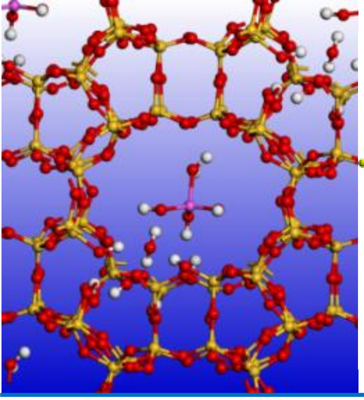
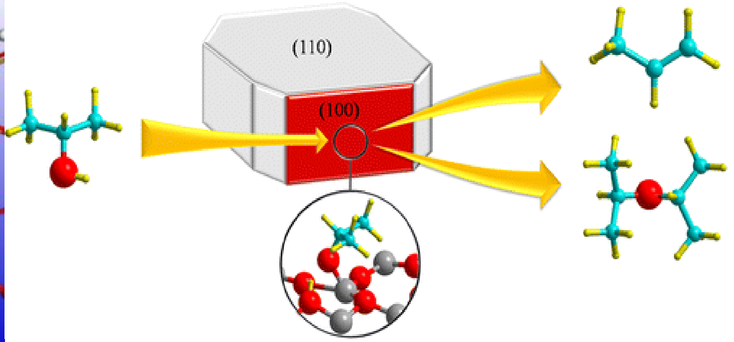
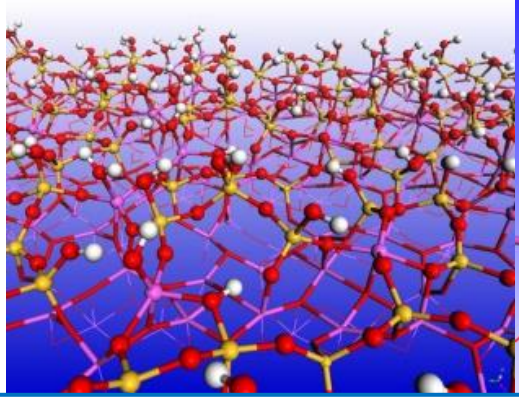
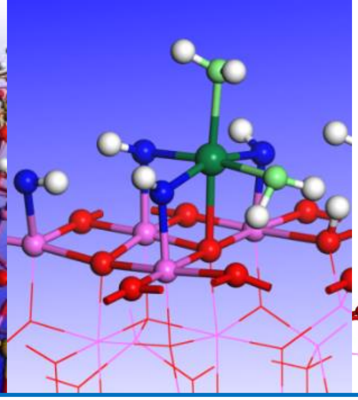
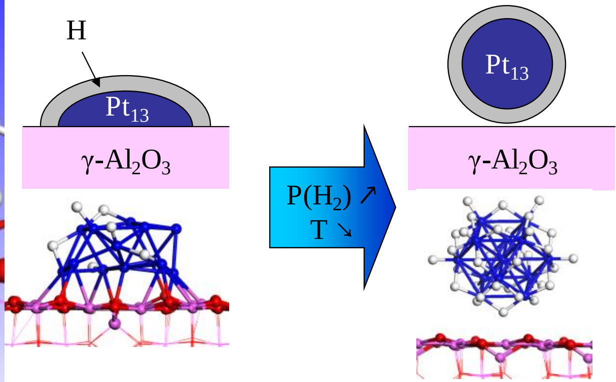










LA CHIMIE THÉORIQUE AU SERVICE DE LA CARACTÉRISATION DES CATALYSEURS HÉTÉROGÈNES

CELINE CHIZALLET

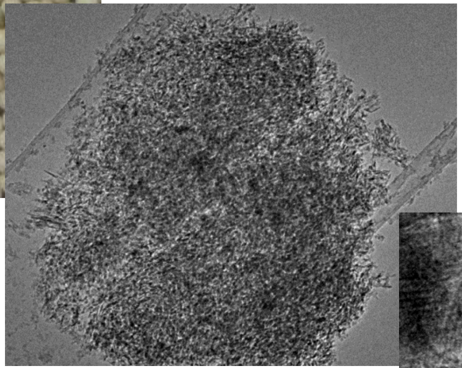
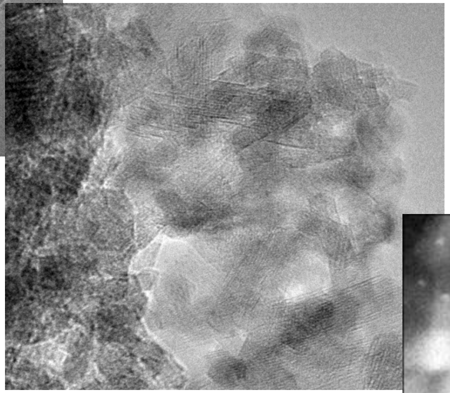
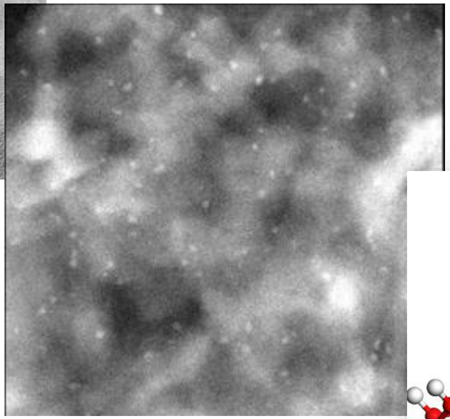
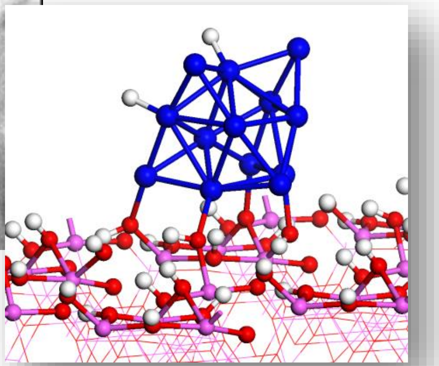
IFP Energies nouvelles
Catalysis and Separation Division
Rond Point de l'échangeur de Solaize, BP3
69360 Solaize, FRANCE

celine.chizallet@ifpen.fr

Energies nouvelles

WHY DO WE NEED MOLECULAR MODELLING IN INDUSTRIAL CATALYSIS ?

Zoom at the atomic scale
On a heterogeneous catalyst

Reforming catalyst
Pt/γ-Al_2O_3-Cl

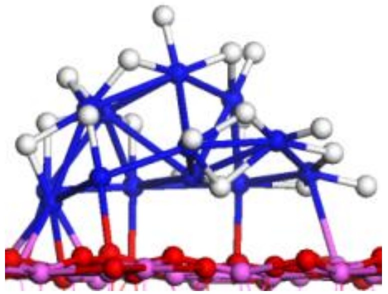
$$H\Psi = \varepsilon\Psi$$

aCLIMAX

TWO FAMILIES OF CATALYTIC SYSTEMS OF INDUSTRIAL RELEVANCE

1. Models for ultradispersed Pt/γ-Al_2O_3 catalysts in reactive environment

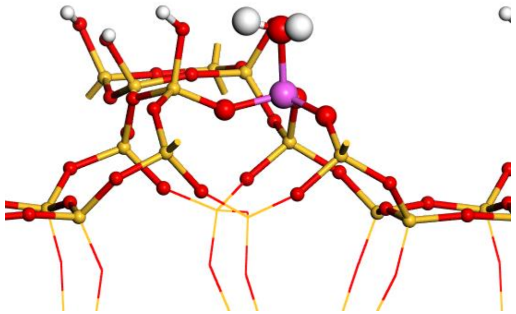
   Ductility of the particles



2. Models for the external surface of zeolite catalysts:

   Structural sources of complexity

   Variety of acid sites



FIRST EXAMPLE: SUPPORTED ULTRA-DISPERSED Pt/γ-Al_2O_3 CATALYSTS

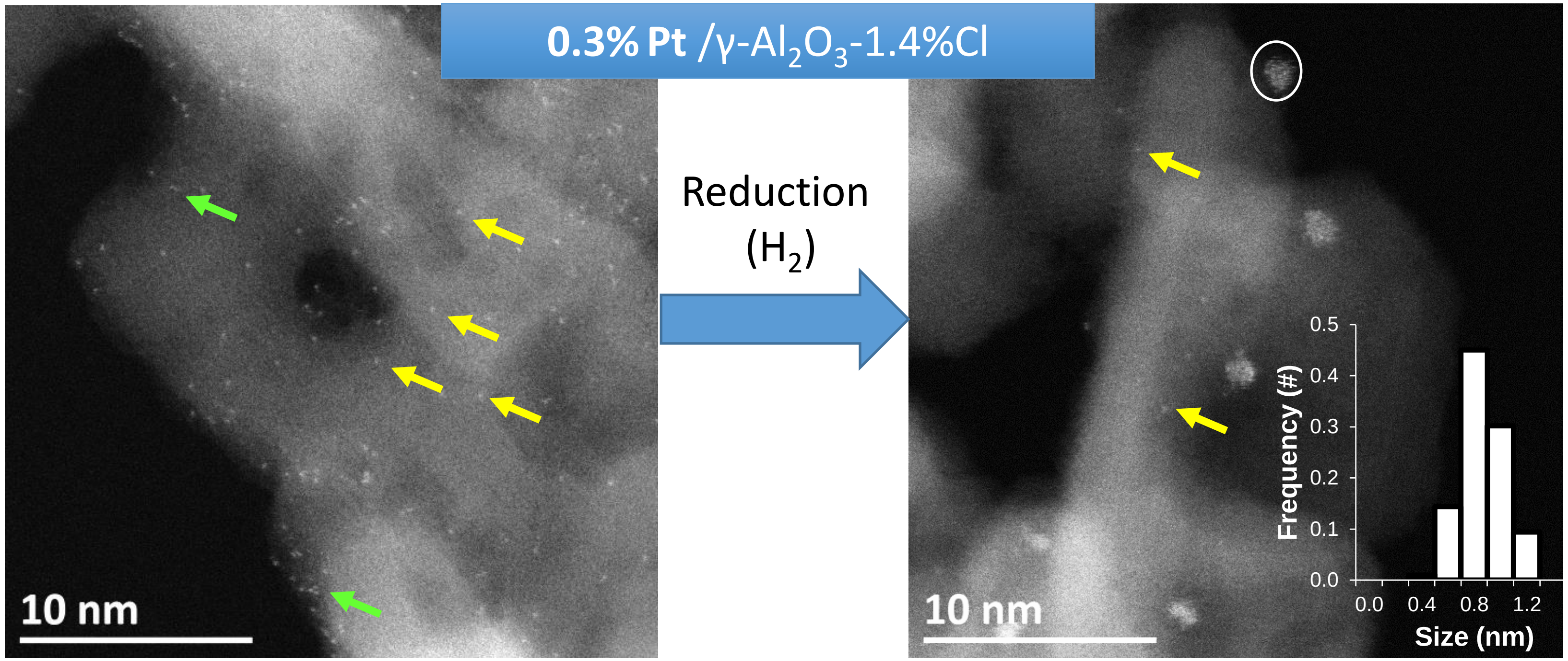
Relevant systems for PDH, catalytic reforming, etc. → importance of P(H_2)

