Ab initio molecular modelling of the mechanisms of dealumination and desilication of relevant zeolite frameworks

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Introduction

- **Aluminosilicates: porous acidic materials**
  - Hydrocracking, Fluid Catalytic Cracking (FCC)
    - Zeolites (MOR, ZSM-5, FAU)
      - strong Brønsted acidity and micropores
        → diffusion limitations, confinement effect (shape transition state selectivity)
  - Mesostructured Aluminosilicates (e.g. MCM-48, MCM-41)
    - amorphous silica: long range ordered framework structure
    - better diffusion but amorphous walls leading to an instability

Hierarchical Zeolites

Introduction of Mesopores

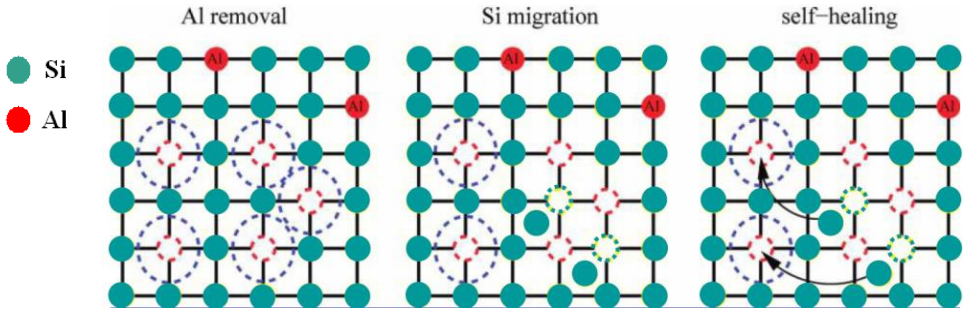
- Dealumination: steaming and acid treatment
→ extra-framework Al (EFAL)
- Desilication: aqueous basic treatment
→ extra-framework Si (EFSI)

Pérez-Ramírez et al., *Chem. Soc. Rev.*, **2008**

Mechanism and Formation of Mesopores

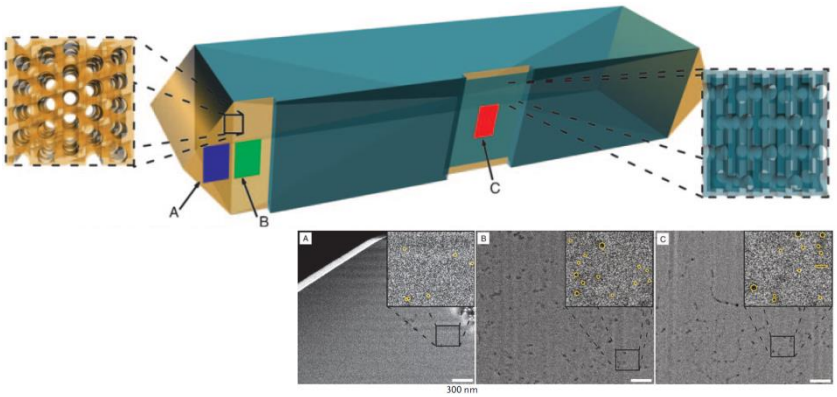
- **Dealumination**
  - Marcilly's Mechanism

Marcilly, Pétrole et Techniques, **1986**



Ban et al., *J. Phys. Chem.*, **2010**

- **steamed ZSM-5 displays formation of vast areas of mesopores** Karwacki et al., *Angew. Chem. Int. Ed.*, **2011**
  - sinusoidal channels more susceptible to dealumination
  - extraction of EFAL hindered within straight channels



