Materials Design

2024 UGM Webinar Series

Mechanistic and Structural Sources of Complexity in the Atomic Scale Simulation of Brønsted Acidic Zeolite Catalysts

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Dr. Céline Chizallet

IFP Energies nouvelles

October 15, 2024

Materials Design UGM

UGM 2024

The Materials Design annual user event will be online for 2024.

Tuesdays and Thursdays
October 15 – November 7

Plenary Speakers:

Professor Sir Richard Catlow - University College London, England
Professor Georg Kresse, Dr. Martijn Marsman,
and Dr. Manuel Engel - The University of Vienna, Austria
Professor Greg Olson - Massachusetts Institute of Technology, USA
Dr. Céline Chizallet - IFP Energies Nouvelles, France

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October 15, 2024

Materials Design UGM Presenter

Dr. Céline Chizallet

Project leader

Catalysis, Biocatalysis and Separation Division

IFP Energies nouvelles, France

Webinar Speakers

Katherine Hollingsworth

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Dr. Alexander Mavromaras

amavromaras@materialsdesign.com

Materials Design UGM Webinar Series

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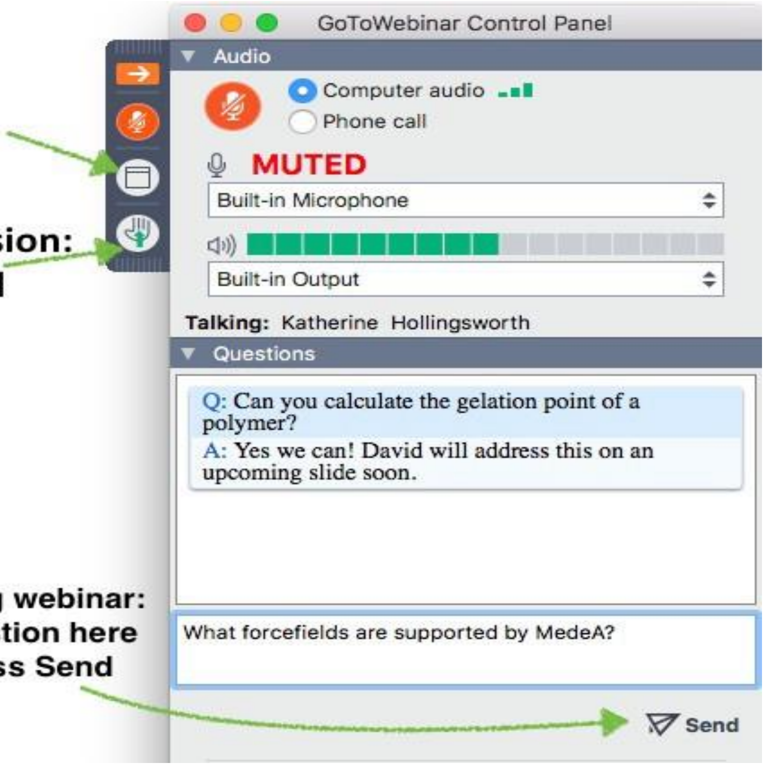
Please Ask Questions!



Talking: Katherine Hollingsworth

Q: Can you calculate the gelation point of a polymer?
A: Yes we can! David will address this on an upcoming slide soon.

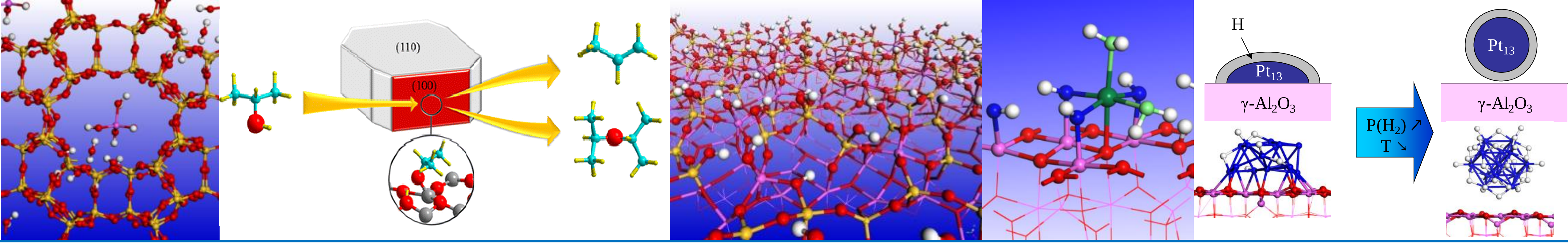
What forcefields are supported by MedeA?

full screen

during discussion:
raise hand
to speak

Use the raise hand icon to bring attention to your question

any time during webinar:
type your question here
and then press Send



MECHANISTIC AND STRUCTURAL SOURCES OF COMPLEXITY IN THE ATOMIC SCALE SIMULATION OF BRØNSTED ACIDIC ZEOLITE CATALYSTS

CELINE CHIZALLET

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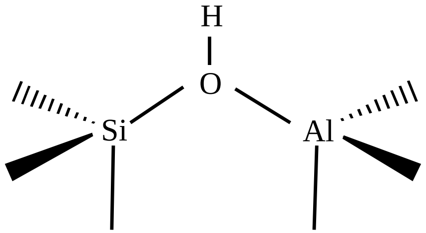
BRØNSTED ACIDIC ZEOLITE CATALYSTS

* Practical relevance of proton exchanged zeolites in catalysis

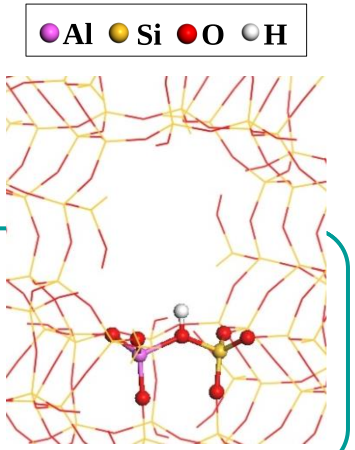
- Refining, petrochemistry, biomass conversion, plastic recycling
- Cationic or cationic-like intermediates invoked (carbenium/carbonium chemistry)
- Mechanisms still questioned

Molecular Views on Mechanisms of Brønsted Acid-Catalyzed Reactions in Zeolites
C. Chizallet, C. Bouchy, K. Larmier, G. Pirngruber, ***Chem. Rev.,*** 2023, 123, 6107

* Bulk sites in micropores

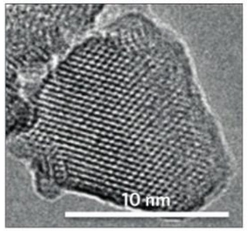


Uytterhoeven, Christner, Hall, JPC 1965
Haag, Lago, Weisz, Nature 1984
Mortier, Sauer, Lercher, Noller, JPC 1984

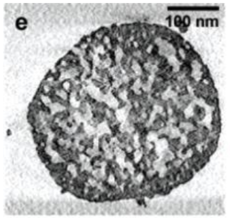


* Beyond the crystal bulk approach

- External surface / surface at mesopores

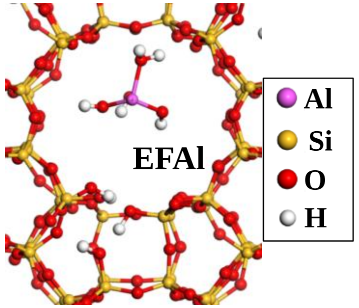


Nano-FAU, Mintova et al.
Nature Materials 2015

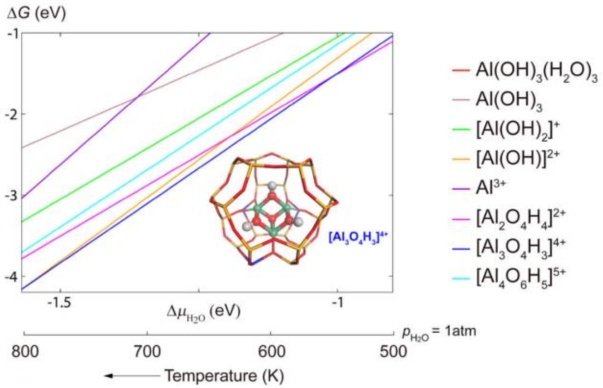


Hierarchical-MFI, Perez-Ramirez et al.
JACS 2005

- Defects, EFAls



J. Catal. **2016**, *339*, 242



Pidko et al. *ACS Catal.* **2015**, *5*, 7024

Need for molecular approaches

C. Chizallet, *ACS Catal. 2020, 10, 5579−5601*

FROM RATIONALIZATION TO PREDICTION OF COMPLEX CATALYTIC SYSTEMS

I- Structure understanding

-**Model** construction for active sites
-Electronic and stability analysis
- Comparison with experimental **spectral feature**

Quantum chemistry approach:

$$H\Psi = \varepsilon\Psi$$

II- Chemical reactivity investigations

-Adsorption of **reactants**
-Determination of **intermediates** and **transition structures**
-Calculation of **free energy profiles and** full reaction **pathways**

$$k = \frac{k_B T}{h}\exp\left(-\frac{\Delta_r H^\ddagger - T\Delta_r S^\ddagger}{RT}\right)$$

III- Towards prediction

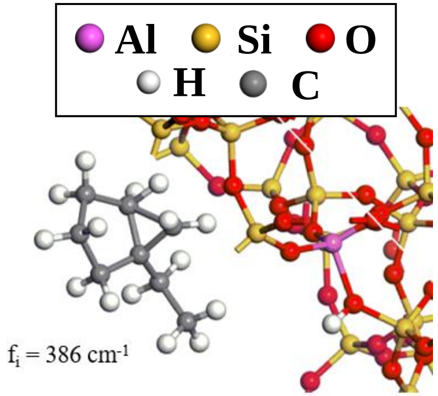
Multiscale modeling : prediction of macroscopic **activity** / **selectivity**

Rate of elementary step =
- d[R]/dt = k [R]