HR-HAADF-STEM

Cs-corrected JEOL JEM 2100F microscope (200kV)
JEOL HAADF detector
Electron probe size: 0.11 nm

Ovidiu Ersen, Walid Baaziz

IPCMS



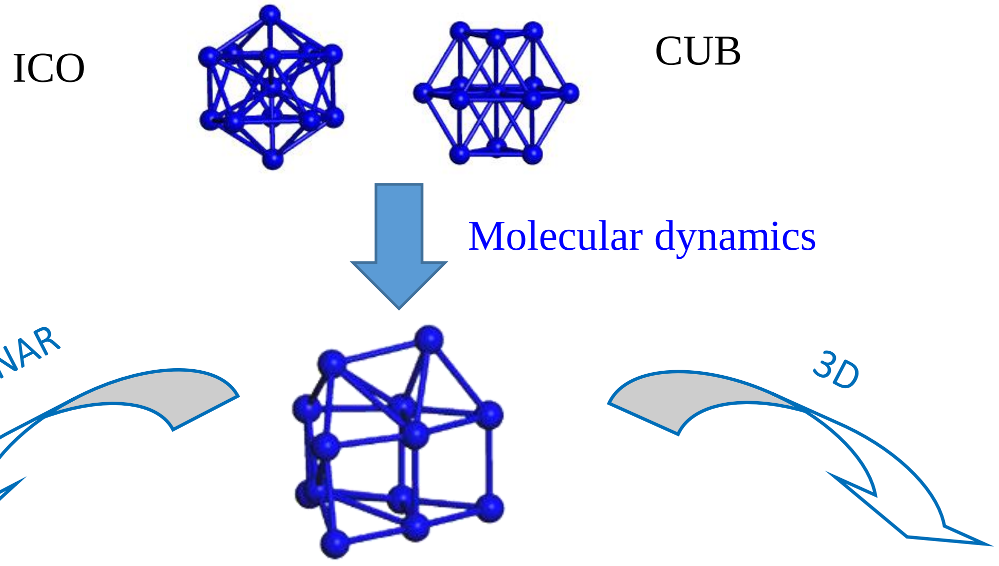
« Oxide » « Reduced »

Single atoms prevail in the oxide state

Consistent control of nanoparticle size at 0.9 nm

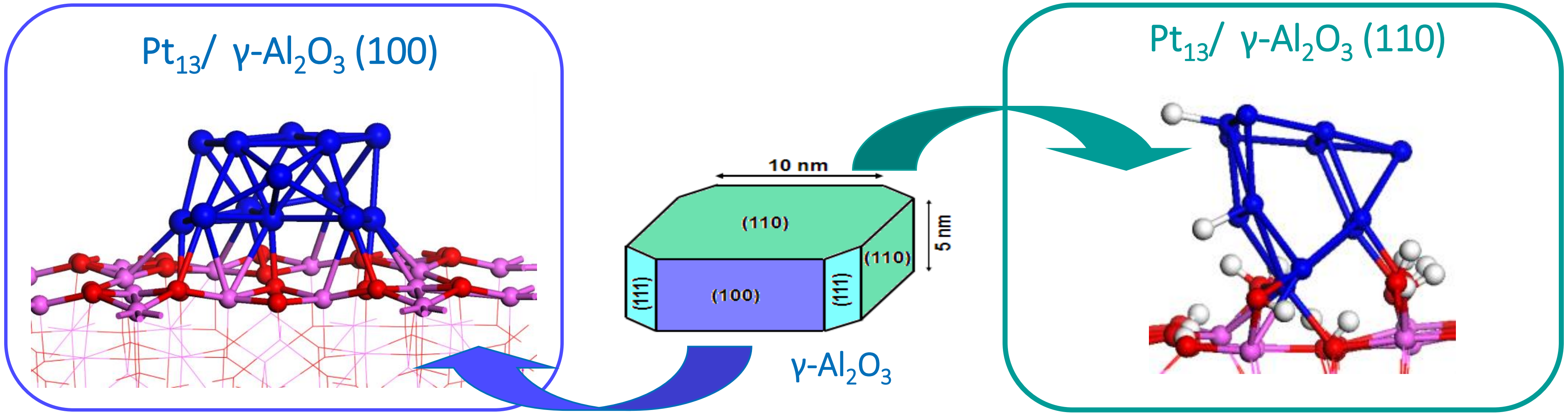
A.T.F. Batista et al., ***ACS Catal***., 2020, 10, 4193

$Pt_{13}/\gamma\text{-}Al_2O_3$



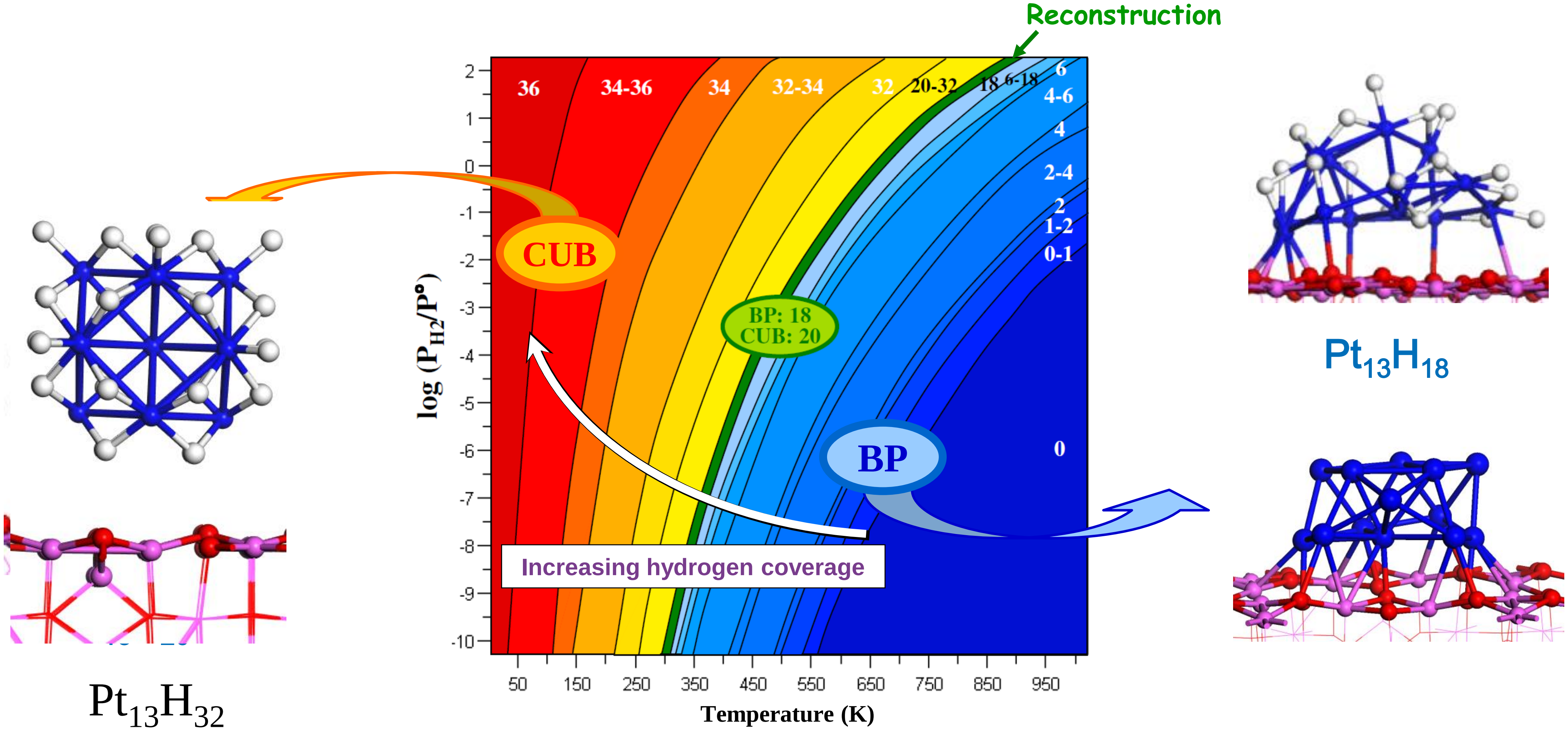
Phys. Rev. B, **2009**, 79, 195416

J. Catal. **2010**, *274*, 99–110
ACS Catal. **2012**, *2*, 1346–1357



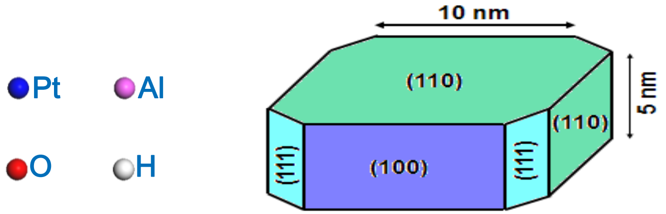
Morphology depends on the alumina facet and hydroxylation level
Far form symmetric !