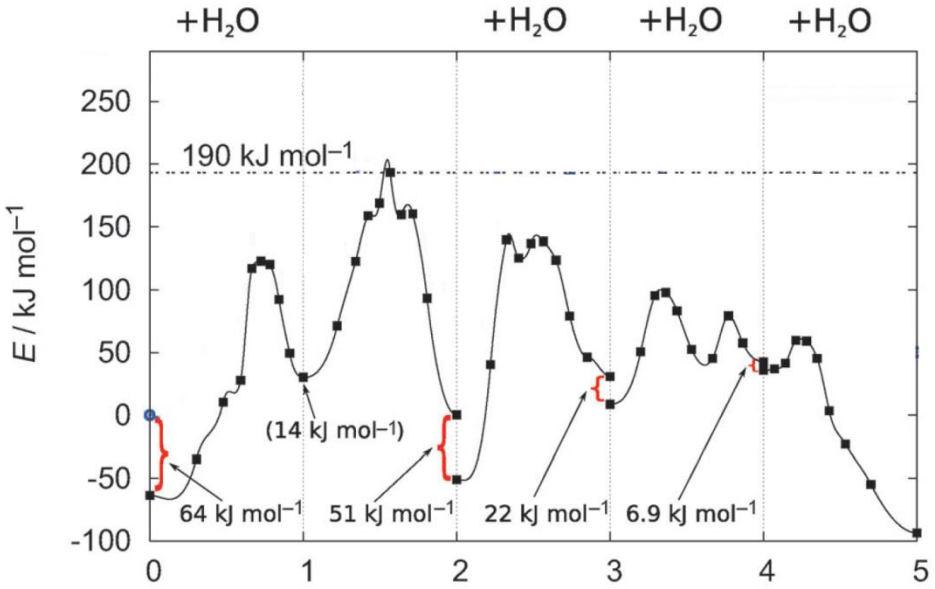
Motivation

- **understanding the mechanism on the molecular scale**
  - why are certain T sites more susceptible to the dealumination?
  - how does the water initiate an Al-O/Si-O bond break?
  - how do mesopores form/propagate?

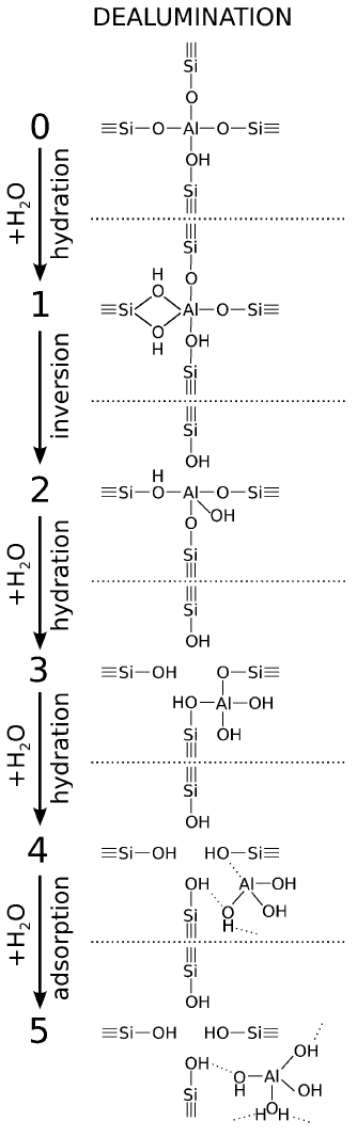
- **only few mechanistic approaches by dint of ab initio calculations for the dealumination/desilication**

Dealumination – Reaction Path

Zeolitic System: H-Chabazite



Malola et al., *Angew. Chem Int. Ed.*, **2011**



first kinetic reaction path of the dealumination mechanism using periodic DFT (functional: PBE)

Motivation

- **understanding the mechanism on the molecular scale**
  - why are certain T sites more susceptible to the dealumination?
  - how does the water attack initiate a bond break?
  - how do mesopores propagate?

- **only few mechanistic approaches by dint of ab initio calculations for the dealumination/desilication**

- **recent periodic DFT analysis only on H-CHA**
  Malola et al., *Angew. Chem Int. Ed.*, **2011**

- **MOR, ZSM-5, (FAU) of great interest since largely used in petroleum refining**

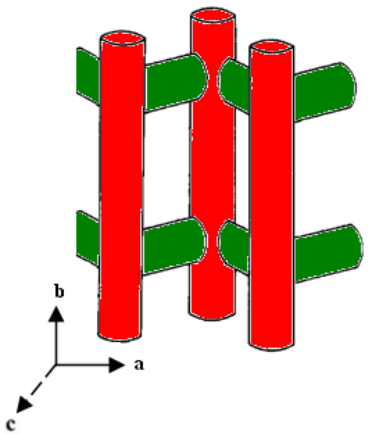
Strategy & Methods

- Hydrolysis/adsorption reactions involving one water molecule
- Mechanistic approach for the Dealumination/Desilication
- Theoretical approaches
  - periodic DFT+D (VASP) and QM/QM (QMPOT)