Topics in Catalysis, **2022**, *65*, 69-81

A SUCCESSFUL EXAMPLE WITH “LOW EFFORT”: BIFUNCTIONAL HYDROISOMERIZATION OF ETHYL-CYCLOHEXANE IN EU-1

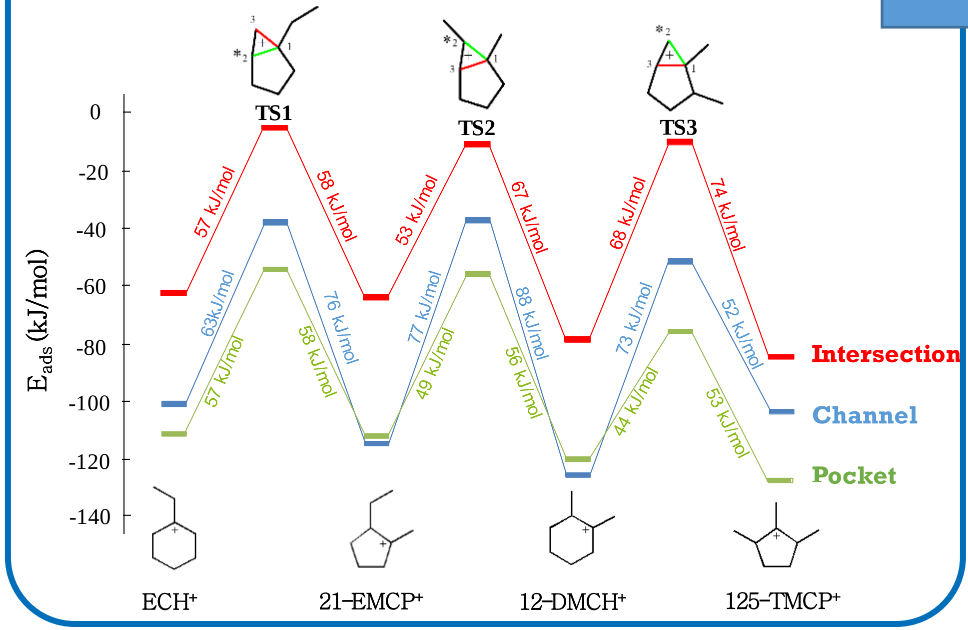
DFT calculations



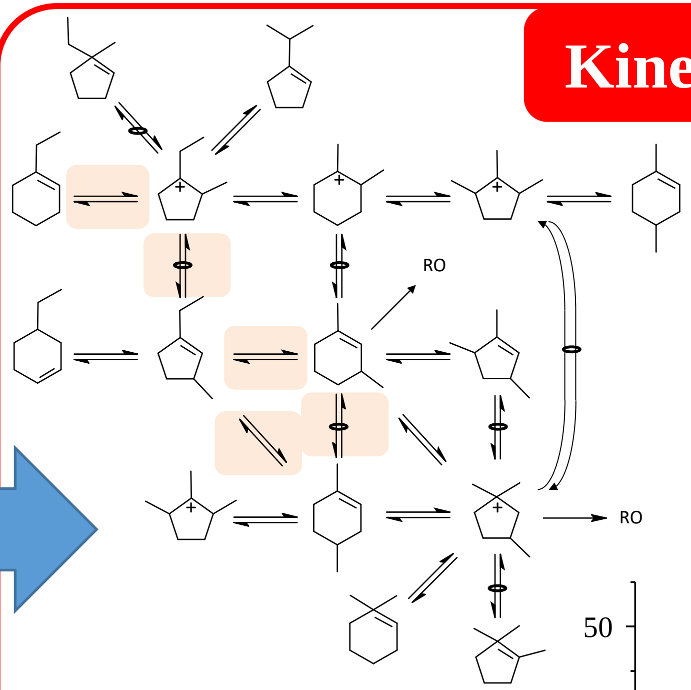
Bulk sites
at various locations

Static approach

PBE+D2

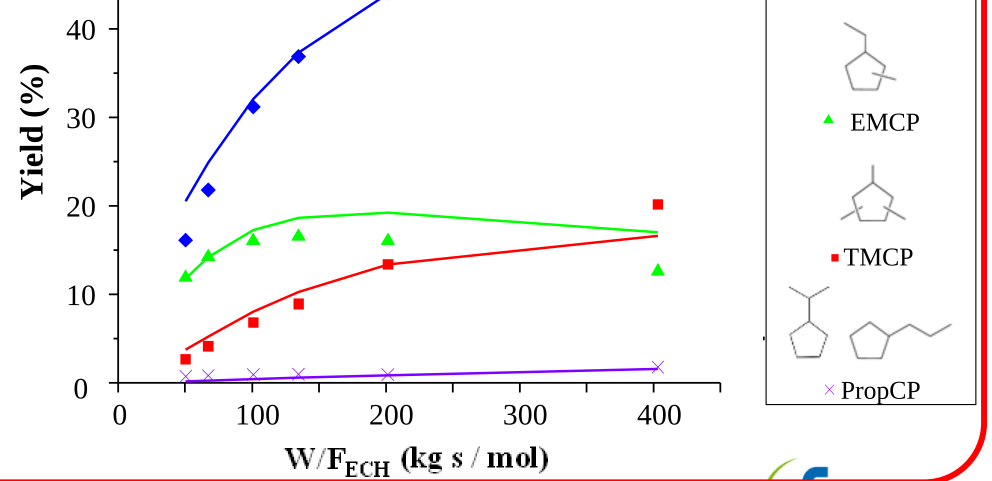


Kinetic model



Micro-kinetics
31 parameters fitted over 134
103 parameters come from DFT

POINTS: 1%Pt/Al_2O_3 + EU-1, 285 °C
LINES: model



ACS Catal. **2019**, 9, 1692-1704

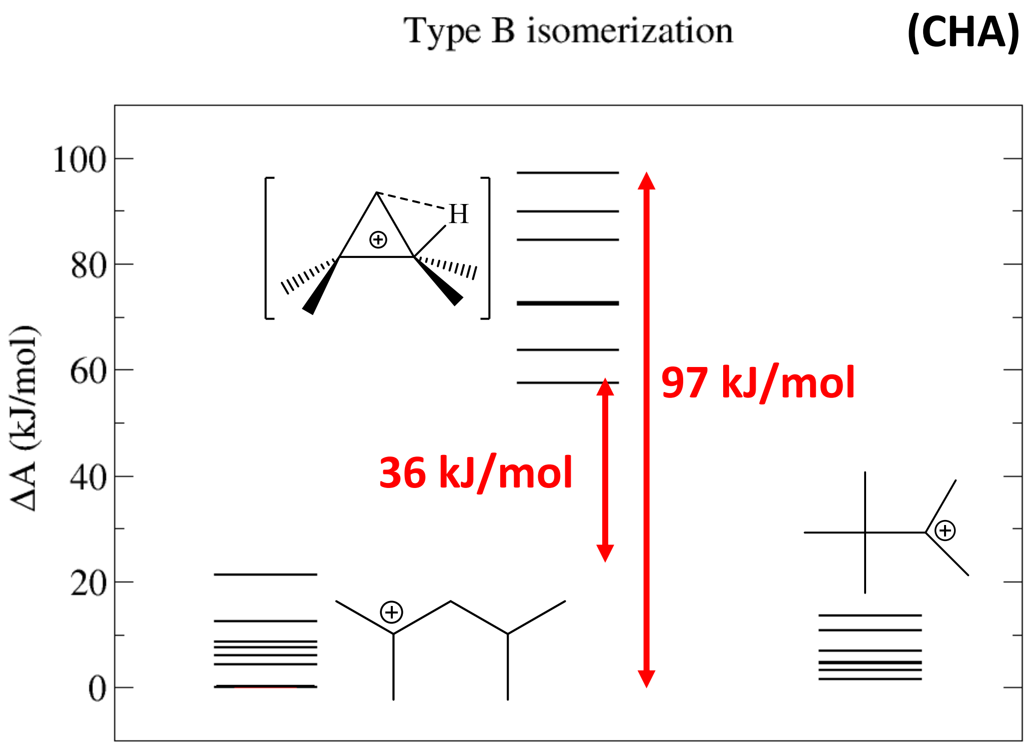
ChemCatChem, **2021**, 13, 3434

SAMPLING PROBLEMS WITH THE STATIC APPROACH

Carbenium chemistry in Brønsted acid zeolites : variety of local minima and saddle points

Deviation of ~60 kJ/mol on barriers
→ Ratio ~ 2.10^6 on rate constants k at 500 K !

	Static		**AIMD**
Typical computational time scale ratio:	**1**	➞	**10^3-10^4**

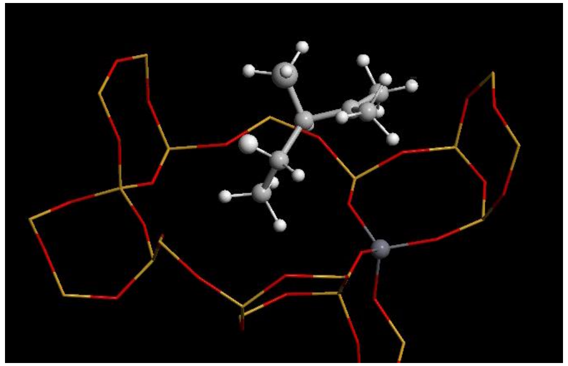


Rey, Gomez , Raybaud, Chizallet , Bučko, *J. Catal.*, **2019**, 373, 361

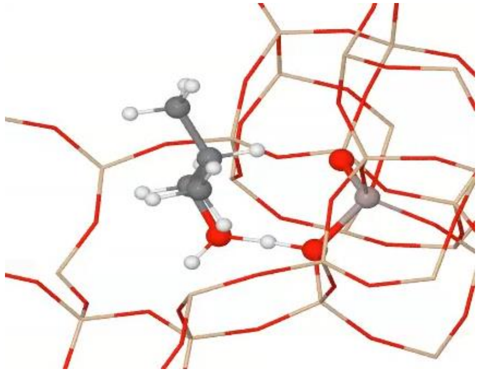
SIMULATION OF INTRICATE ZEOLITE CATALYSTS

Static investigation of the reactivity of bulk sites

Alkene isomerisation and cracking

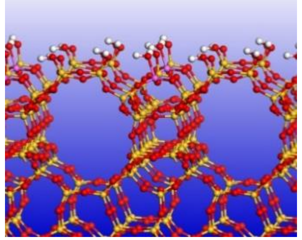


Alcohol dehydration

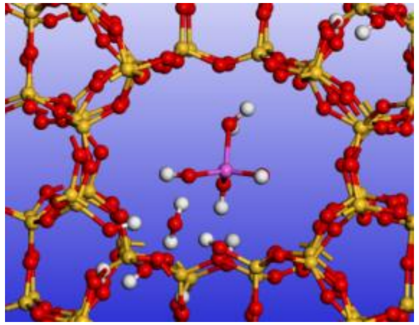


Complexity of chemical reaction investigations: AIMD

Acid sites at the external surface

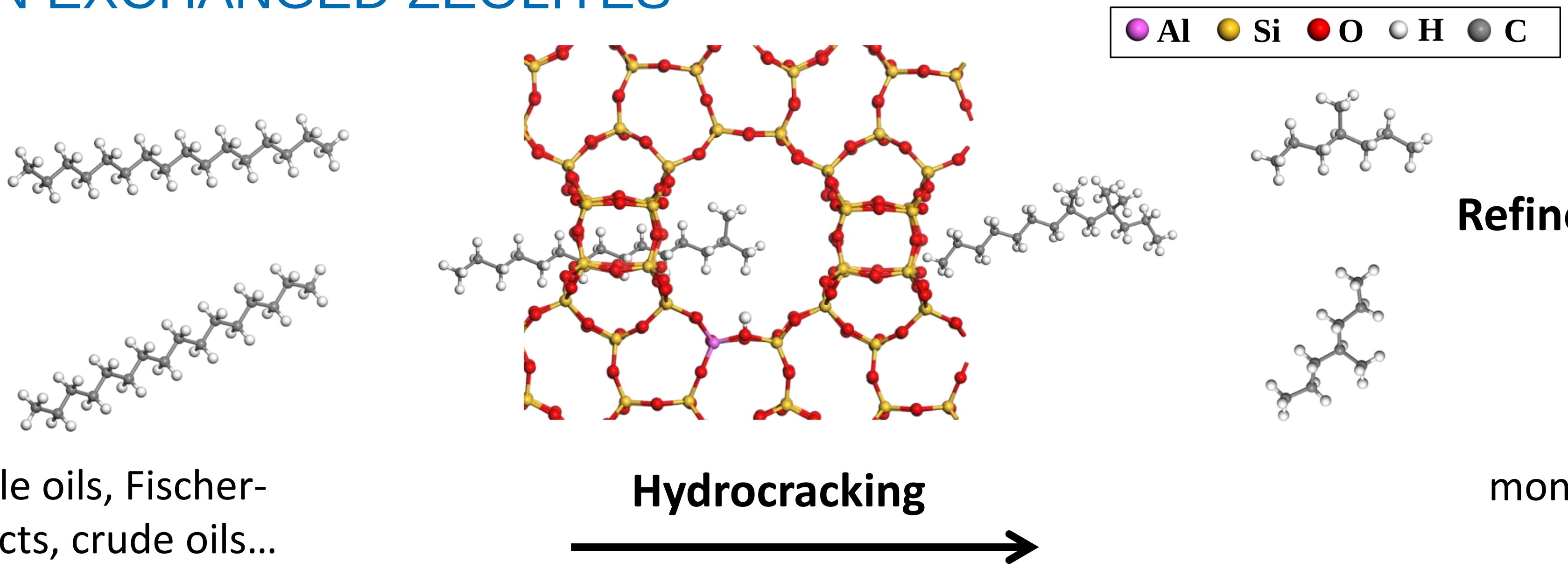


Dealumination mechanisms



Structural complexity

ALKANE ISOMERIZATION AND CRACKING BY PROTON EXCHANGED ZEOLITES



Heavy feedstocks

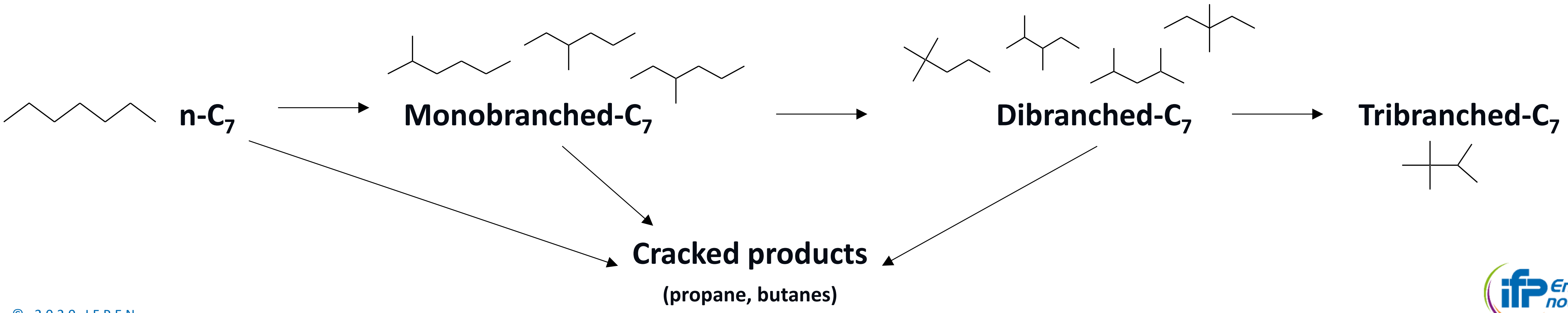
Plastic waste, vegetable oils, Fischer-Tropsch process products, crude oils…

Hydrocracking

Refined products

monomers, fuel

Hydroconversion of n-heptane as a model reaction:



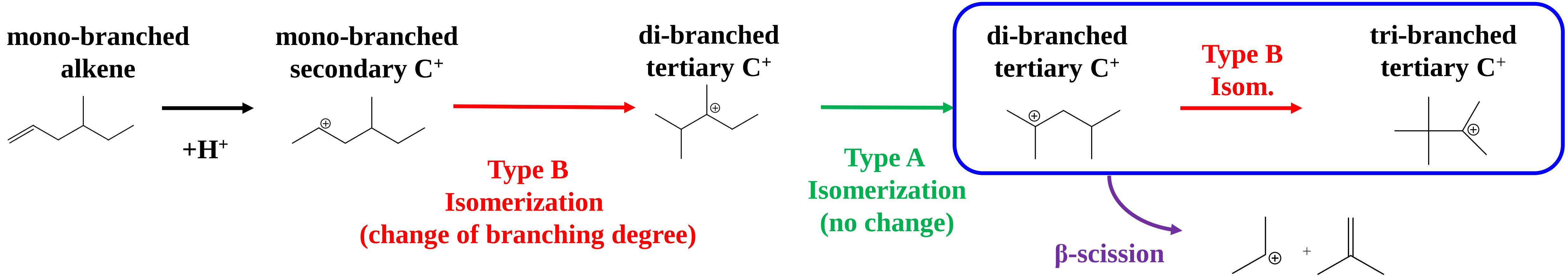
n-C_7 → **Monobranched-C_7** → **Dibranched-C_7** → **Tribranched-C_7**

Cracked products

(propane, butanes)

NATURE OF ELEMENTARY STEPS

Bifunctional: *alkenes* as reactants in the zeolite



mono-branched alkene

+H$^+$

mono-branched secondary C$^+$

Type B Isomerization (change of branching degree)

di-branched tertiary C$^+$

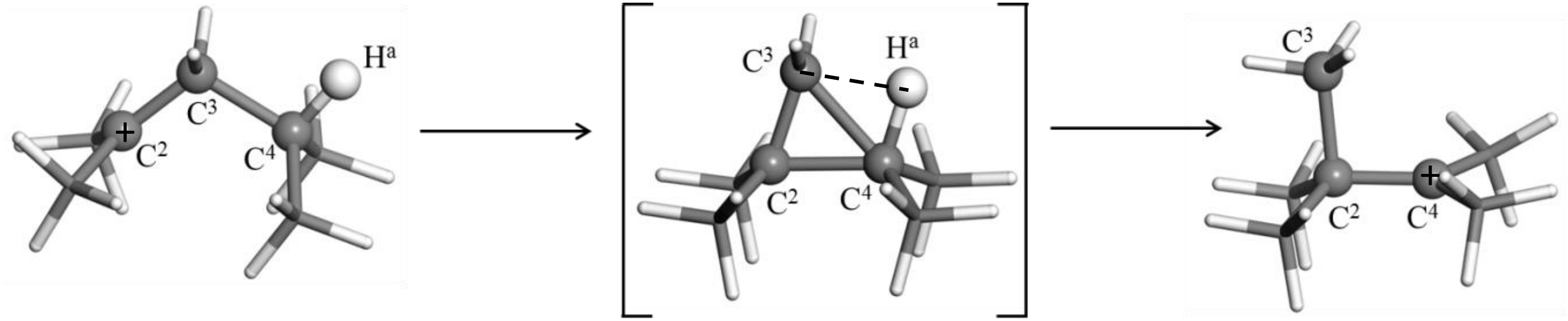
Type A Isomerization (no change)

di-branched tertiary C$^+$

Type B Isom.