RECONSTRUCTION OF THE PARTICLES UPON EXPOSURE TO H_2



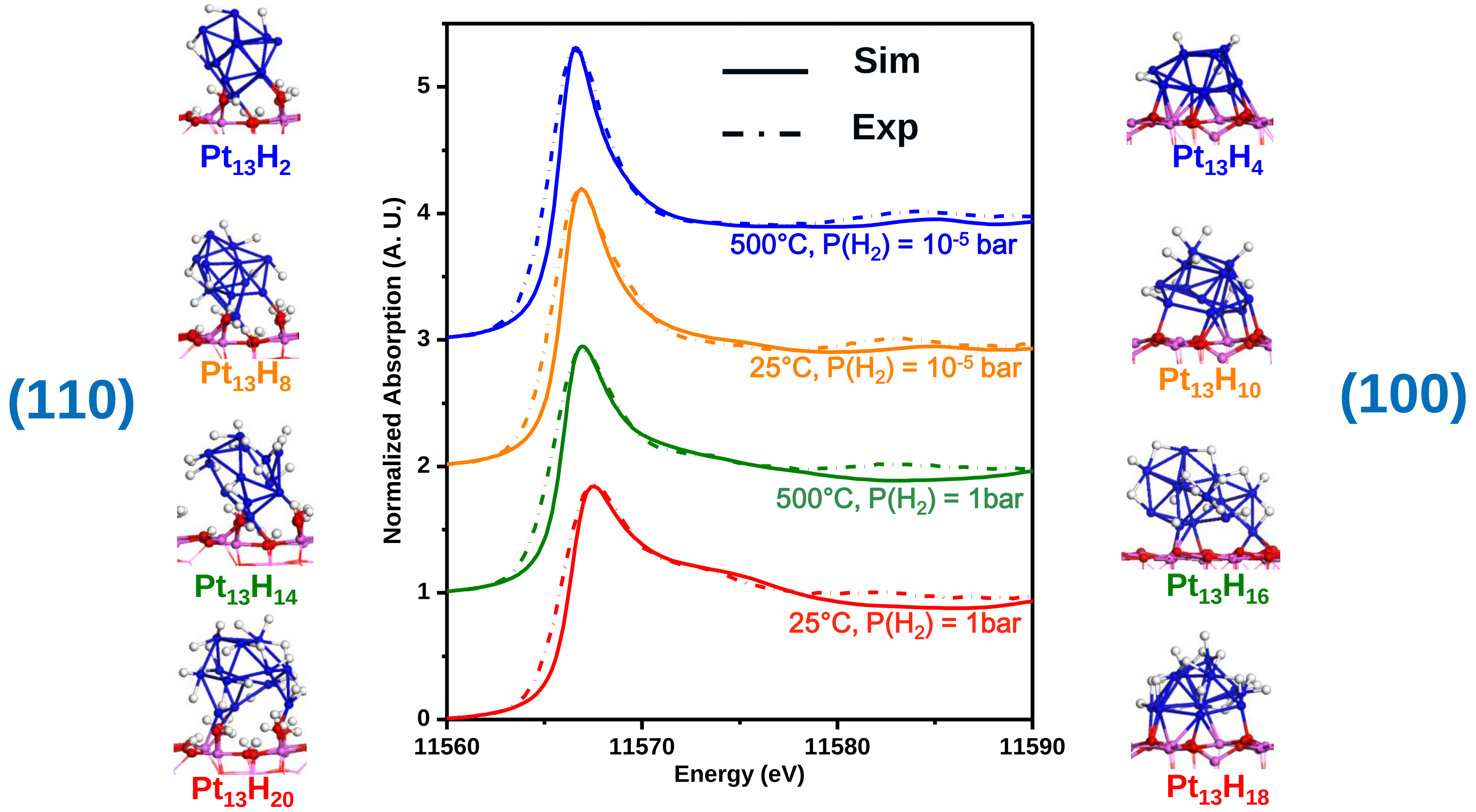
C. Mager-Maury, G. Bonnard, C. Chizallet, P. Sautet, P. Raybaud, ***ChemCatChem*** , 3 (**2011**) 99

HYDROGEN INTERACTION WITH Pt/ALUMINA: XANES



Jean-Louis Hazemann, Olivier Proux

Pt L_3 edge (11564 eV)
Double crystal Si(220) monochromator
Two Rh-coated Si mirrors
Fluorescence mode
Multi-crystal analyzer Ge(100)
+ mono-element silicon drift detector



Identification of hydrogen coverage / morphology on each surface and for each experimental condition

A. Gorczyca, V. Moizan, C. Chizallet, O. Proux, W. Del Net, E. Lahera, J. L. Hazemann, P. Raybaud, Y. Joly, ***Ang. Chem. Int. Ed.***, 53 (**2014**) 12426