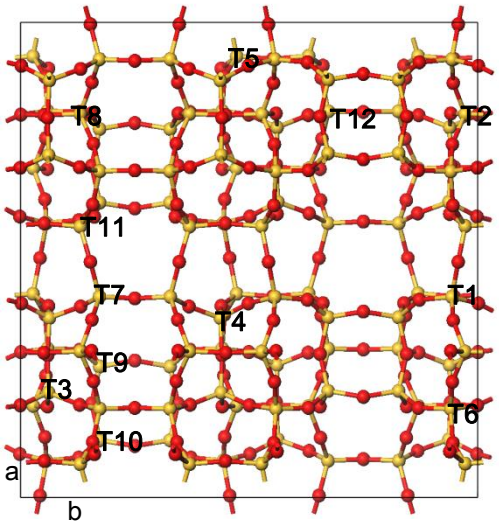
Model System

- ZSM-5: 12 T sites
  Si/Al = 95

10 MR sinusoidal

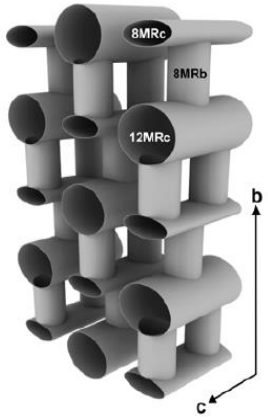


10 MR straight

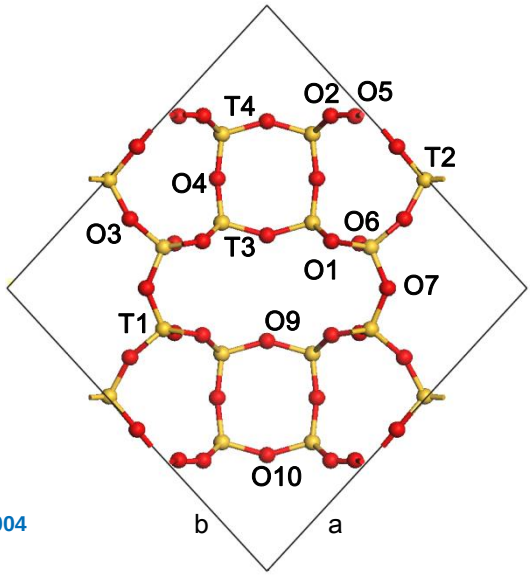


$AlSi_{95}O_{192}H$

- Mordenite: 4 T sites
  Si/Al = 47



Simoncic et al., *Am Mineral,* **2004**



$AlSi_{47}O_{96}H$

Methods

- $\Delta U_{ads} = U_{zeo-n(water)} - U_{zeo} - nU_{water}$

Kresse, Hafner, *Phys Rev B,* **1993**

- **periodic DFT: VASP** PAW / cut-off: 400eV / Γ-point
  - **structure optimization:** SCF convergence: 10^{-6} eV / forces on atoms < 0.02 eV/Å²
    - **DFT+D2:** dispersion forces added semi-empirically to PBE

      Grimme, *J. Comput. Chem.*, **2006**
  - **Nudged Elastic Band:** SCF convergence: 10^{-4} eV / forces on atoms < 0.03 eV/Å²
    - estimate reaction barriers (8 intermediate images)

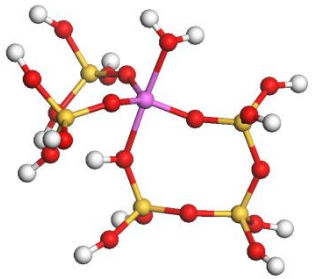
      Jonsson, *Classical and Quantum Dynamics in condensed Phase Simulations,* **1998**