tri-branched tertiary C$^+$

β-scission

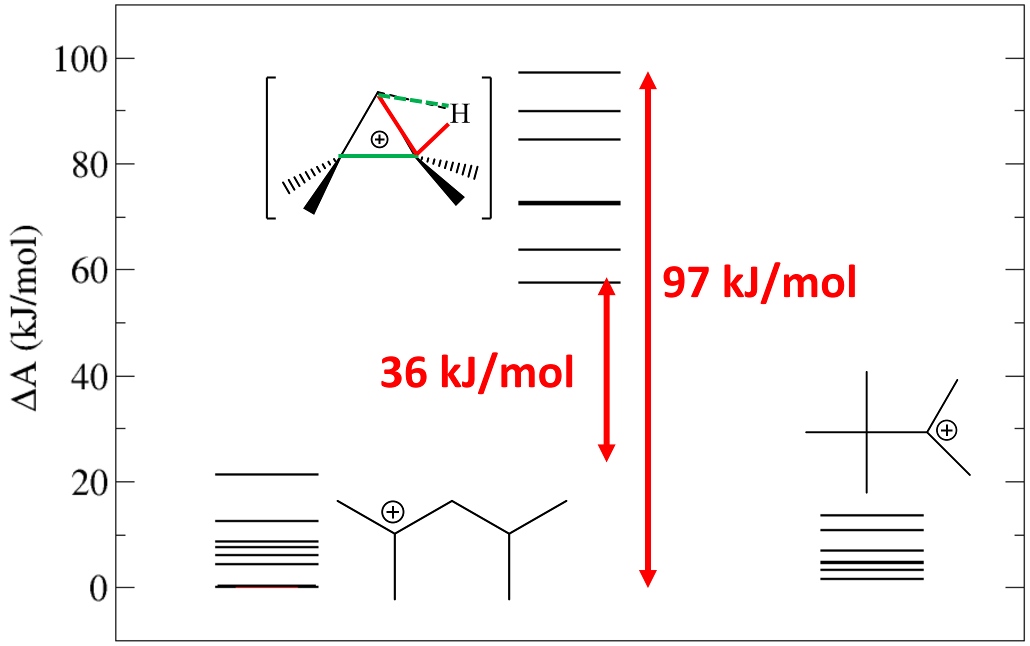


Edge-protonated PCP

TYPE B ISOMERIZATION BETWEEN TWO TERTIARY CARBENIUM IONS

Static approach

Variety of local minima and saddle points

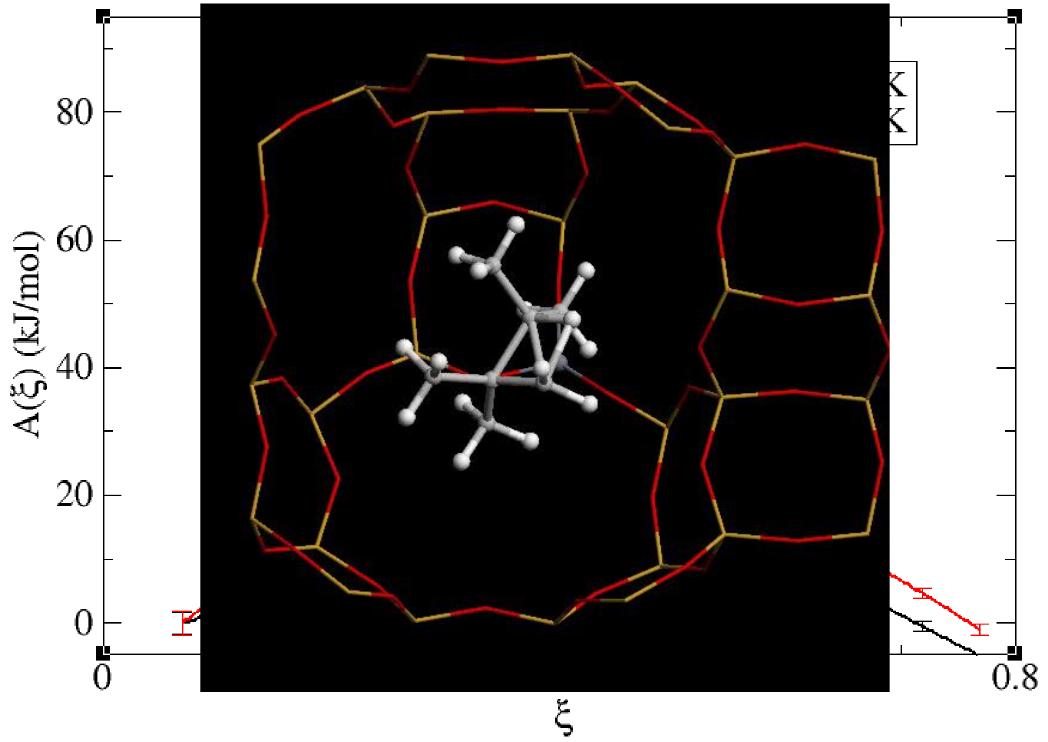


Free energies given at 300 K

PBE+D2

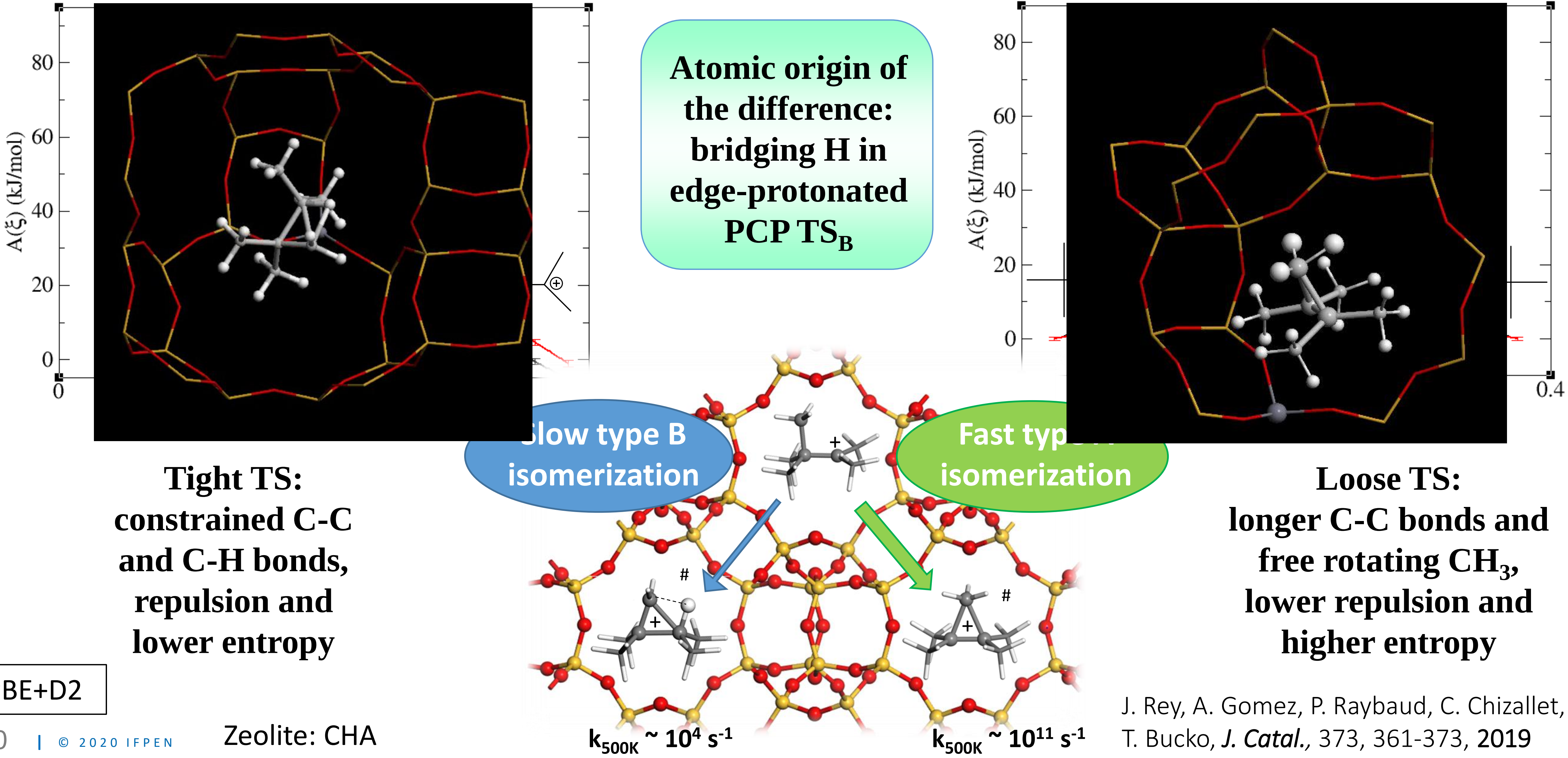
Ab initio molecular dynamics (AIMD)

Constrained molecular dynamics (Blue Moon Sampling)



J. Rey, A. Gomez, P. Raybaud, C. Chizallet, T. Bucko, *J. Catal.*, 373, 361-373, 2019

TYPE A VERSUS TYPE B ISOMERIZATION



Type B

Tight TS:
constrained C-C and C-H bonds, repulsion and lower entropy

Atomic origin of the difference: bridging H in edge-protonated PCP TS_B

Slow type B isomerization

k_{500K} ~ 10^4 s^{-1}

Fast typ
isomerization

k_{500K} ~ 10^{11} s^{-1}

Type A

Loose TS:
longer C-C bonds and free rotating CH_3, lower repulsion and higher entropy

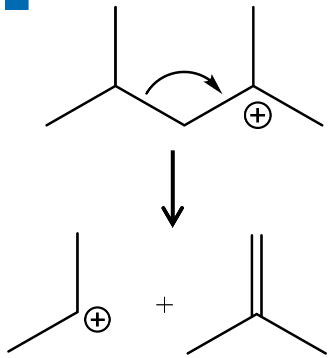
PBE+D2

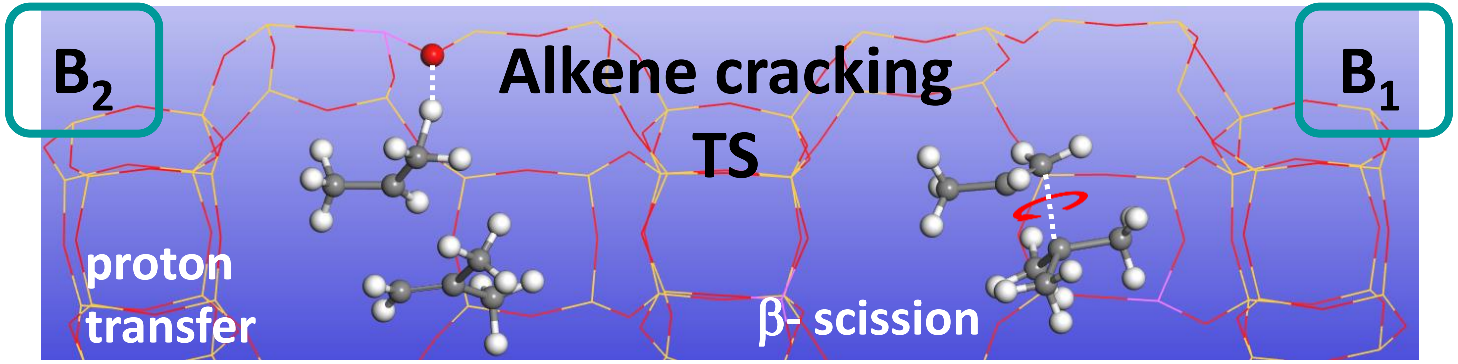
Zeolite: CHA

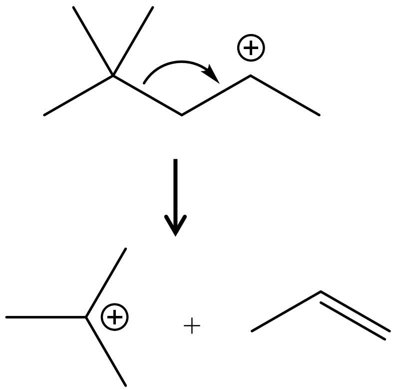
J. Rey, A. Gomez, P. Raybaud, C. Chizallet, T. Bucko, *J. Catal.*, 373, 361-373, 2019