HYDROGEN INTERACTION WITH Pt/ALUMINA: INELASTIC NEUTRON SCATTERING

Elena Groppo, Andrea Piovano

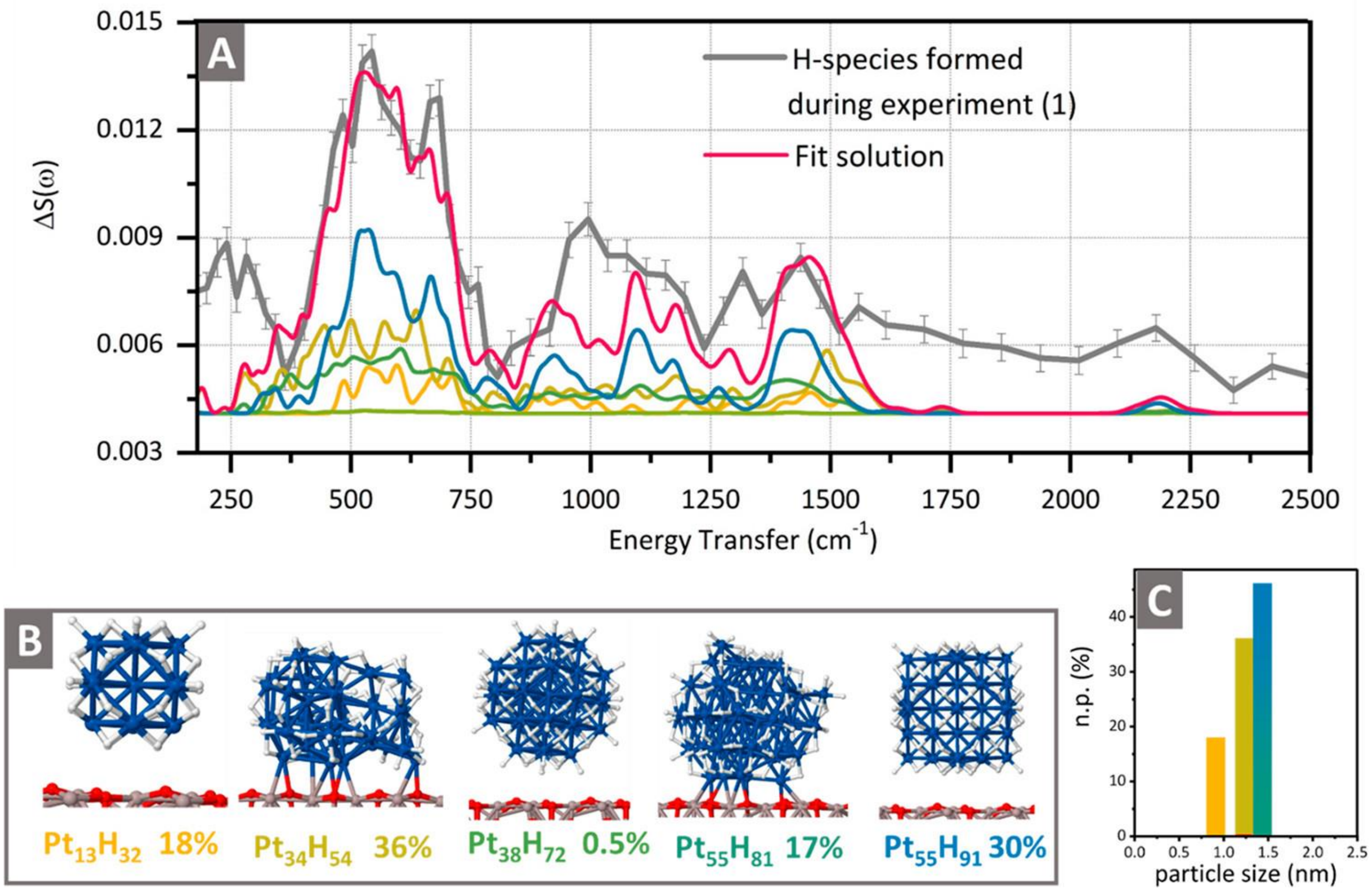
5 wt % Pt/Al_2O_3

1.4 ± 0.4 nm

393 K outgasing

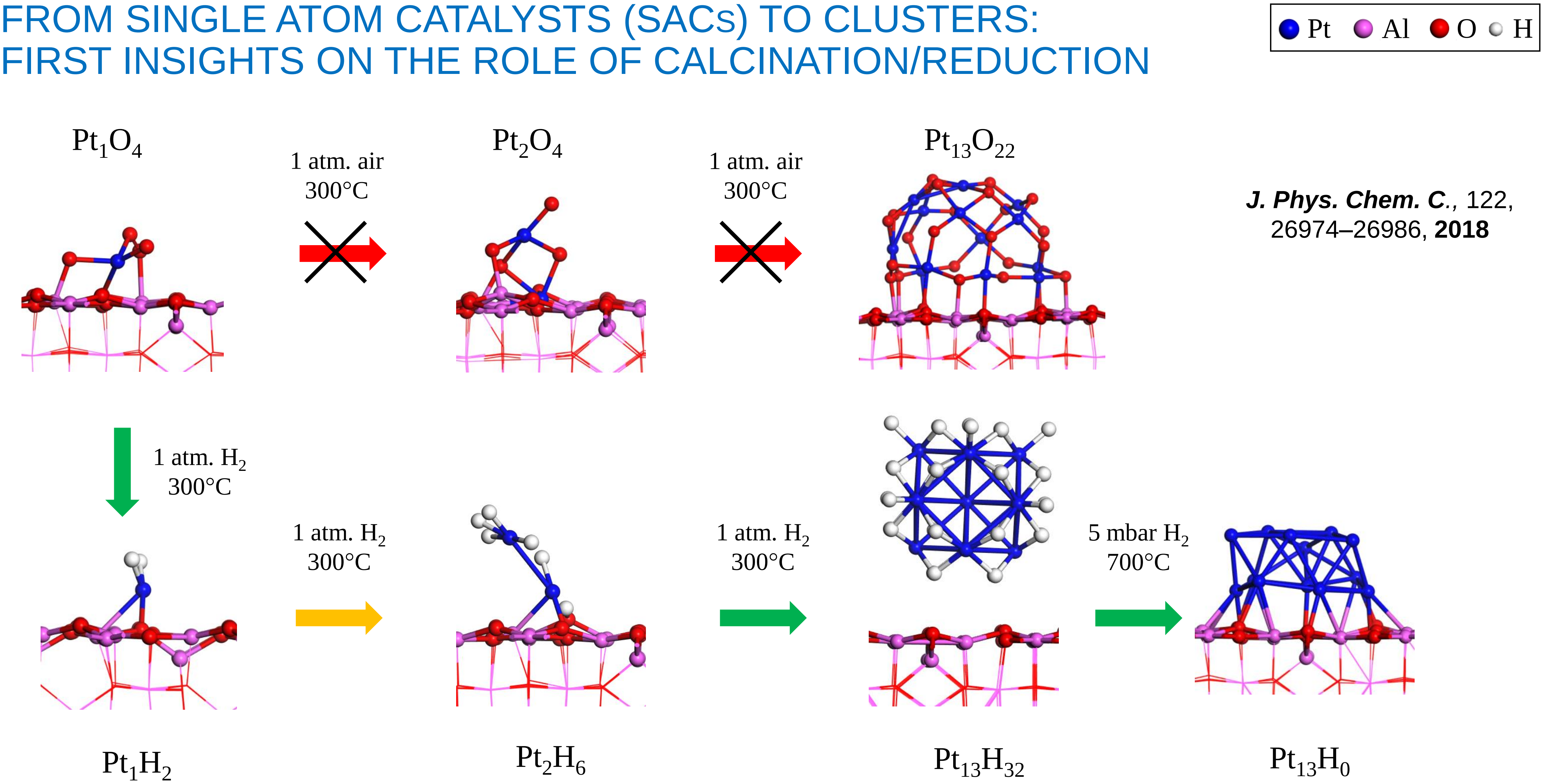
IN1-Lagrange

Si311 and Cu220 monochromators



E. Vottero et al., ***ACS Catal***., 12 (**2022**) 5979

FROM SINGLE ATOM CATALYSTS (SACs) TO CLUSTERS: FIRST INSIGHTS ON THE ROLE OF CALCINATION/REDUCTION

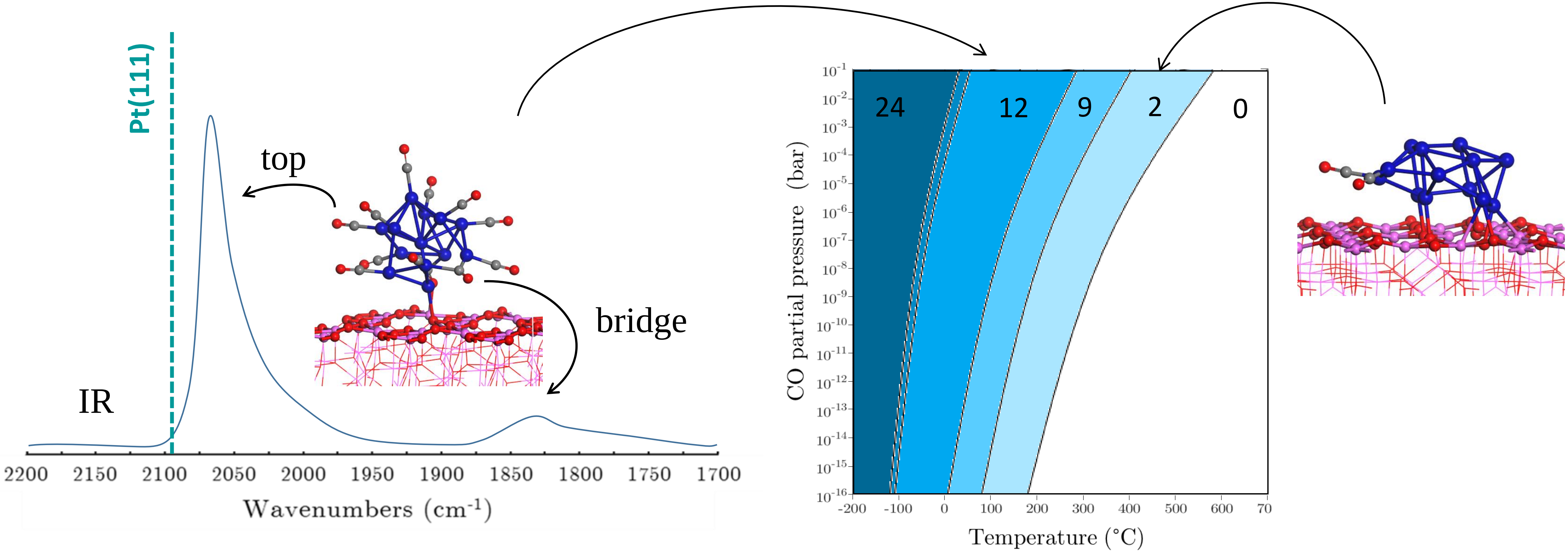


J. Phys. Chem. C, 122, 26974–26986, **2018**

Pt remains in the form of single atoms under oxidizing atmosphere, mobile clusters form upon reduction
Confirmed by EXAFS and E-HR-STEM

Nanoscale, 11, 6897- 6904, **2019**

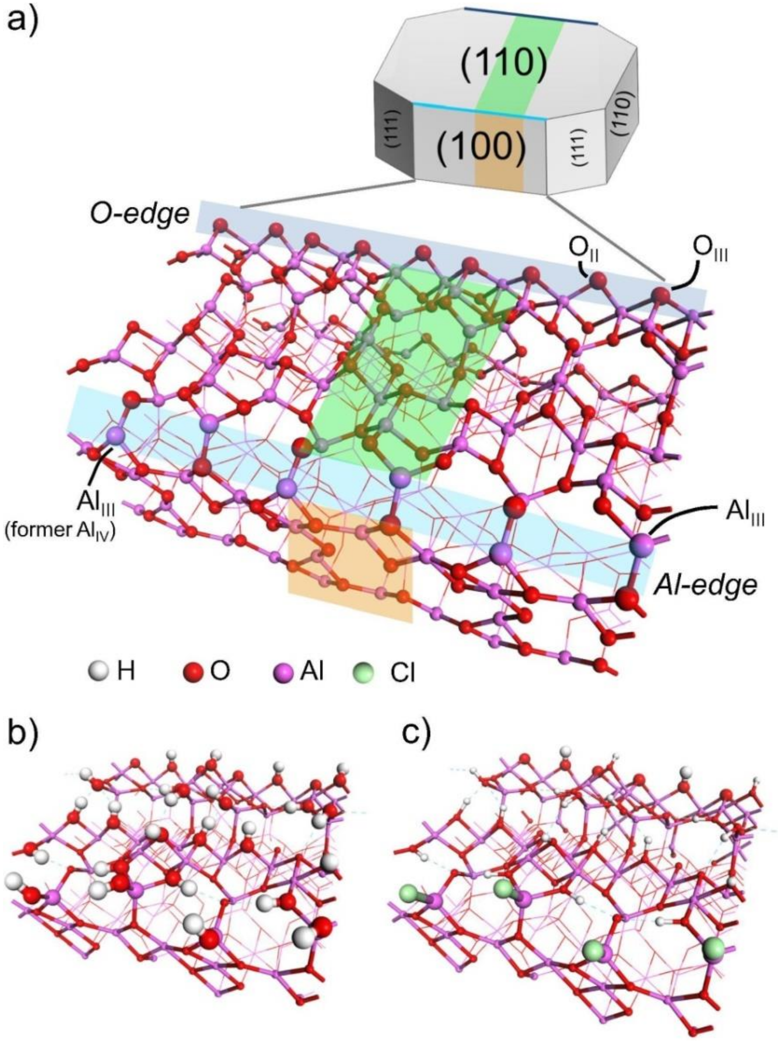
ADSORPTION OF CO ON SUPPORTED PLATINUM CLUSTERS



Reconstruction upon exposure to CO.
Size effect: ↗ strenght of interaction , ↘ IR frequency

A. Sangnier, E. Genty, M. Iachella, P. Sautet, P. Raybaud, M. Matrat, C. Dujardin, C. Chizallet, ***ACS Catal.*** 2021, 11, 13280

IMPORTANCE OF THE EDGES OF THE ALUMINA PLATELETS

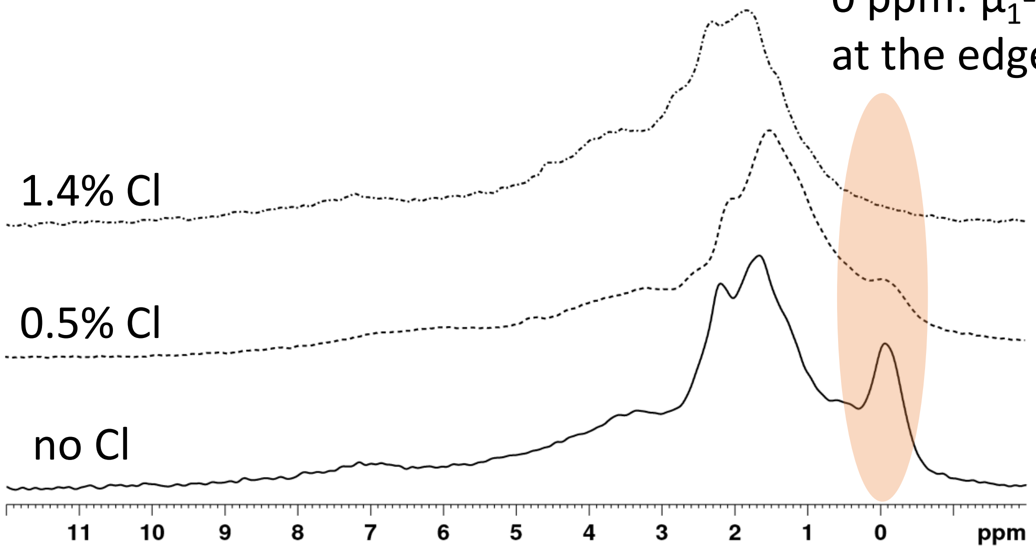


Batista et al., ***J. Catal***. 2019, 378, 140

Assignment of the ^{1}H NMR spectra

^{1}H Nuclear Magnetic Resonance

0 ppm: μ_1-OH at the edge



Bruker Avance III 800 SB 800 MHz
30 kHz MAS
DEPTH sequence

All Cl up to 1.4% are located on the edges

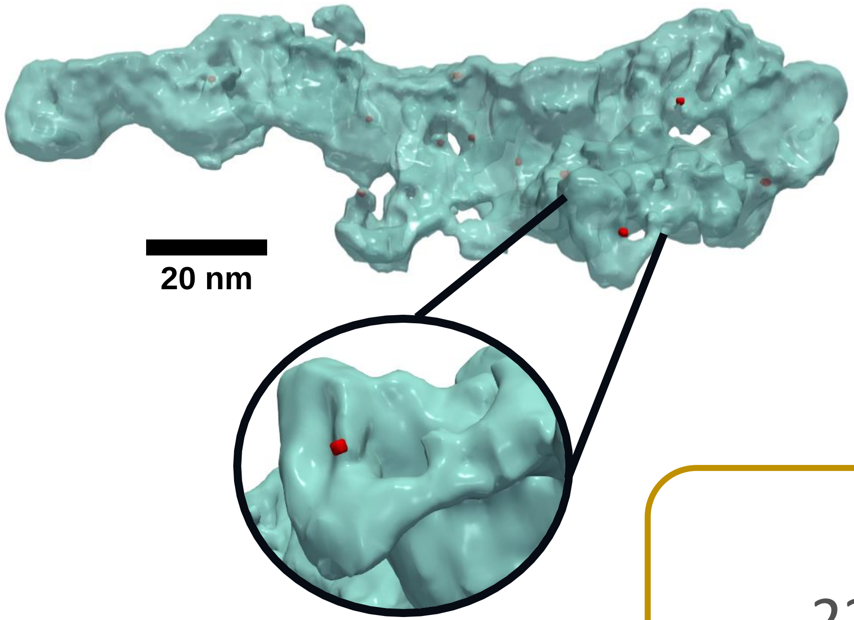
Bruker Avance III 800 SB 800 MHz
30 kHz MAS
2.5 mm rotor with Vespel® caps
DEPTH sequence