- **post-HF: Møller-Plesset Perturbation Theory (MP2)**
  - adding a certain dynamic correlation as a perturbative potential

$$\hat{H} = \hat{H}_0 + \lambda \hat{A}$$

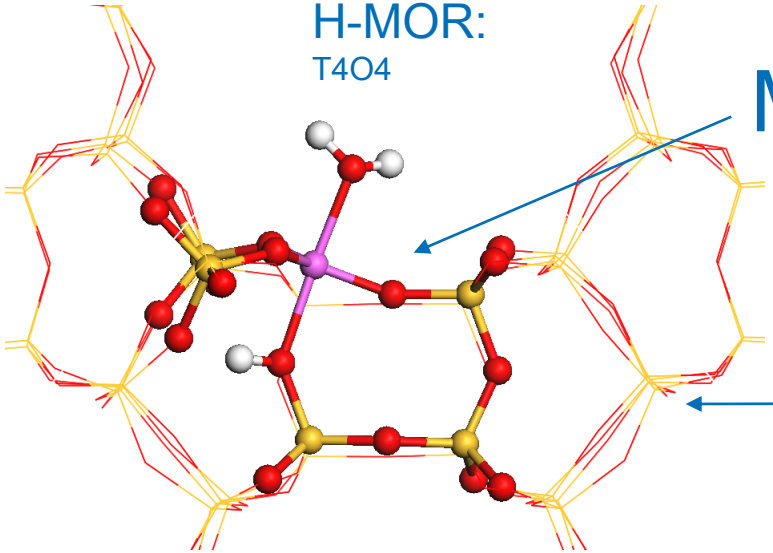
Methods

- **QMPOT** Sierka, Sauer, *J. Chem. Phys.*, **2000**



6T cluster

H-MOR:
T4O4



MP2 high level

Turbomole: R. Ahlrichs et al., *Chem. Phys. Lett.*, **1989**

PBE+D low level

VASP: Kresse, Hafner, *Phys Rev B,* **1993**

1. optimization $PBE + D$
2. Single Point calculations with Turbomole on 6T cluster $\Delta MP2_{SP}$
   - HF, MP2: cc-pVXZ (X = T, Q) for CBS
   - no BSSE correction
   - no CCSD(T) verification possible (not implemented in TM 5.9)

$$\Delta E_{tot} = E^{S}_{PBE+D} + \Delta MP2 = E^{S}_{PBE+D} + E^{T6}_{MP2,CBS} - E^{T6}_{PBE+D}$$

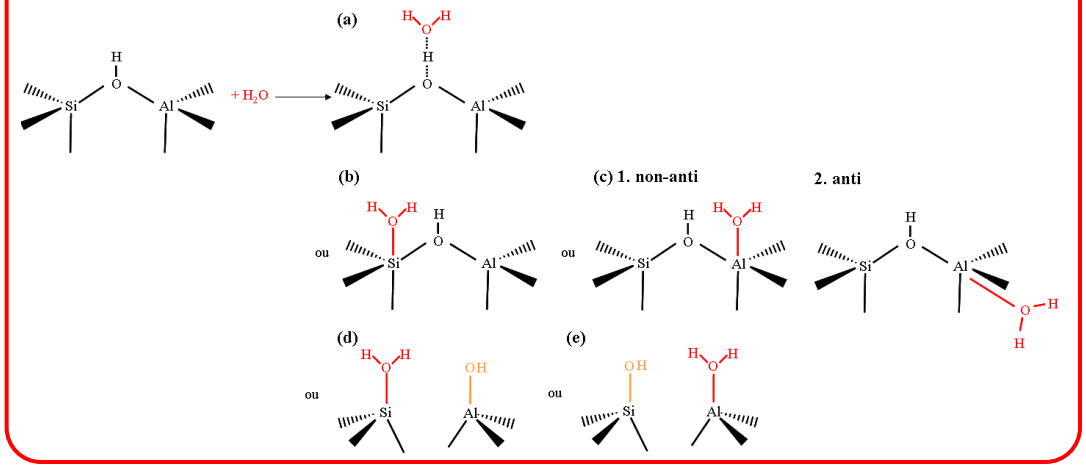
pbc PBE+D	pbc PBE+D; MP2
-56.9 kJ/mol	-57.1 kJ/mol