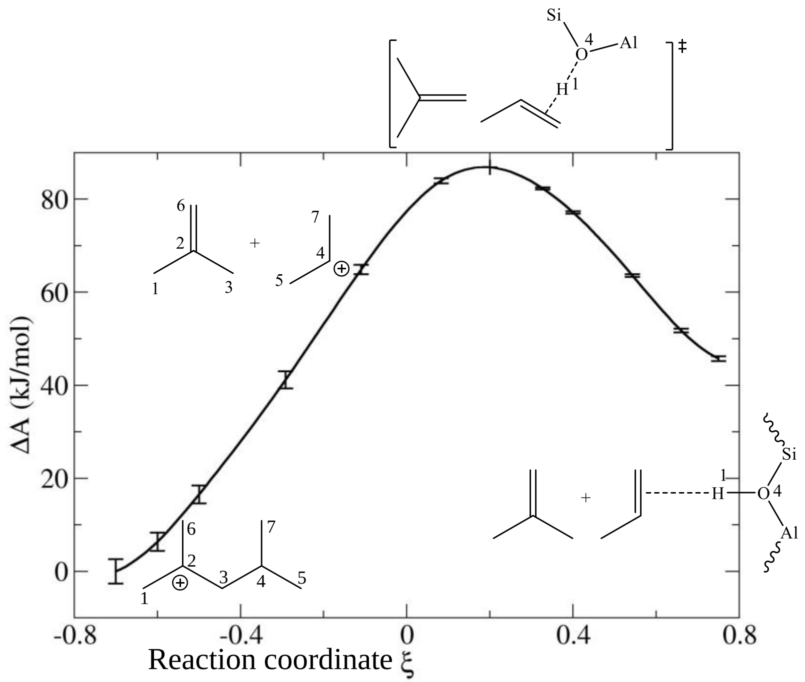
CRACKING REACTIONS

AIMD,
PBE+D2



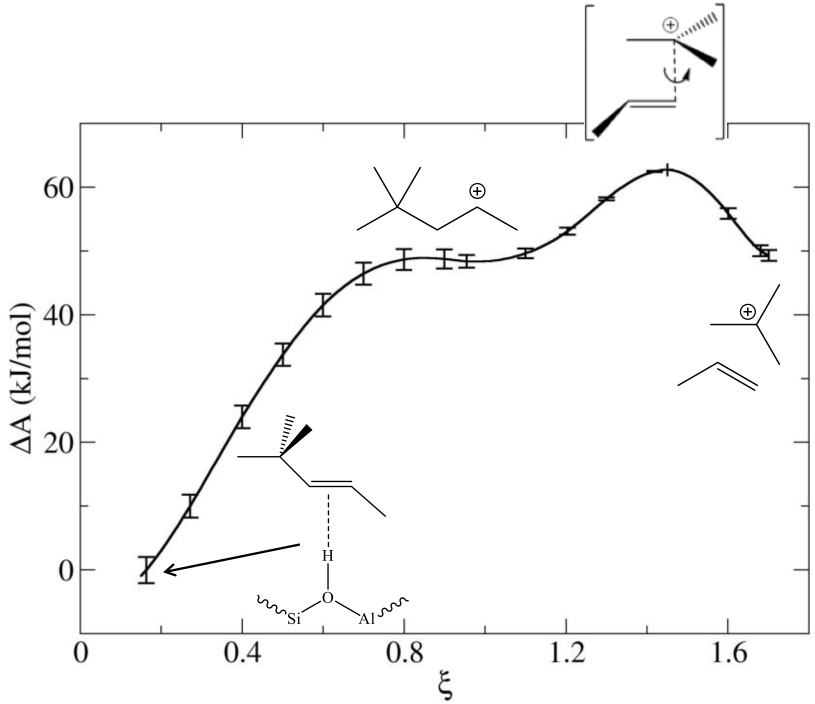






B_2 cracking: not the usually admitted TS, secondary cation produced is not a stable intermediate

B_1 cracking:
- not the usually admitted reactant,
- high entropy of the β-scission TS due to dynamic effects



J. Rey, C. Bignaud, P. Raybaud, T. Bucko, C. Chizallet, *Angew. Chem. Int. Ed.*, 59, 18938-18942, 2020

KINETIC MODELLING, COMPARIZON WITH EXPERIMENTS

Ab initio based microkinetic model

Tabulated data for hydro-dehydrogenations of alkenes/alkanes in gas phase, equilibrium at each simulation step

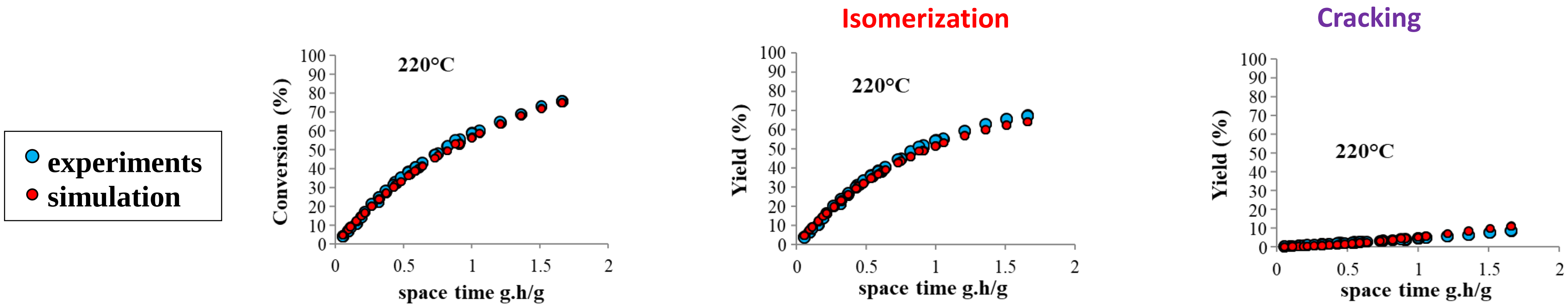
Ab initio rate constants for reactions undergone by alkenes in the zeolite: adsorption, protonation, isomerization, cracking → lumping

High Throughput Experiments

Catalyst: Pt/Beta (BEA)

HTE: 16 reactors, Flowrence Avantium

Kinetic study: variation of %Pt, T, P_{tot}, H_2/HC, τ



Adjustments of barriers:

data	original value	adjusted value
$\Delta G_{+}^{\ddagger}$ (type C cracking) $(\mathrm{kJ\cdot mol^{-1}})$	24	40
$\Delta G_{+}^{\ddagger}$ (type B1 cracking) $(\mathrm{kJ\cdot mol^{-1}})$	15	30
$\Delta G_{+}^{\ddagger}$ (type B2 cracking) $(\mathrm{kJ\cdot mol^{-1}})$	84	93

DFT underestimates by 10-15 kJ/mol the difference between the cracking barriers and the isomerization barriers

Improvements to be made: lack of accuracy of DFT ? Effect of the level of theory ?

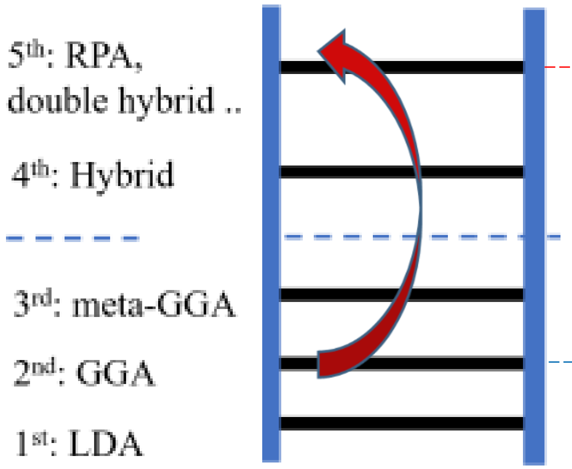
JM. Schweitzer, C. Bouchy, C. Chizallet et al., *ACS Catalysis,* 12, 1068-1081, 2022

COMPUTING FREE ENERGY BARRIERS WITH AIMD AT THE RPA LEVEL

Jacob's ladder of DFT functionals

$$H\Psi = \varepsilon\Psi$$

Heaven of chemical accuracy



Hartree world
No exchange-correlation

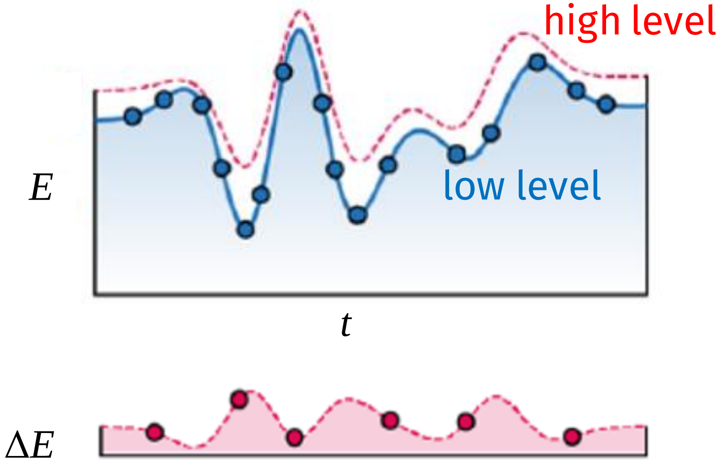
Typical computational time scale (AIMD):

10^3 years !

~ a few months

MLPT: Machine Learning Perturbation Theory

- **Step 1**: AIMD at a "low" production level (PBE+D2)
- **Step 2**: Compute only a few (~100) single point energy calculations on some configurations at the high target level

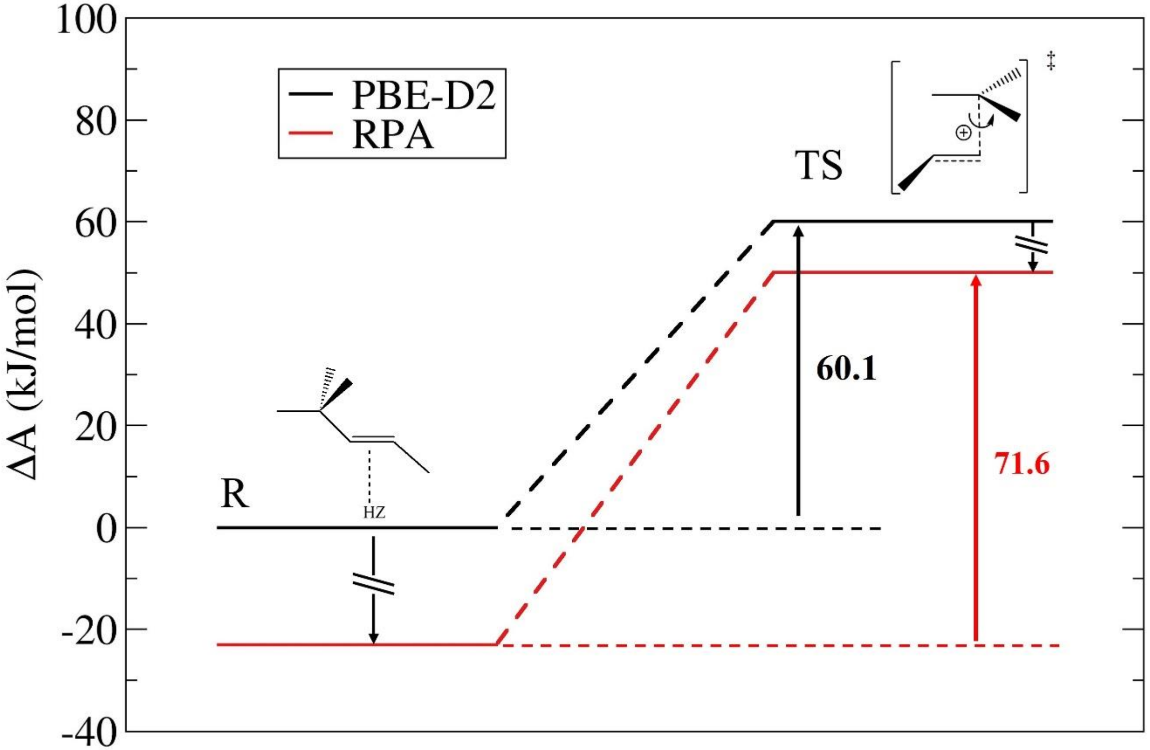


- **Step 3**: Train a Machine Learning model to quantify the difference in energy between the two levels thanks to structural descriptors
- **Step 4**: Apply Perturbation Theory to deduce the free energy at the high level of theory

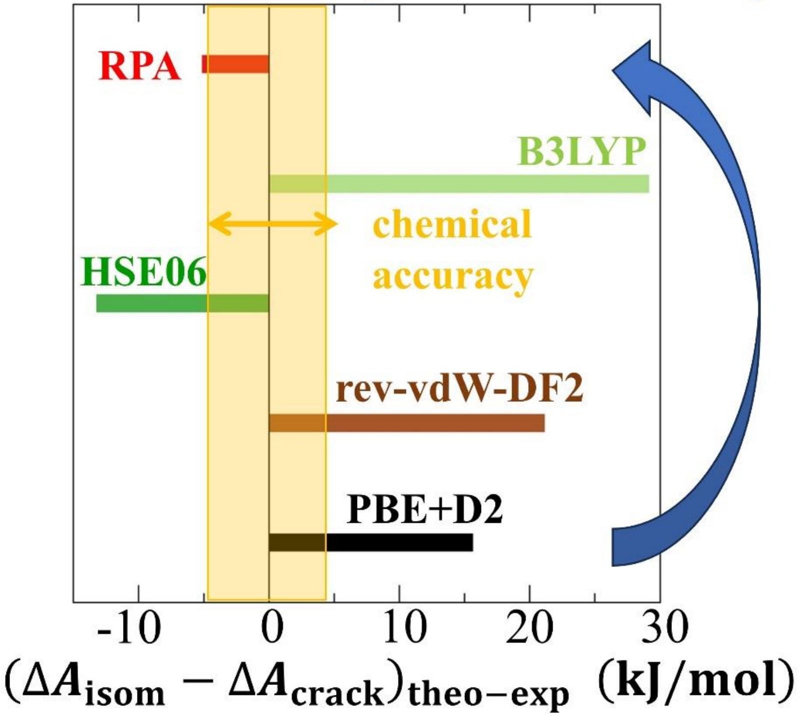
Rocca, Bucko et al, *J. Chem. Theory Comput.* **2019**, *15*, 6333; **2020**, *16*, 6049; **2022**, *18*, 1382

FREE ENERGY BARRIERS OF ISOMERIZATION VERSUS CRACKING

Correction of the B_1 cracking free energy profile:



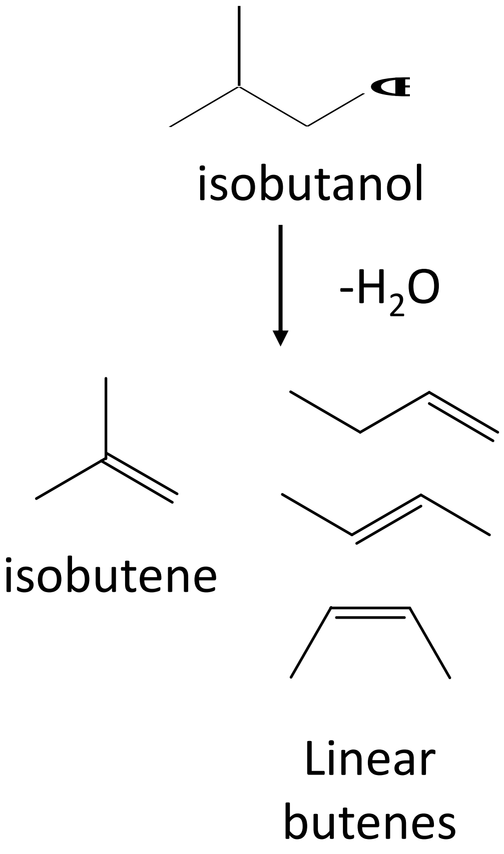
Climbing the Jacob's ladder by Machine Learning Perturbation Theory



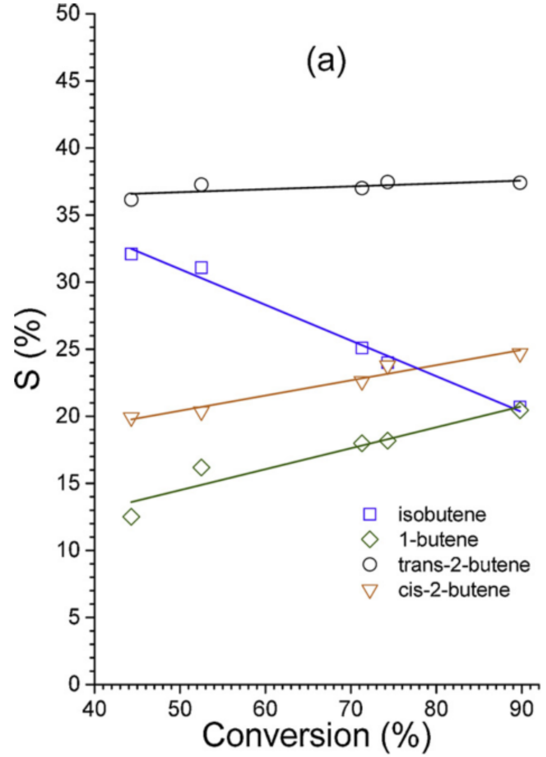
RPA-MLPT provides the best (and necessary) accuracy
Combining AIMD and RPA would not have been possible without Machine Learning Perturbation Theory

J. Rey, C. Chizallet, D. Rocca, T. Bucko, M. Badawi, *Angew. Chem. Int. Ed.,* 63, e202312392, 2024
J. Rey, M. Badawi, D. Rocca, C. Chizallet, T. Bucko, *Catal. Sci. Technol.,* in press, 2024

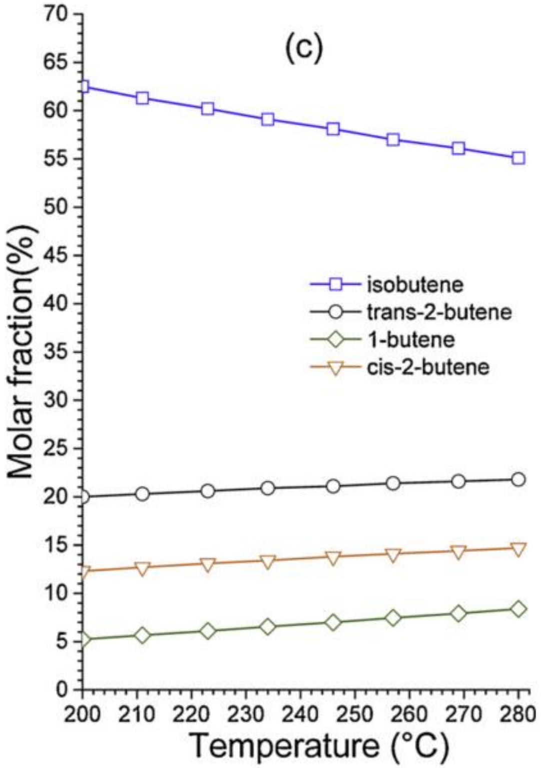
ISOBUTANOL DEHYDRATION INTO LINEAR ALKENES



Isobutanol dehydration (250°C, ferrierite):

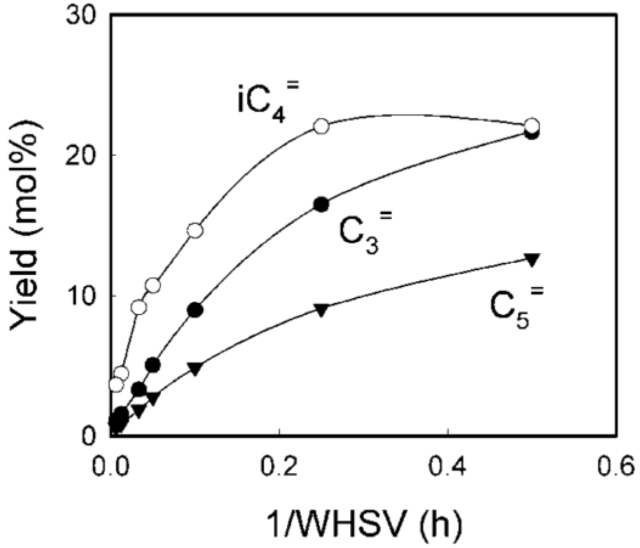


Equilibrium composition:



Appl. Catal. B 243 (2019) 594-603

Conversion of but-1-ene (350°C):



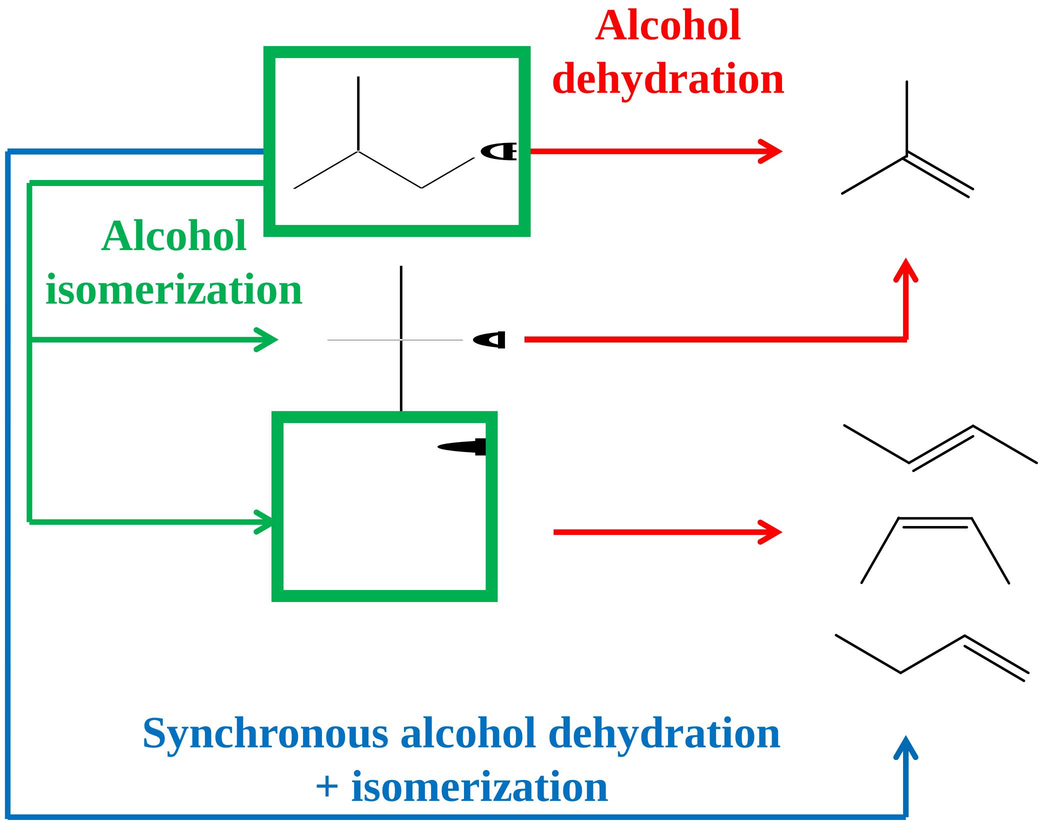
J. Catal. 197 (2001) 68-80

Practical interest: conversion of biosourced molecules into chemicals and fuels

Contradictory results ! How do linear alkenes form ?

NEW MECHANISMS FOUND BY STATIC DFT

PBE+D2

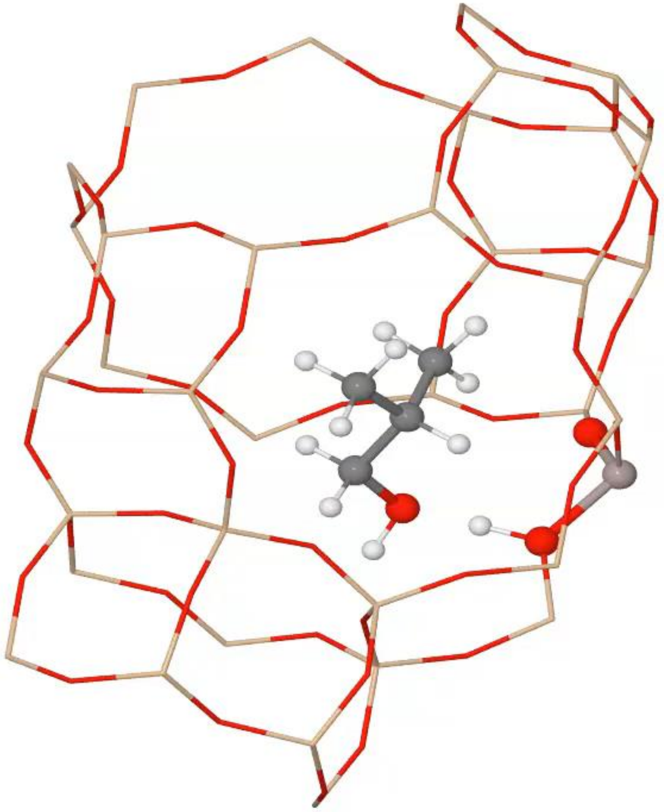


Alcohol dehydration

Alcohol isomerization

Synchronous alcohol dehydration + isomerization

Isomerization of isobutanol into butan-2-ol (CHA):

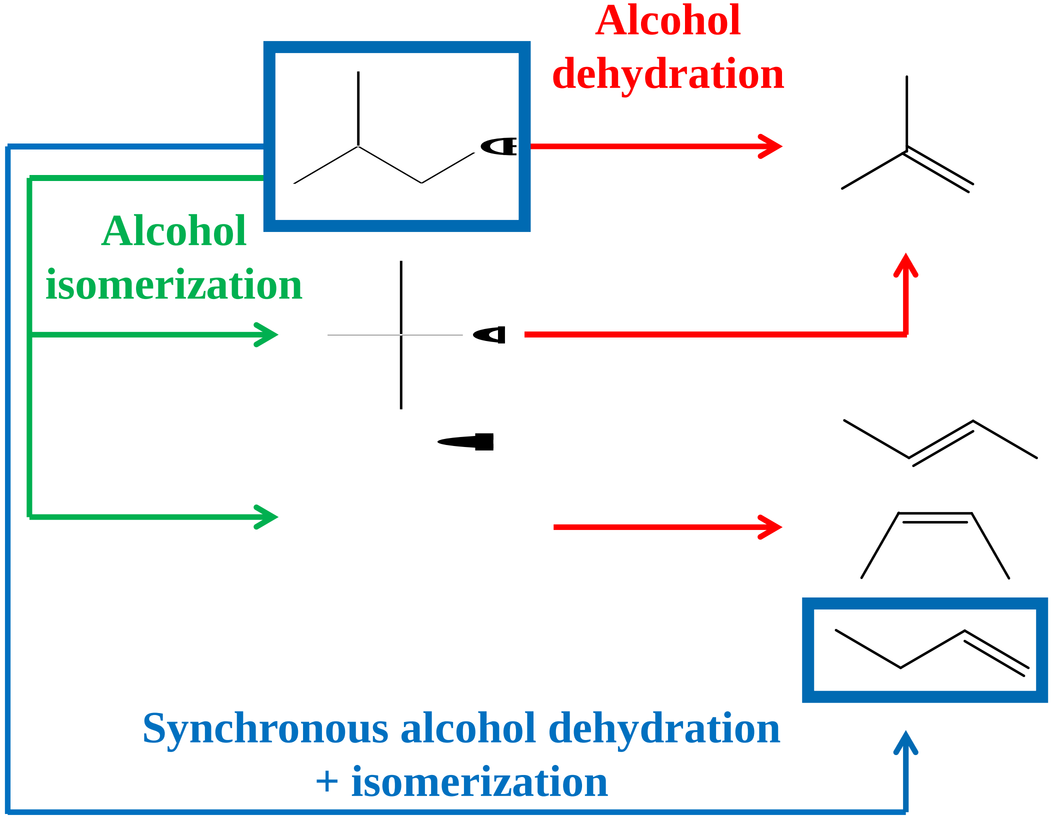


Intrinsic Reaction Coordinate analysis

M. Gešvandtnerová; T. Bučko; P. Raybaud; C. Chizallet ***J. Catal***. *413*, 786, **2022**

NEW MECHANISMS FOUND BY STATIC DFT

PBE+D2

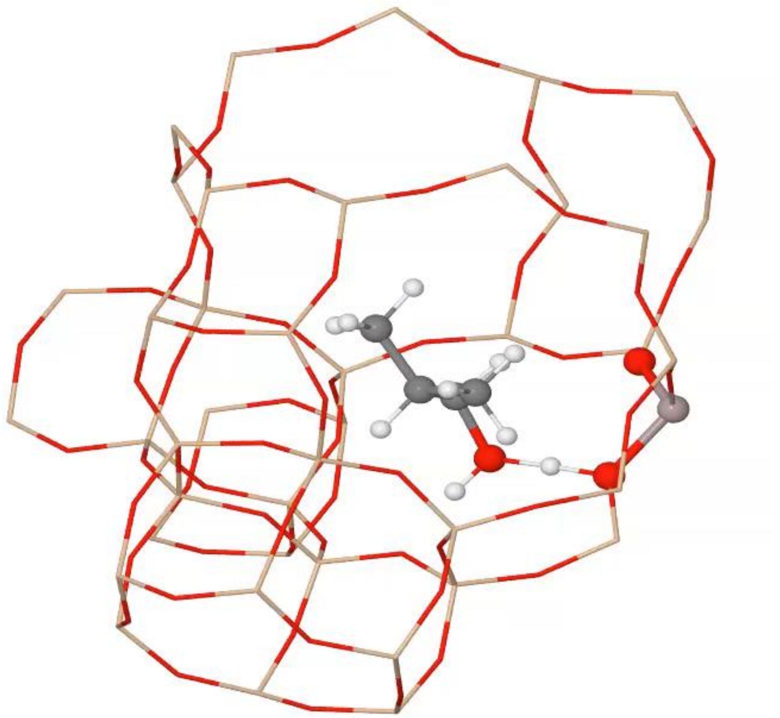


Alcohol dehydration

Alcohol isomerization

Synchronous alcohol dehydration + isomerization

Synchronous isobutanol dehydration and isomerization (CHA):