Centre de RMN à Très Hauts Champs

Anne Lesage, David Gajan, Dorothea Wisser

LOCATION OF PLATINUM NANOPARTICLES ON THE ALUMINA SUPPORT
ELECTRON TOMOGRAPHY

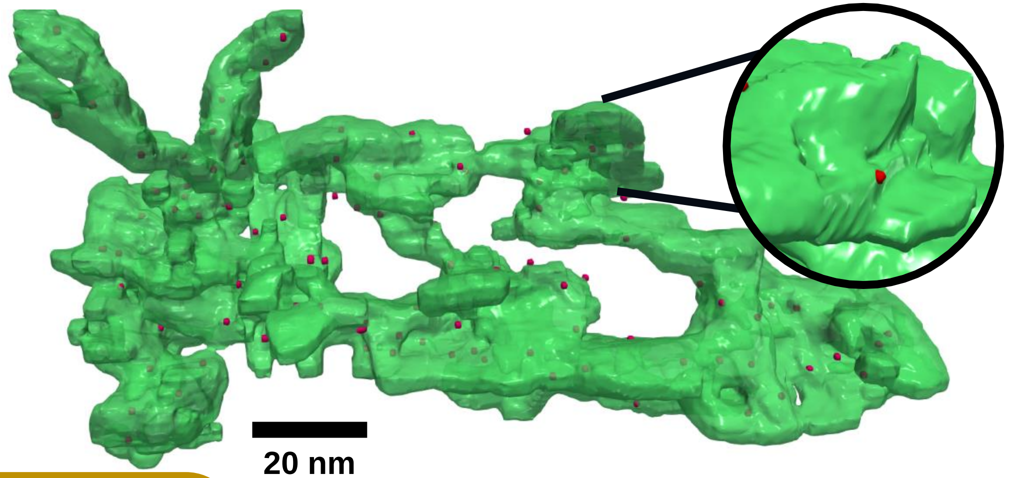
0.3%Pt/γ-Al_2O_3-1.4%Cl



Pt NPs

Alumina

1%Pt/γ-Al_2O_3-1.4%Cl

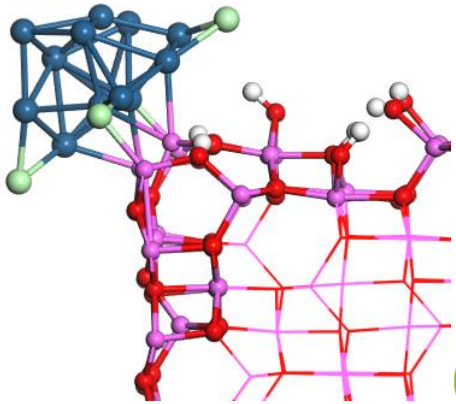


NP Location: **n=80**

22% of NPs on surfaces

78% of NPs on edges

A.T.F. Batista et al., ***ACS Catal***., 2020, 10, 4193



DFT: Pt_{13}/edge is energetically competitive with Pt_{13}/surface

Ovidiu Ersen, Walid Baaziz

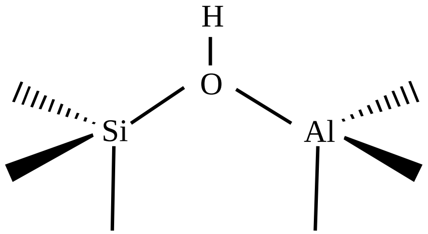
IPCMS

CATALYTIC ACTIVE SITE OF ALUMINOSILICATES?

* Framework and compensation cations in micropores

This work: protonic zeolites, Brønsted acid sites

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

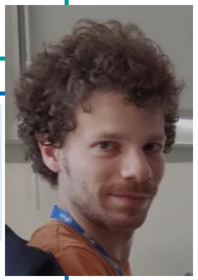


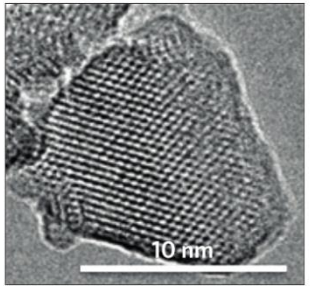
* Beyond the crystal bulk approach

- External surface / surface at mesopores

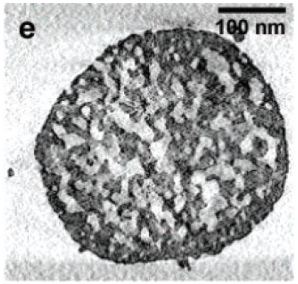
- Defects, EFAls

in CARMEN: poster of Thomas JARRIN

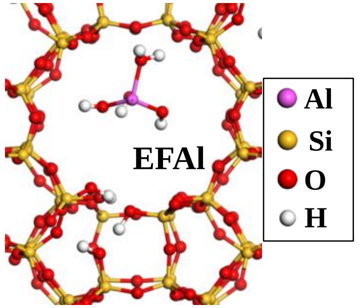




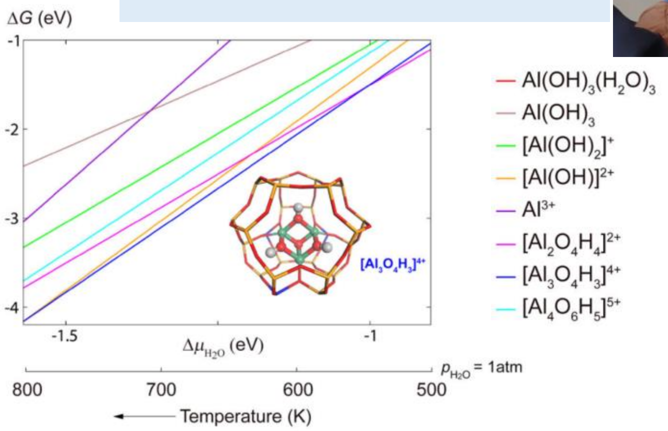
Nano-FAU
Mintova et al.
Nature Materials 2015



Hierarchical-MFI
Perez-Ramirez et al.
JACS 2005



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



ACS Catal. **2015**, *5*, 7024

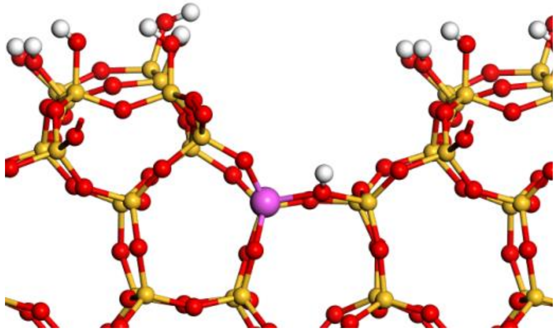
Need for molecular approaches

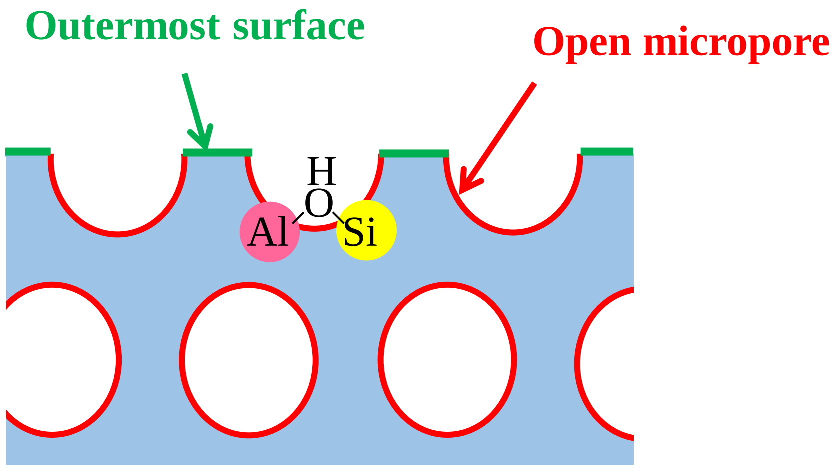
C. Chizallet, *ACS Catal.* **2020**, 10, 5579

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

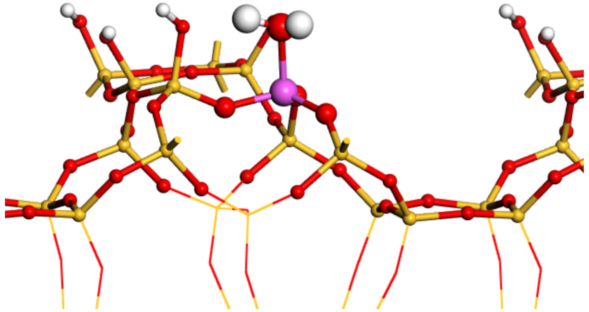
Al Si O H

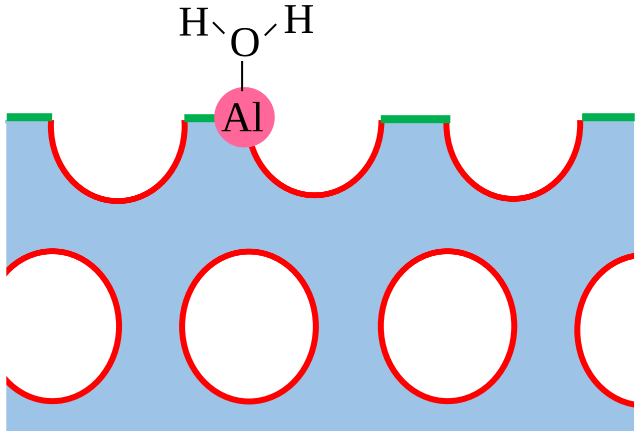
Similar stability as in bulk micropores:





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

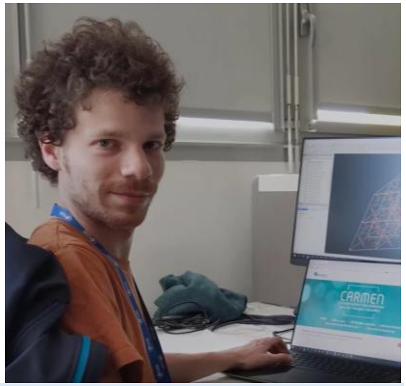




The surface promotes Al-(H_2O) at the outermost surface rather than Si-(OH)-Al

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

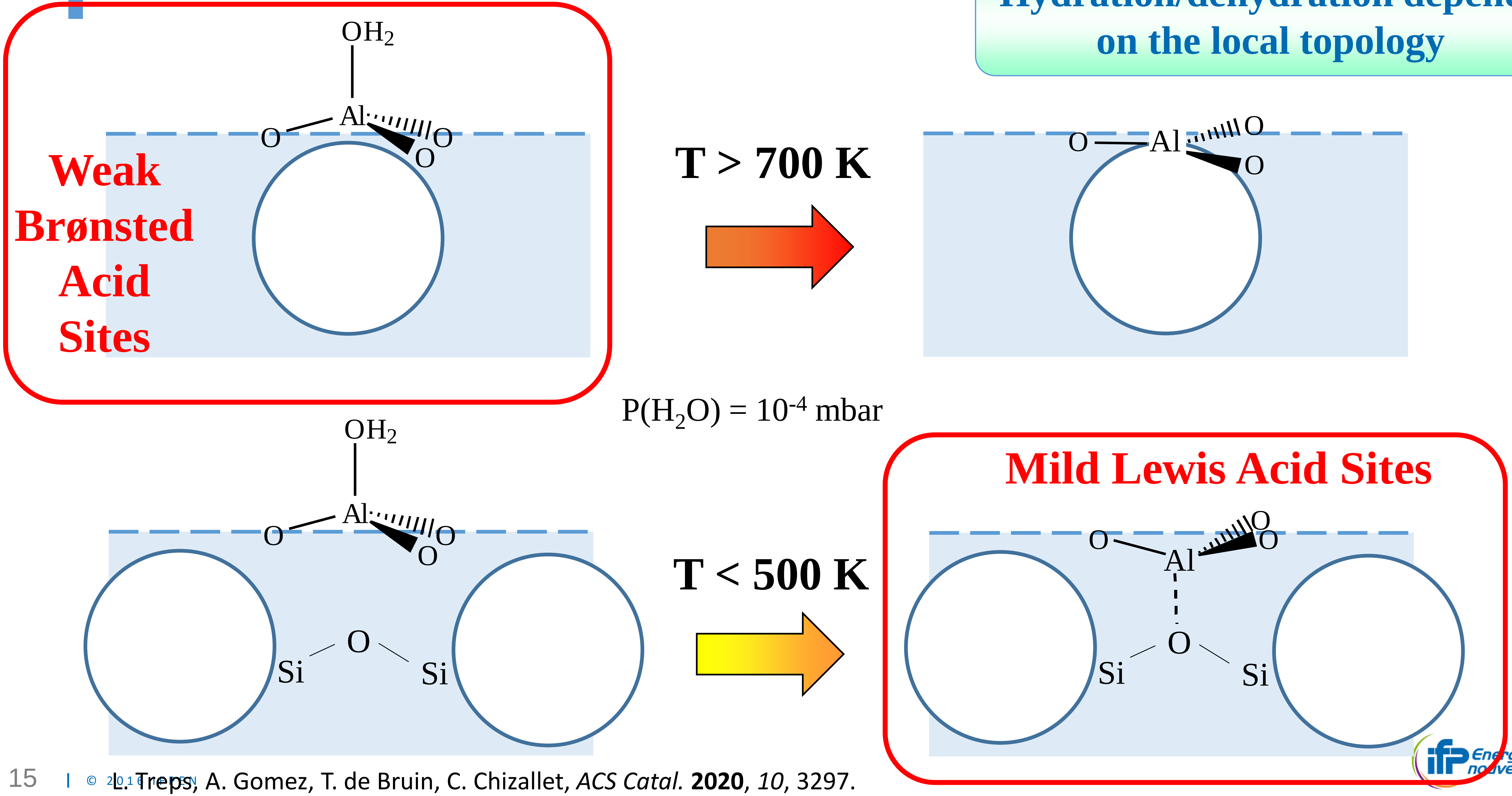
ZSM-5: L. Treps, A. Gomez, T. de Bruin, C. Chizallet, *ACS Catalysis*, **2020**, 10, 3297



Faujasite: see poster of Thomas JARRIN

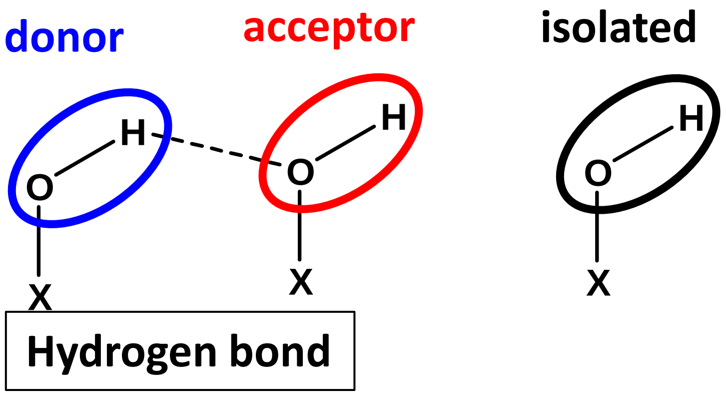
BRØNSTED (BAS) OR LEWIS (LAS) ACID SITES ?

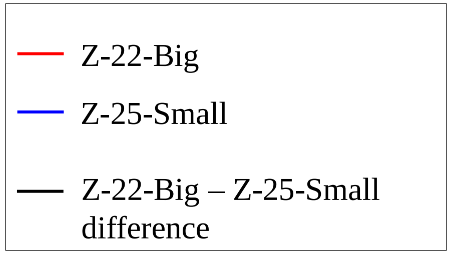
Hydration/dehydration depends on the local topology

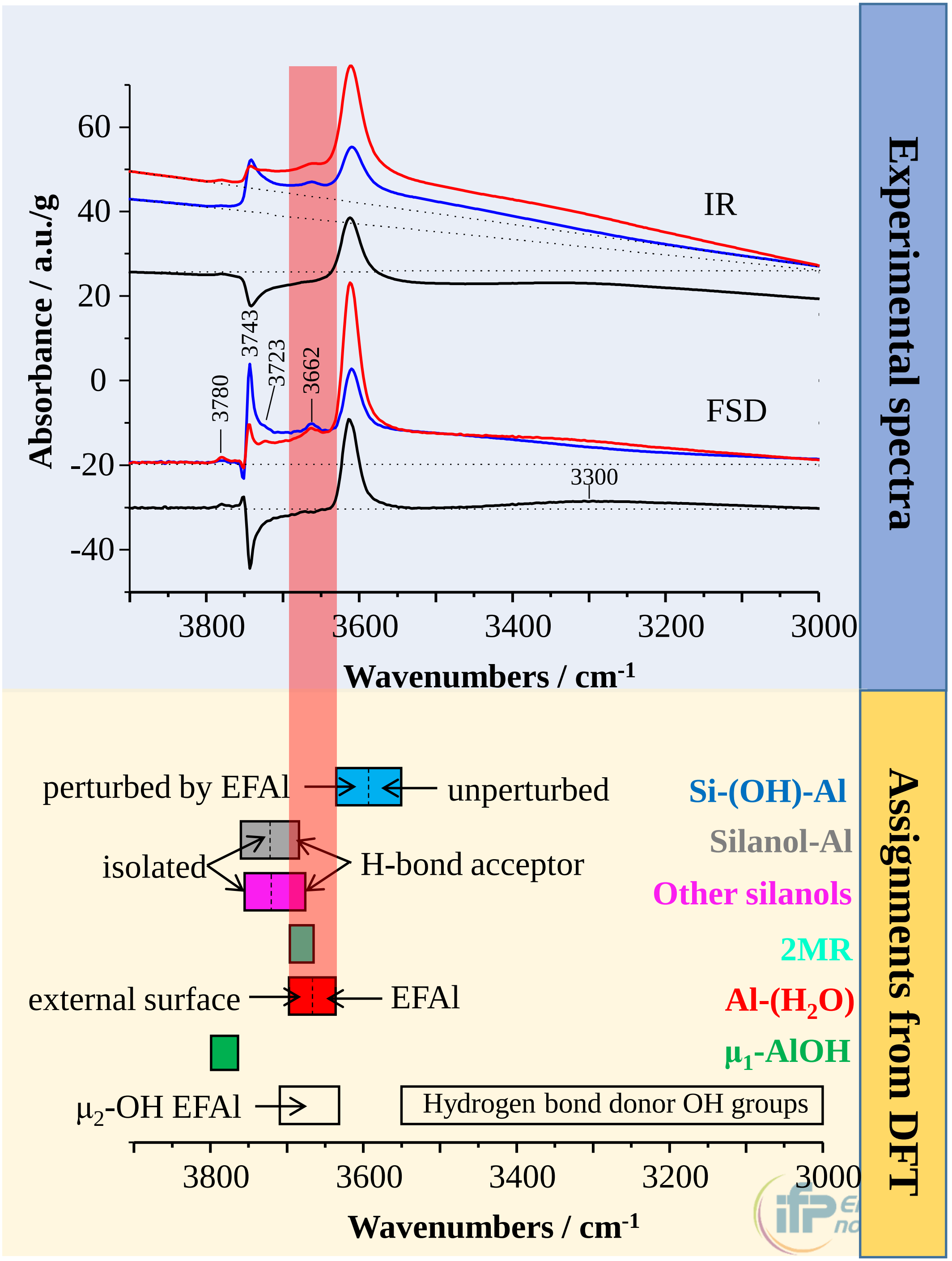


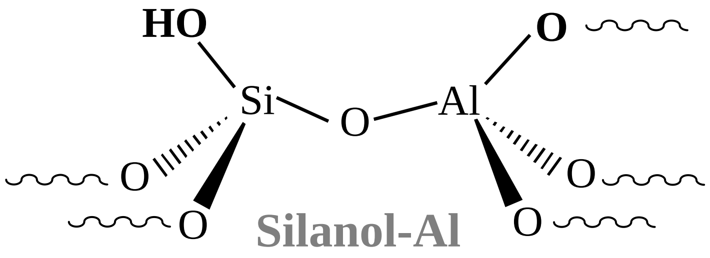
L. Treps, A. Gomez, T. de Bruin, C. Chizallet, *ACS Catal.* **2020**, *10*, 3297.