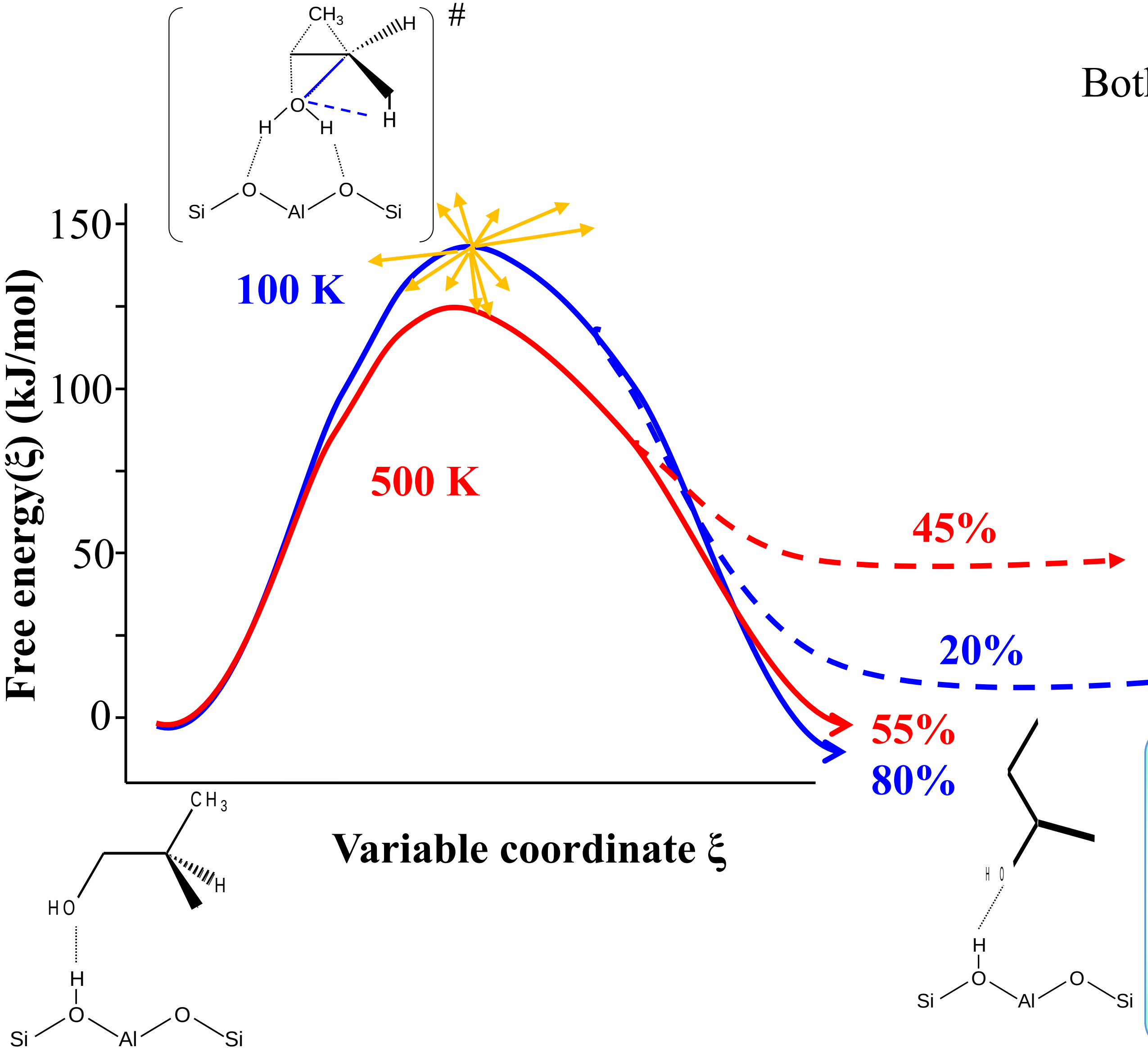
Intrinsic Reaction Coordinate analysis

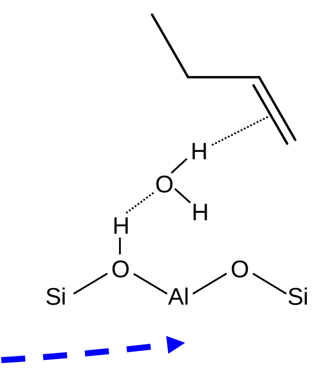
M. Gešvandtnerová; T. Bučko; P. Raybaud; C. Chizallet ***J. Catal***. *413*, 786, **2022**

COMPETITION BETWEEN ALCOHOL ISOMERIZATION *VERSUS* SYNCHRONOUS DEHYDRATION/ISOMERIZATION: DYNAMIC EFFECTS

PBE+D2

Both reactions actually share a common transition state !
→ Post-TS bifurcation
→ Transition state theory does not apply





At low temperature, isobutanol isomerization into butan-2-ol dominates

At 500 K, both route are nearly equally contributing to the formation of linear alkenes

Scheme based on Blue Moon ensemble simulations
% obtained from 5000 TS crossing trajectories (2 ps each)

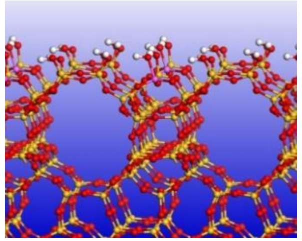
M. Geševandtnerová; P. Raybaud; C. Chizallet, T. Bučko
ACS Catal., 14, 7478, **2024**

SIMULATION OF INTRICATE ZEOLITE CATALYSTS

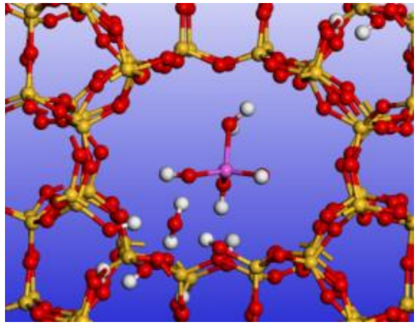
Static investigation of the reactivity of bulk sites

Structural complexity

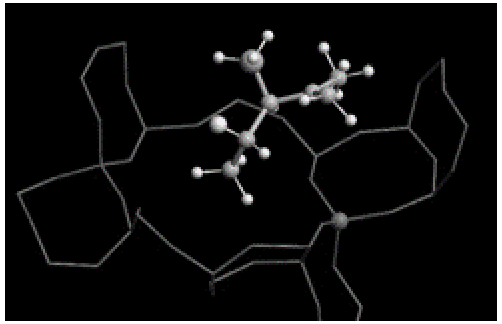
Acid sites at the external surface



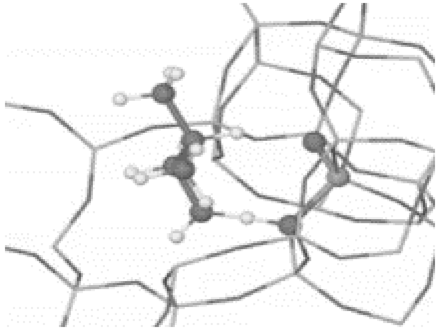
Dealumination mechanisms



Alkene isomerisation and cracking



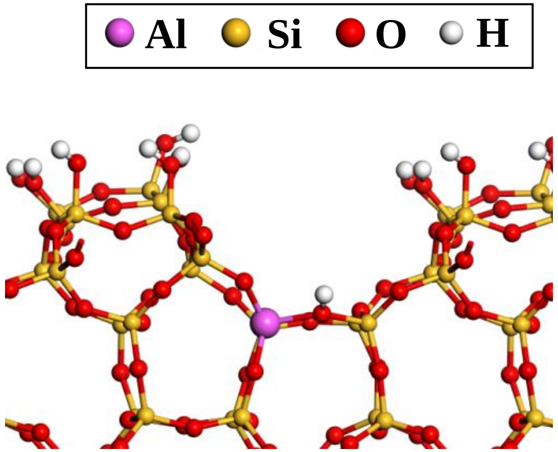
Alcohol dehydration

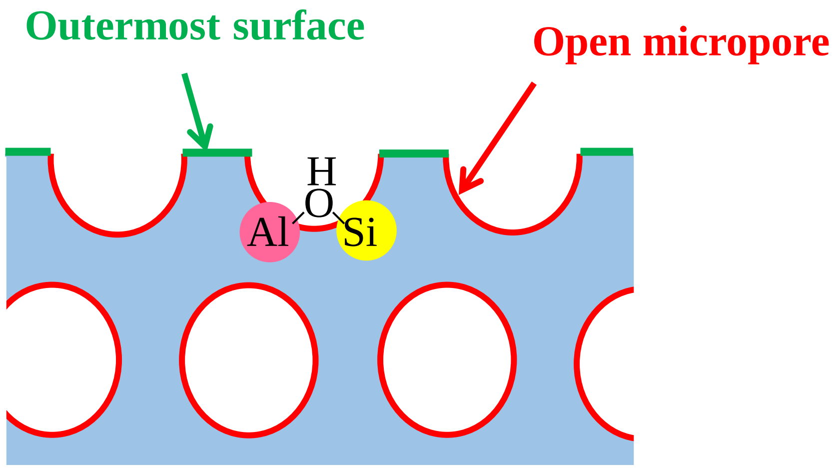


Complexity of chemical reaction investigations

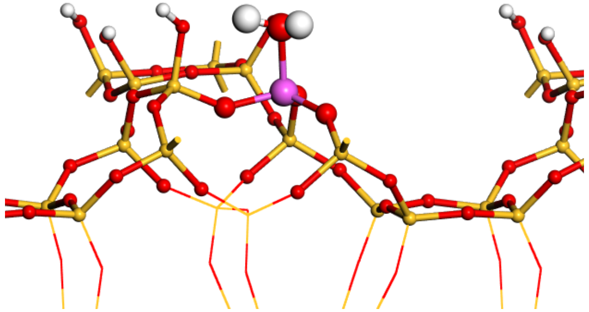
SURFACE MODELS FOR THE EXTERNAL SURFACE OF ZEOLITE BETA AND ZSM-5

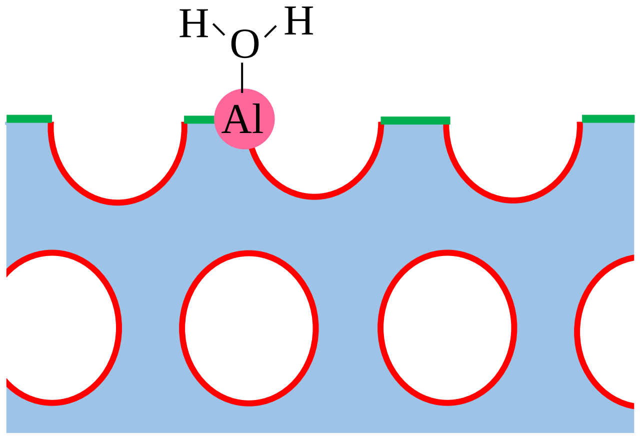
Similar stability as in bulk micropores:





More stable by 20-60 kJ/mol than bulk micropores:





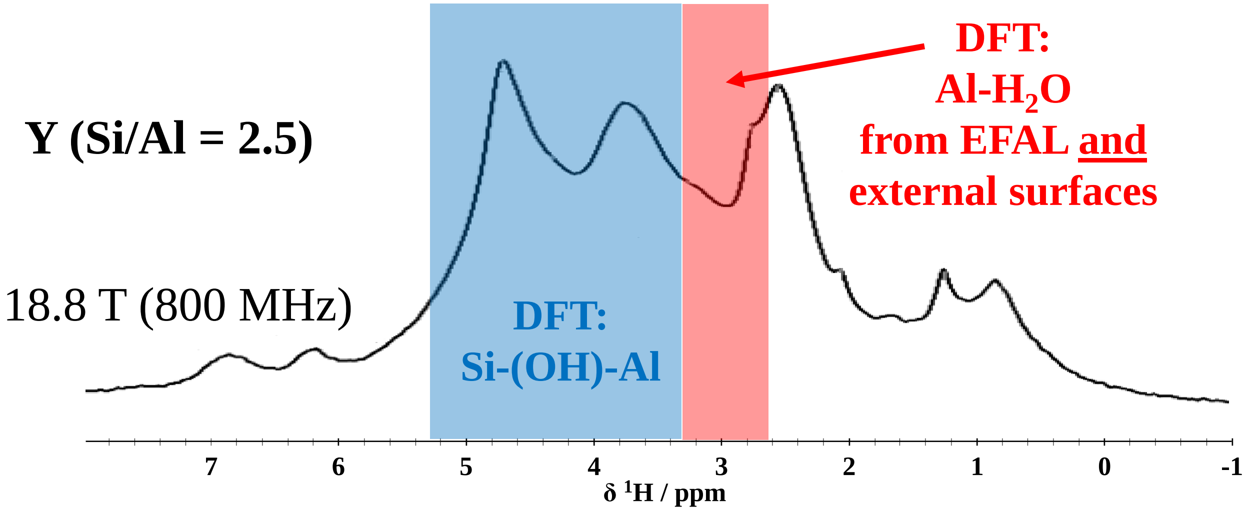
The surface promotes Al-(H_2O) at the outermost surface rather than Si-(OH)-Al

Beta: J. Rey, P. Raybaud, C. Chizallet, *ChemCatChem*, **2017**, 9, 2176

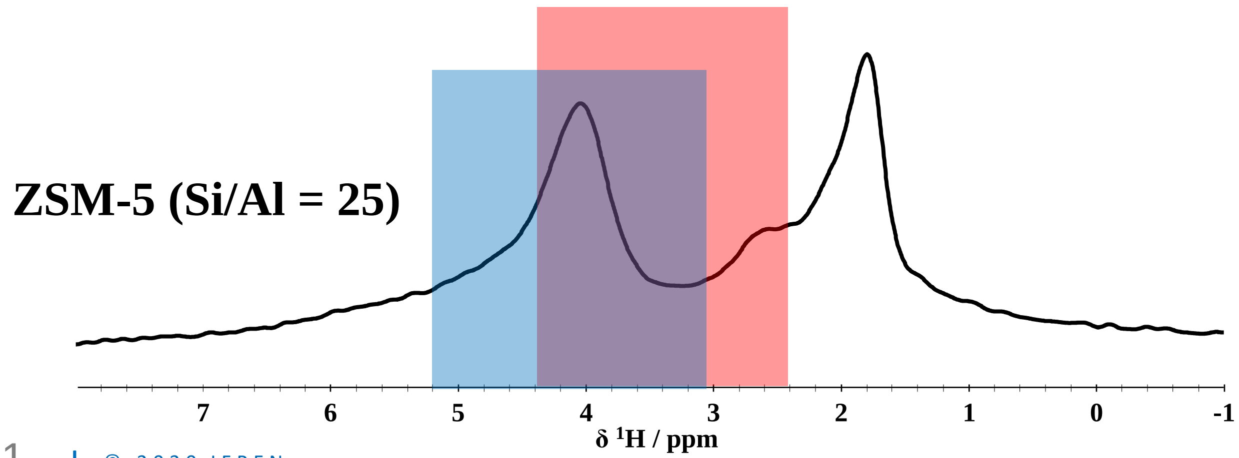
ZSM-5: L. Treps, A. Gomez, T. de Bruin, C. Chizallet, *ACS Catalysis*, **2020**, 10, 3297

Faujasite: T. Jarrin, T. de Bruin, C. Chizallet, *ChemCatChem*, **2023**, 15, e202201302

ASSIGNMENT OF ^{1}H NMR SPECTRA

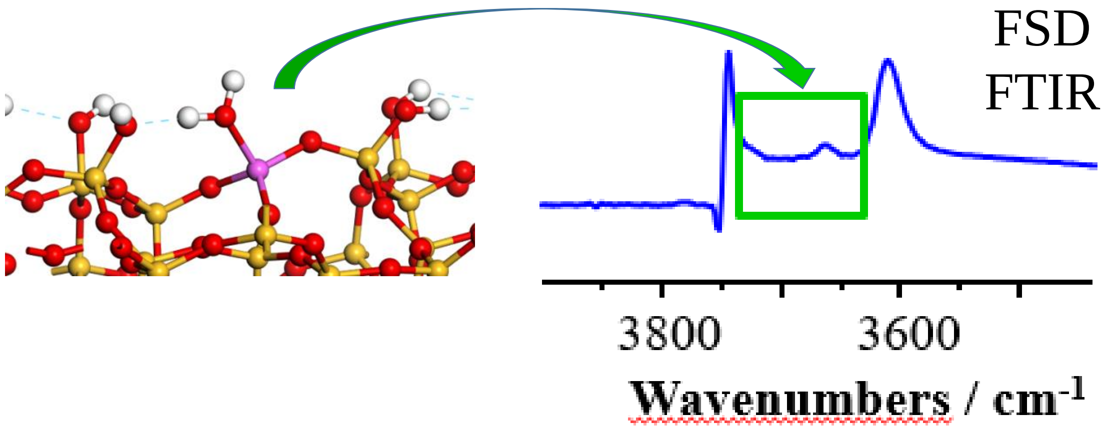


Usual assignment: Si-(OH)-Al ↔ EFALs ↔ Silanols



Zones usually assigned to EFALS are not exclusively due to EFALS for both zeolites
$Al-H_2O$ species from external surface also contribute

Same observation for FTIR on ZSM-5:

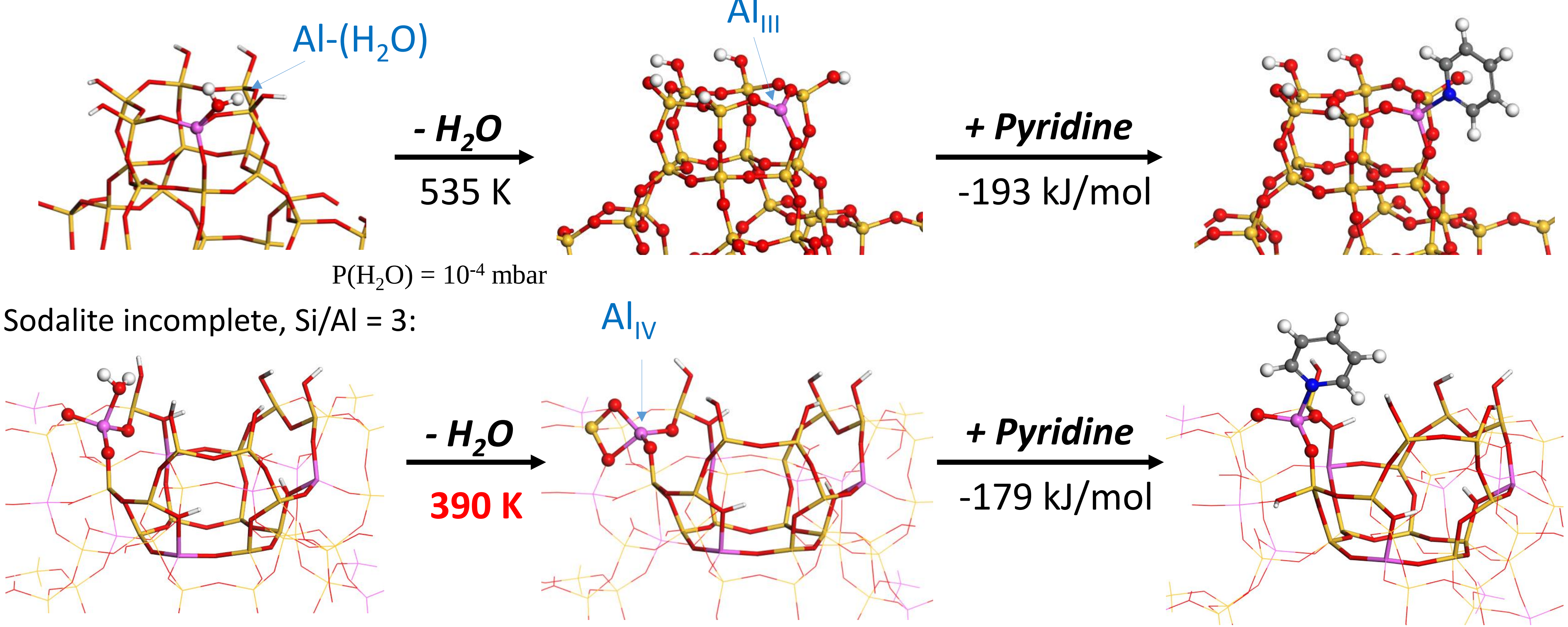


^{1}H NMR signals usually assigned to Si-(OH)-Al groups are also due to $Al-H_2O$ for ZSM-5

ZSM-5: L. Treps et al. *J. Phys. Chem. C*, **2021**, *125*, 2163
Faujasite: Z. Wang et al., *submitted*

LEWIS ACIDITY OF FAUJASITE

● Al ● Si ● O ● H ● C ● N



D6R complete surface, high Si/Al:

Probing Lewis acid sites

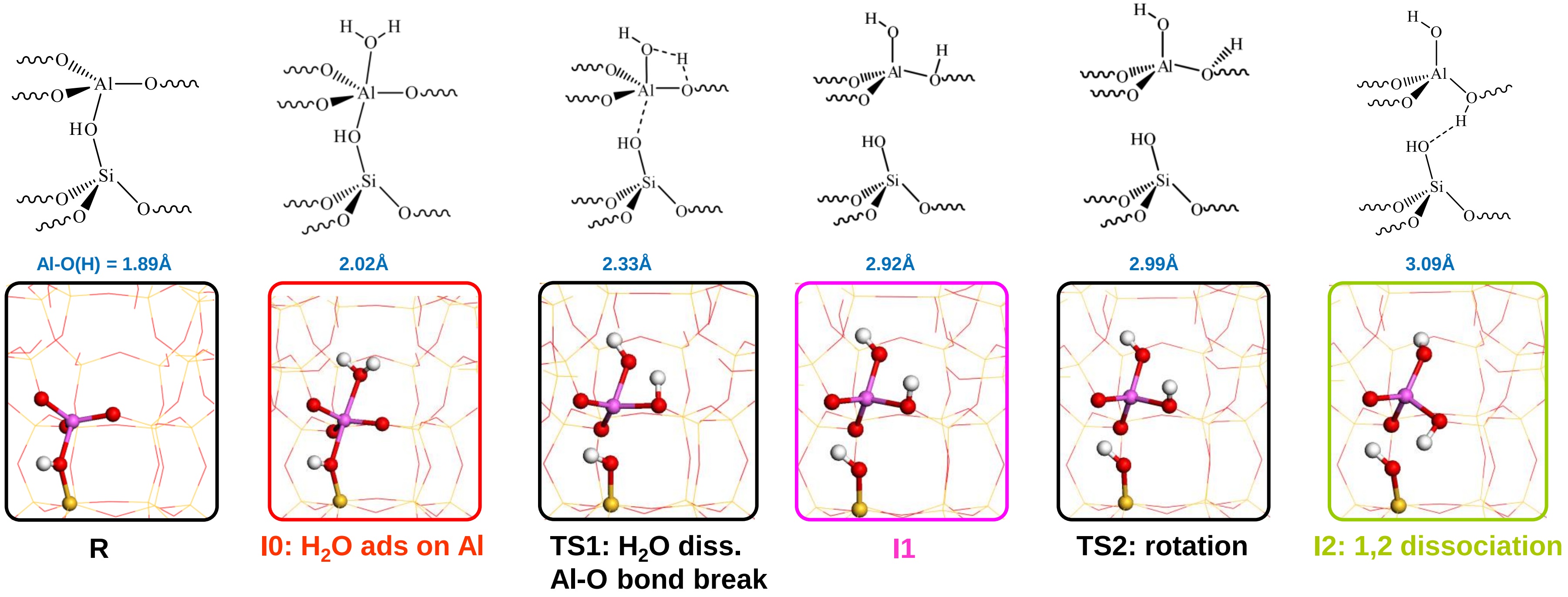
P(H_2O) = 10^{-4} mbar

Sodalite incomplete, Si/Al = 3:

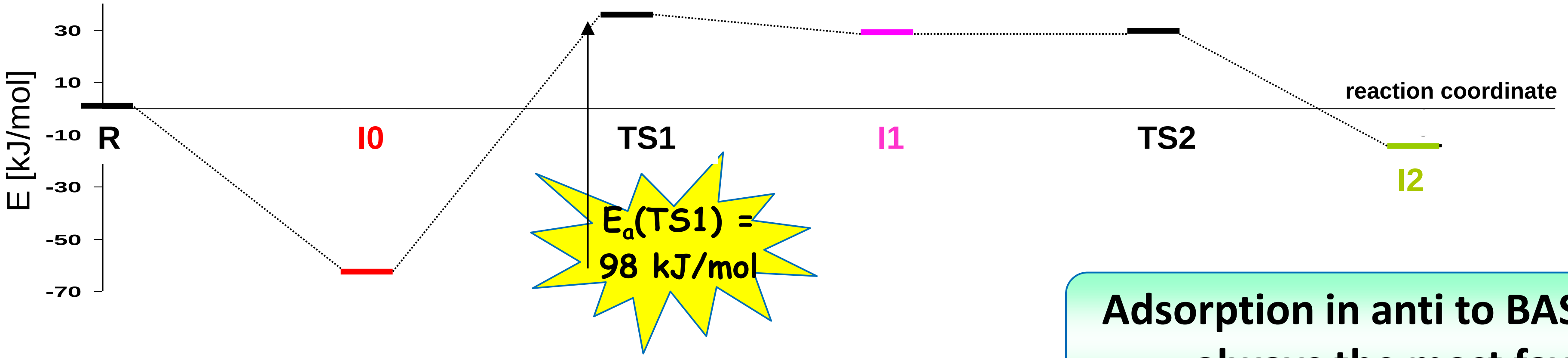
Strong Lewis acid sites are present even in the absence of EFALS on faujasite