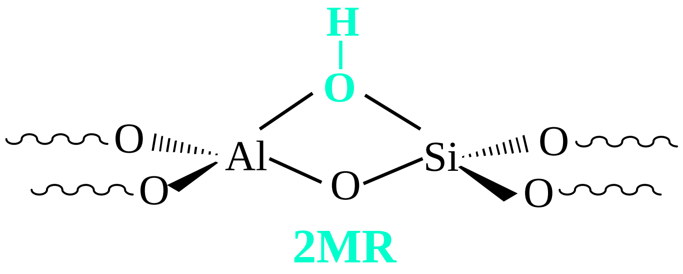
ASSIGNMENT OF FTIR SPECTRA

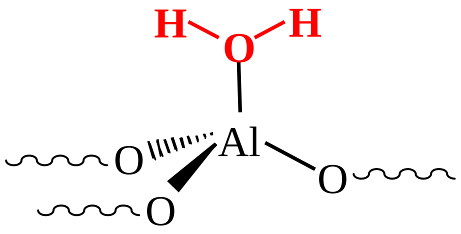


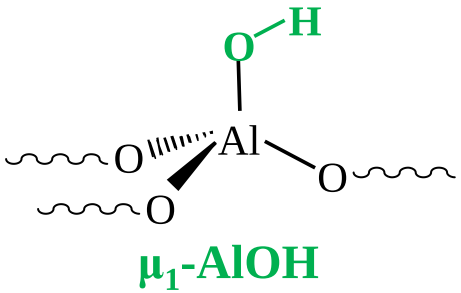


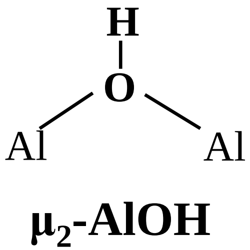












 |

J. Phys. Chem. C, **2021**, *125*, 2163-2181

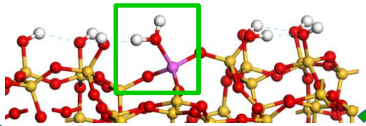
ASSIGNMENT OF ^{1}H NMR SPECTRA

FTIR and ^{1}H NMR are sensitive to:

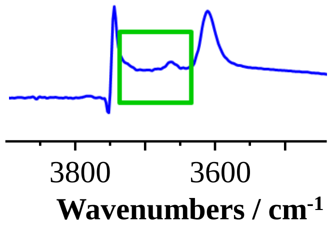
- similar parameters: H-bond, bridging versus silanols
- but not exactly overlapping structure parameters: 2MR, Al-(H_2O)

Zones usually assigned to EFALS are not exclusively due to EFALS
^{1}H NMR: bands usually assigned to Si-(OH)-Al groups are also due to Al-H_2O

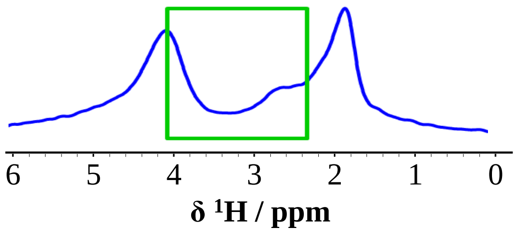
DFT calculations

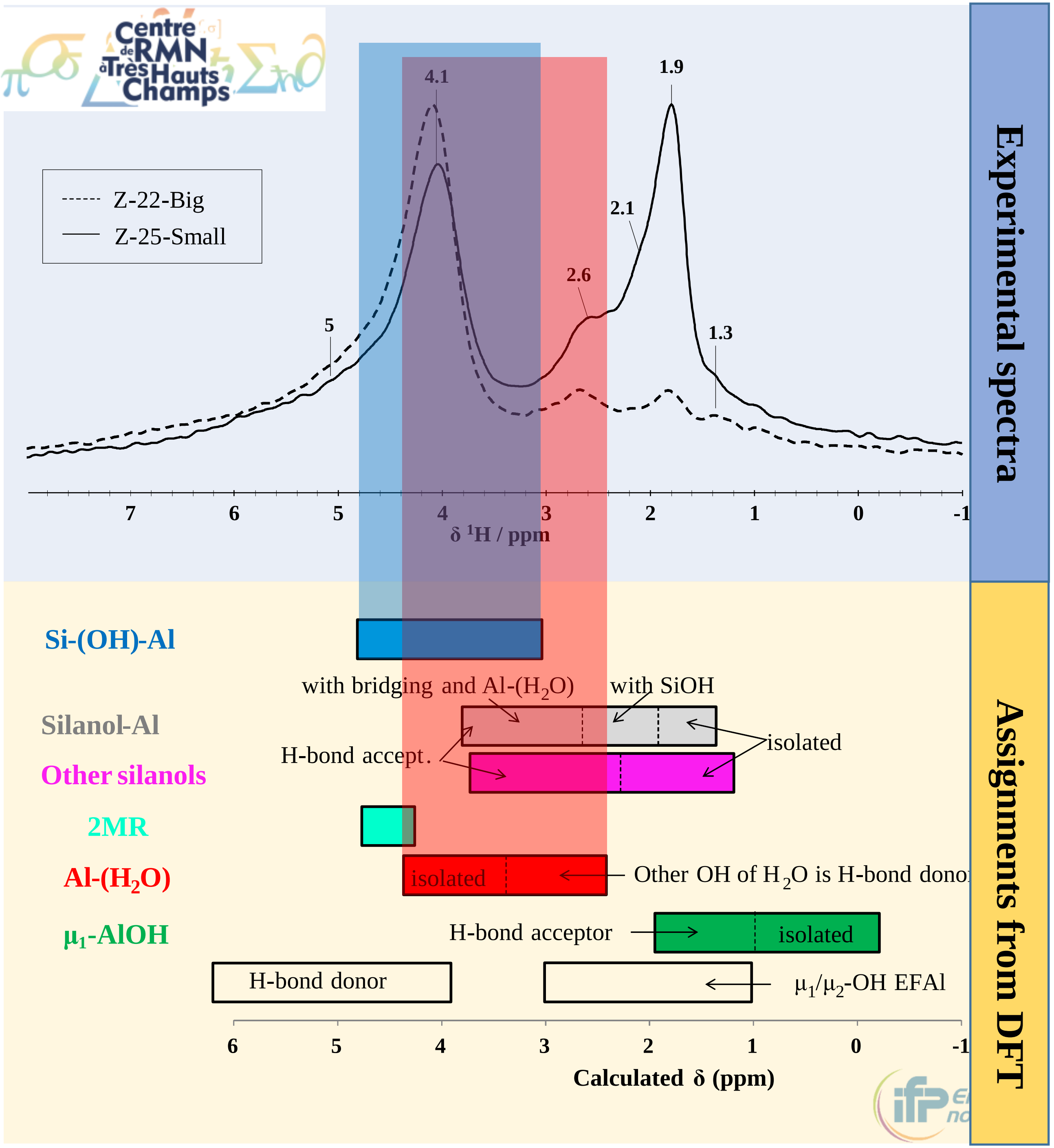


FSD FTIR



800 MHz ^{1}H MAS NMR





J. Phys. Chem. C, **2021**, *125*, 2163-2181

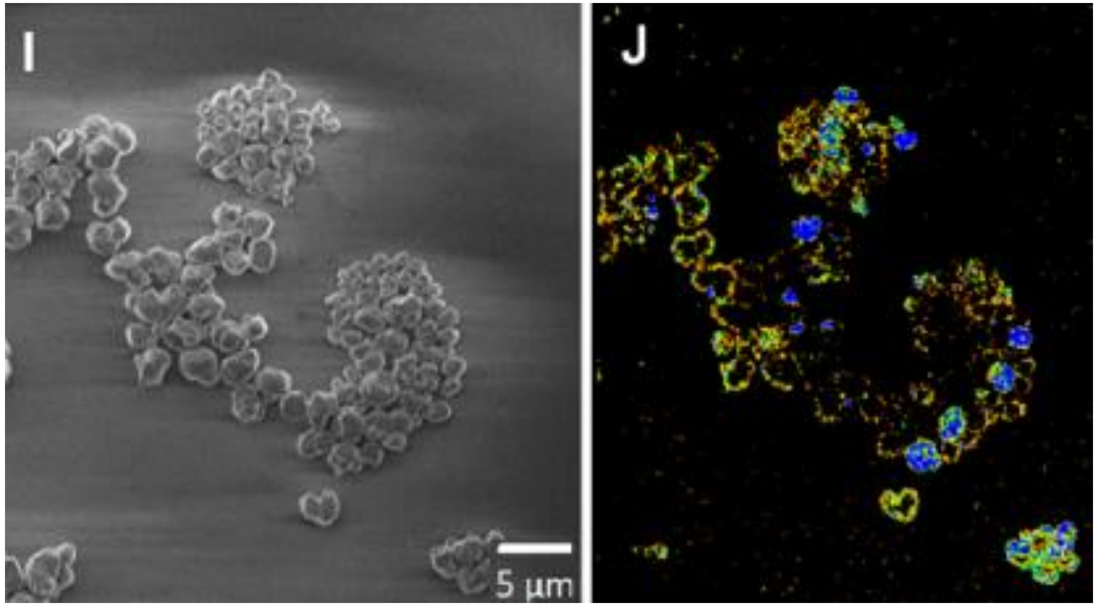
TOWARDS SHAPING: SYNERGY OF FLUORESCENCE MICROSCOPY AND DFT

KU LEUVEN

K. Kennes, A. Kubarev, M. Roeffaers

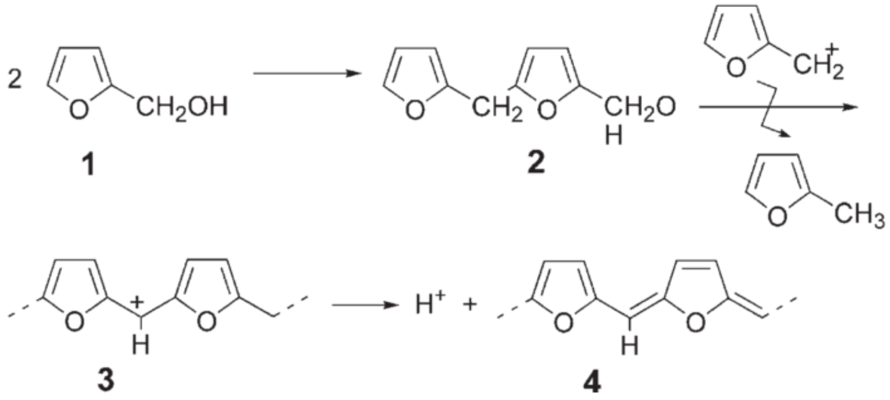
Confocal laser-scanning microscopy (CLSM)
Nanometer accuracy by stochastic chemical reactions (NASCA)

H-ZSM-5, Si/Al = 507



Kennes et al., *ChemCatChem* **2017**, 9, 3440

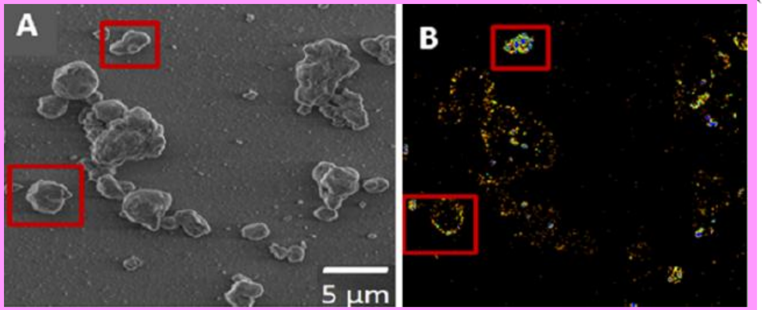
Furfuryl alcohol oligomerization generates fluorescent molecules on acid sites

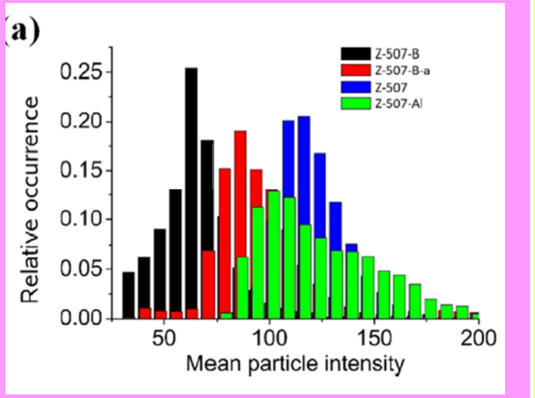


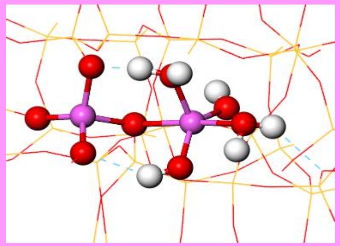
M.B.J. Roeffaers et al., *Angew. Chem. Int. Ed.*, **2007**, *46*, 170

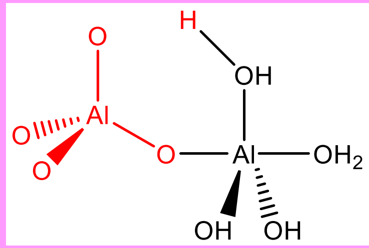
TOWARDS SHAPING: SYNERGY OF FLUORESCENCE MICROSCOPY AND DFT

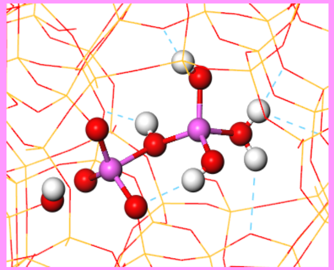
Alumina binders

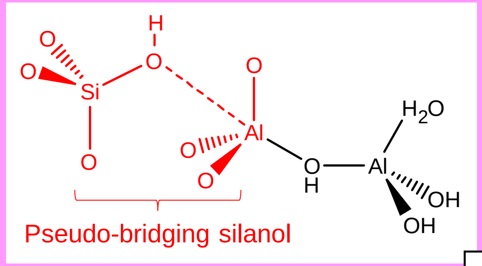




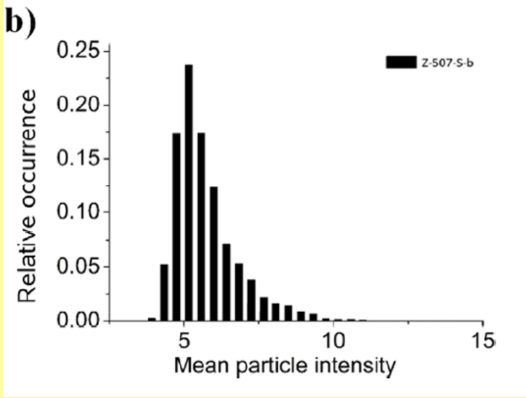


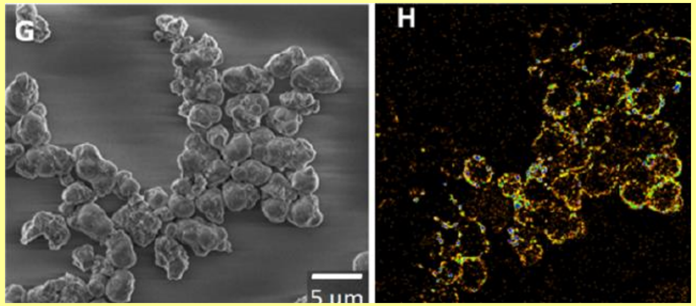


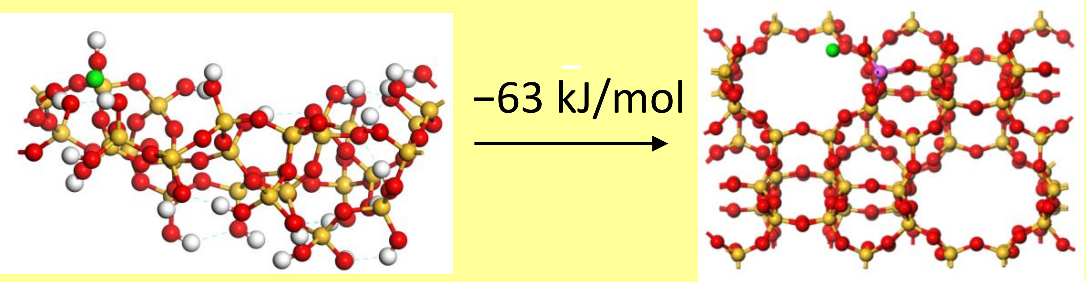


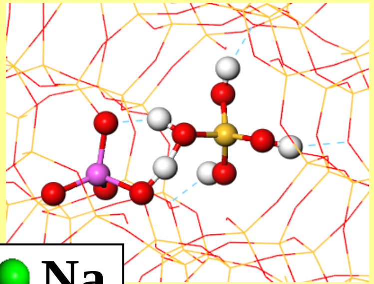


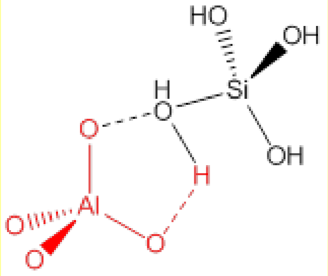
Silica binder







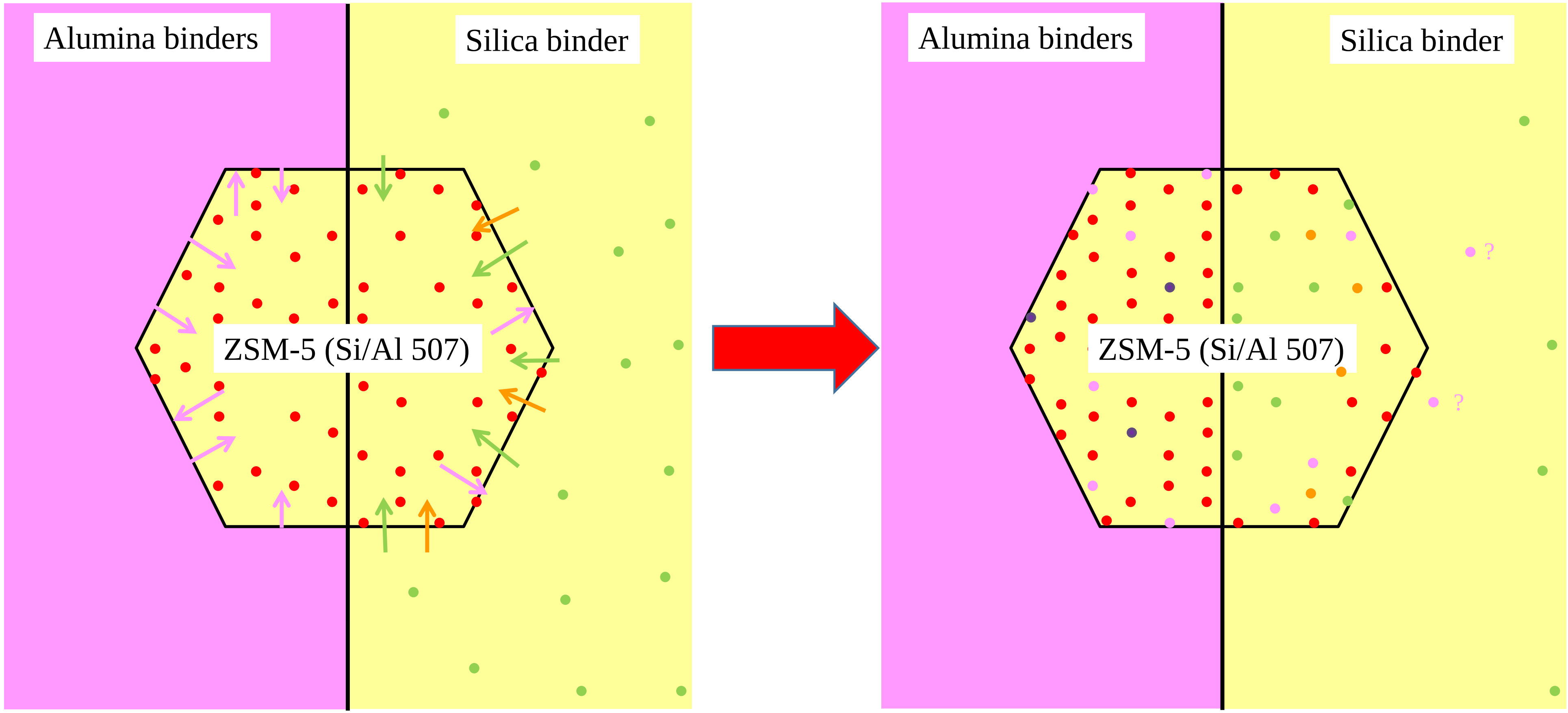




Al Si O H Na

Kennes et al., *ACS Catal*. **2022**, 12, 6794

MECHANISMS INTO PLAY DURING SHAPING



- Framework Brønsted acid site
- Na^+
- Na^+ migration
- Al^{3+} migration
- Si^{4+} migration
- Al^{3+} inducing pore blockage / possibly weak acid sites
- Al^{3+} inducing neutralization / possibly pore blockage
- Si^{4+} inducing pore blockage / possibly weak acid sites

Kennes et al., *ACS Catal*. **2022**, 12, 6794

TAKE HOME MESSAGES

- Quantum chemistry helps for assignment of spectra (IR, NMR, XANES, INS, etc.)
- Synergy effect: comparison with experiments as a validation tool of the models
- More and more feasible to introduce more and more complexity in the models
- Scale change for the simulation of materials: use of forcefields/machine learning as a perspective
- DFT + characterization required as a first step for reactivity investigation by DFT

I- Structure understanding

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

II- Chemical reactivity investigations

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

III- Performance prediction

- Multiscale modeling : prediction of macroscopic **activity** / **selectivity**
- Identification of relevant catalytic **descriptors** for the prediction of **new active phases**

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