T. Jarrin, T. de Bruin, C. Chizallet, *ChemCatChem*, **2023**, 15, e202201302

DEALUMINATION OF ZEOLITES: FIRST AL-O BOND BREAKING



Ex: TO_1H in FAU



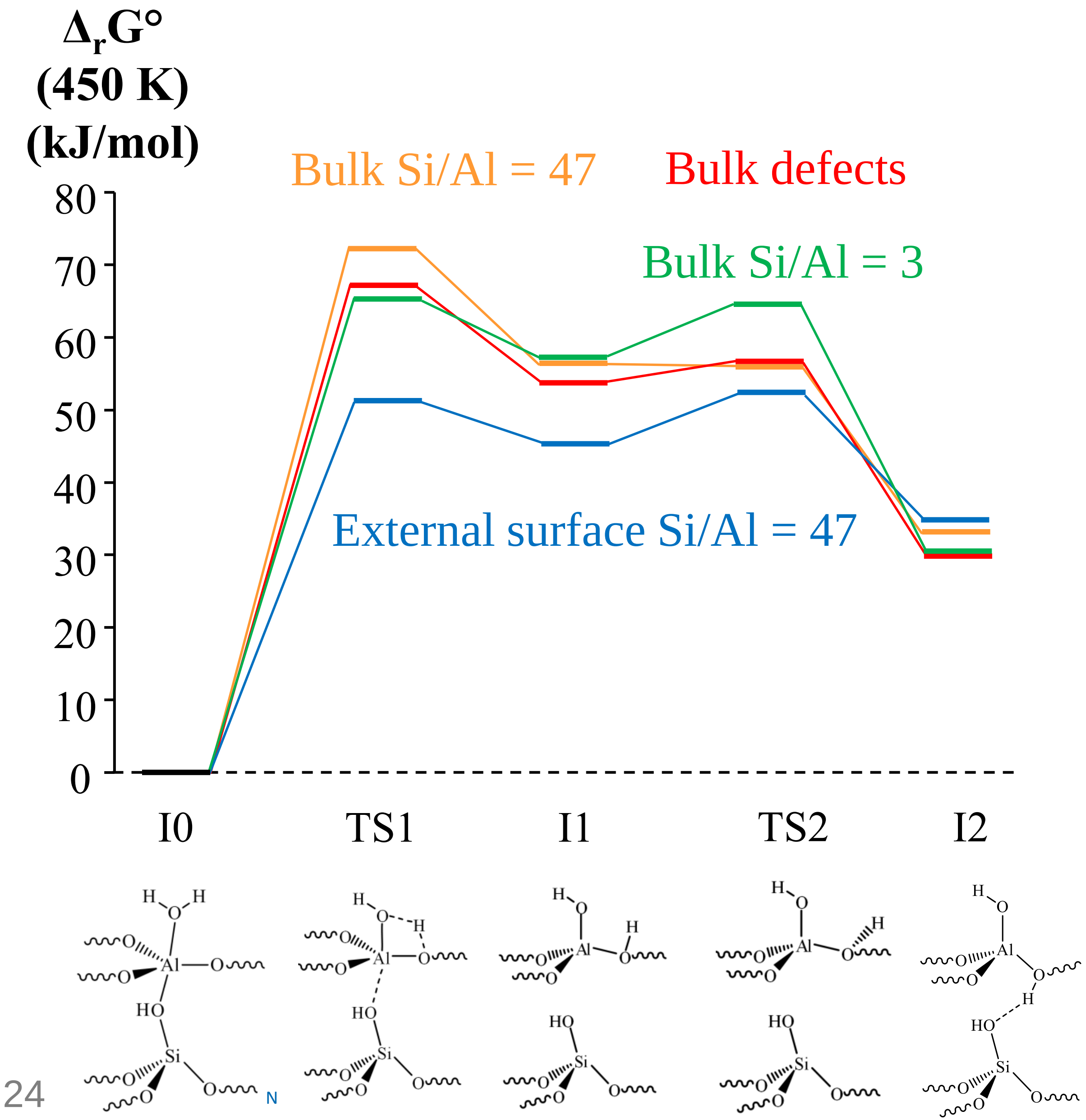
Adsorption in anti to BAS and axial substitution: always the most favorable mechanism

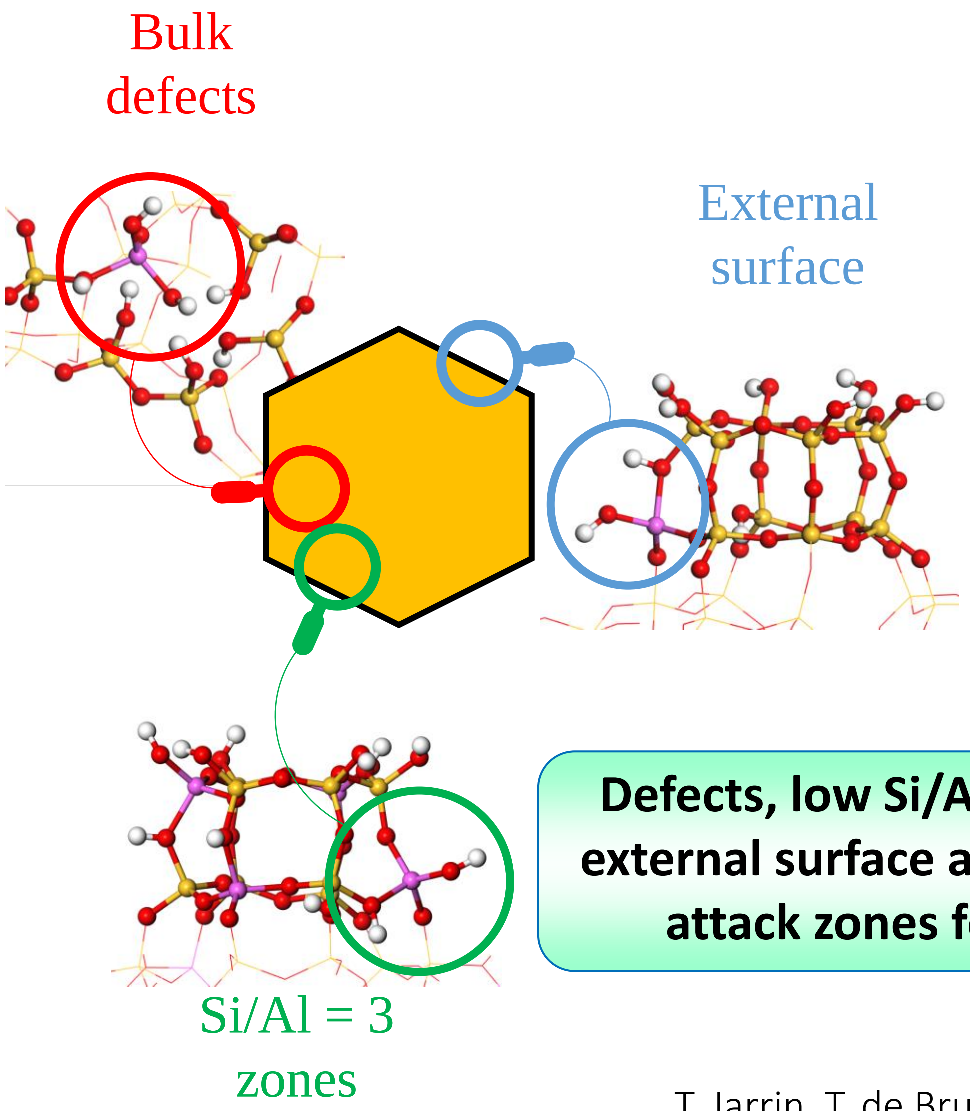
Silaghi et al., ACS Catal., **2015**, 5, 11

IMPACT OF DEFECTS, SI/AL RATIO AND EXTERNAL SURFACE

● Al ● Si ● O ● H

TO_3H faujasite

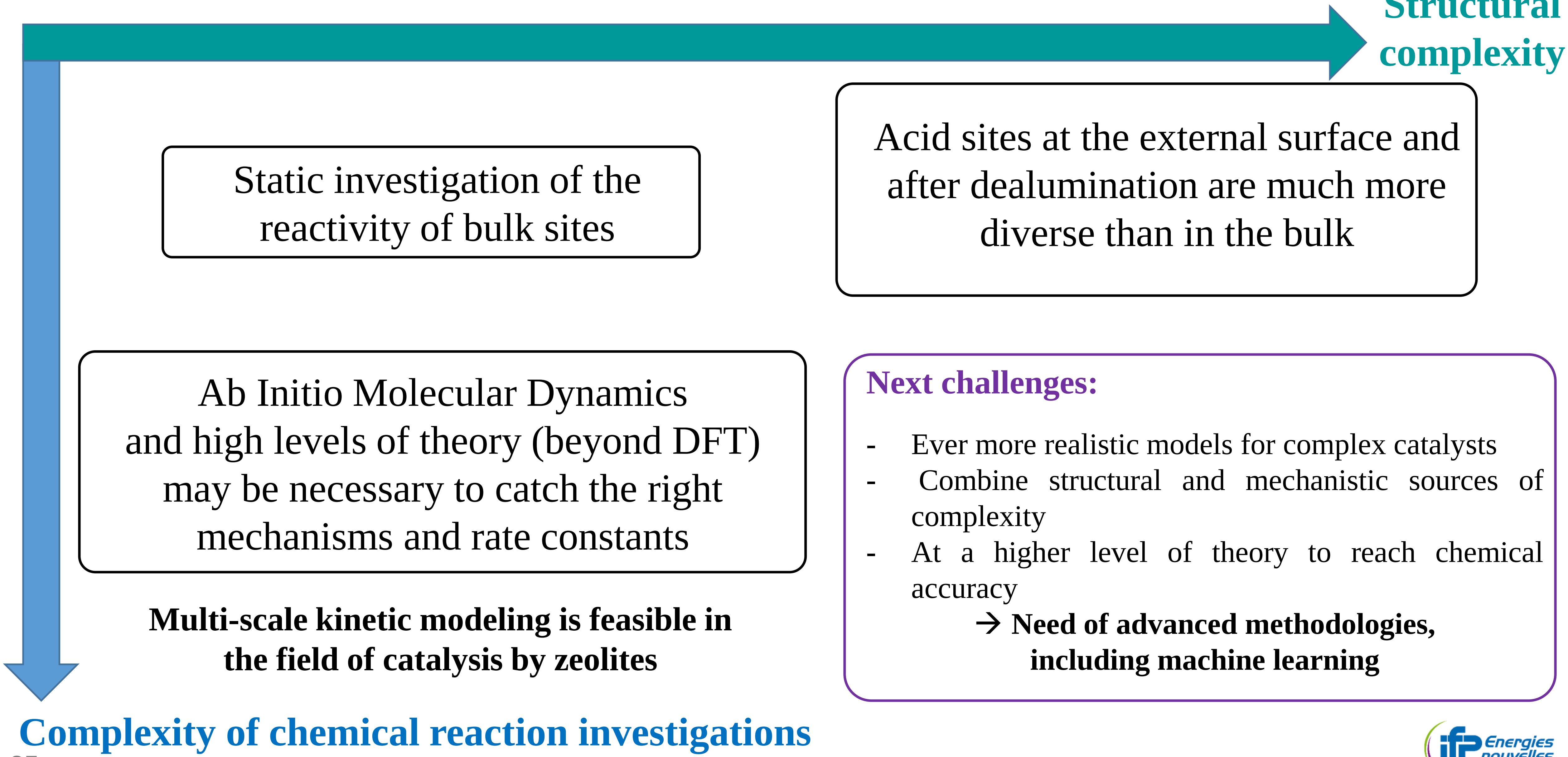




Defects, low Si/Al zones and external surface are preferred attack zones for water

T. Jarrin, T. de Bruin, C. Chizallet, *ACS Catalysis*, **2024**, 14, 1639

SIMULATION OF INTRICATE ALUMINOSILICATE CATALYSTS: STRUCTURAL AND MECHANISTIC COMPLEXITY



Structural complexity

Static investigation of the reactivity of bulk sites

Acid sites at the external surface and after dealumination are much more diverse than in the bulk

Ab Initio Molecular Dynamics and high levels of theory (beyond DFT) may be necessary to catch the right mechanisms and rate constants

Multi-scale kinetic modeling is feasible in the field of catalysis by zeolites

Next challenges:

- Ever more realistic models for complex catalysts
- Combine structural and mechanistic sources of complexity
- At a higher level of theory to reach chemical accuracy

→ **Need of advanced methodologies, including machine learning**

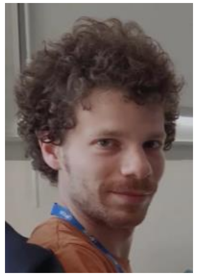
Complexity of chemical reaction investigations

ACKNOWLEDGEMENTS


E. Gutierrez


J. Rey


L. Treps


T. Jarrin

P. Raybaud
A. Gomez
C. Leroux
C. Bignaud
C. Demaret
JM. Schweitzer
V. Rouchon
M. Silaghi

L. Catita
A. Méthivier
E. Guillon
C. James
T. de Bruin
M. Rivallan
B. Harbuzaru
C. Bouchy
G. Pirngruber

T. Bucko
M. Gesvandtnerova

J. Sauer

D. Wisser
Z. Wang
D. Gajan
A. Lesage

M. Badawi
D. Rocca

Y. Schuurman

Question and Answer Session

Dr. Alexander Mavromaras

Materials Design

Dr. Céline Chizallet

IFP Energies nouvelles

Questions about Materials Design UGM

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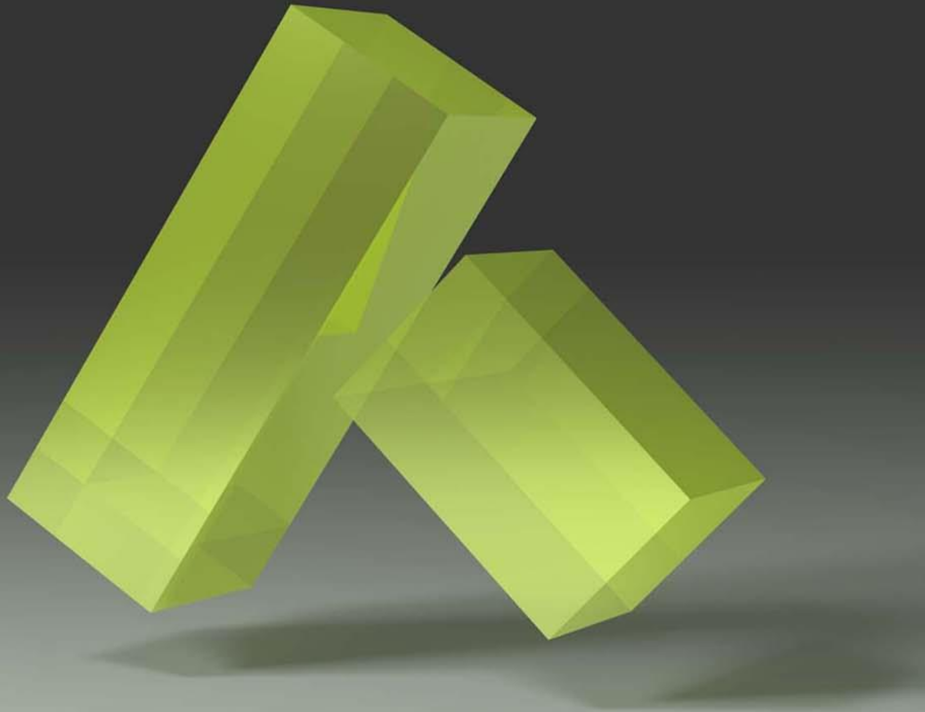

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Innovation by Simulation