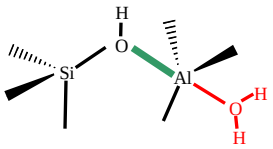
Results

- 1. Hydrolysis/adsorption reactions implicating one water molecule
- 2. Mechanistic approach for the Dealumination/ Desilication

1. Hydrolysis/adsorption reactions implicating one water molecule

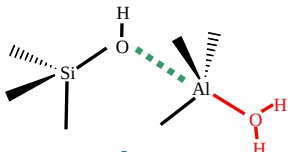
non-dissociative water adsorption





Al_V

or



Al_{IV}

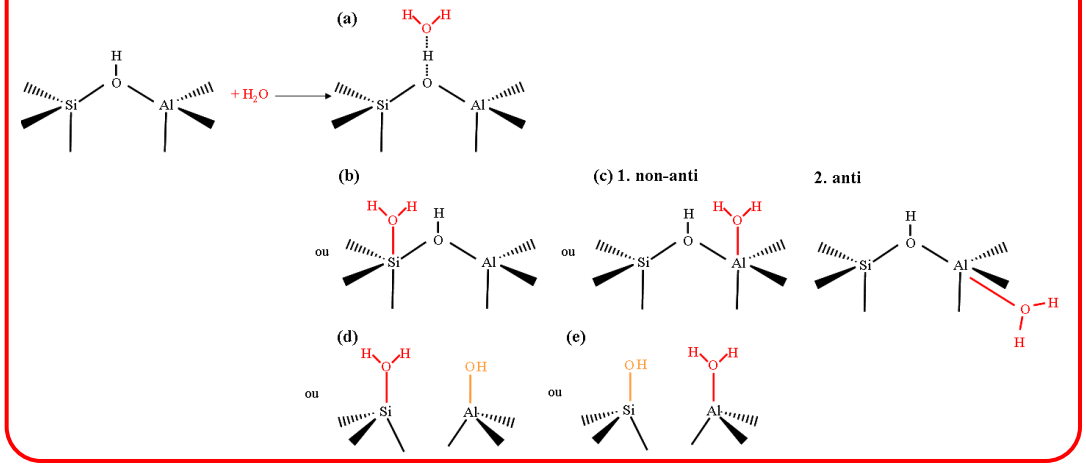
Bond overlap population analyses

Petracovschi et al, Rapport IFPEN 62062, Dec. 2011

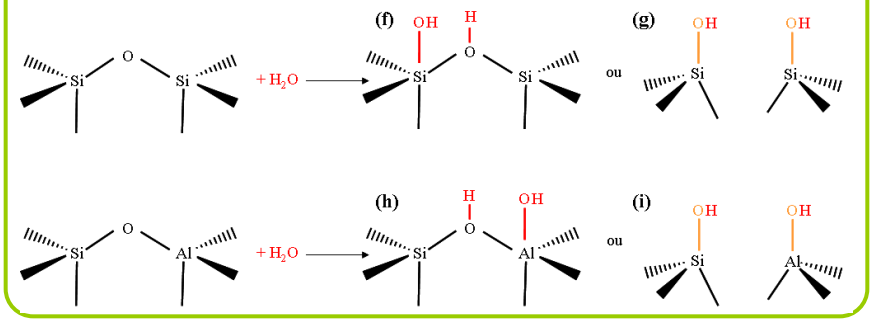
→ Al-O bond break if r(Al-O) > 2.20 Å

1. Hydrolysis/adsorption reactions implicating one water molecule

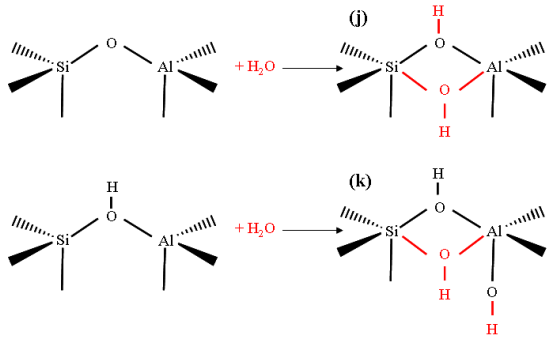
non-dissociative water adsorption



dissociative water adsorption (with hydrolysis)



vicinal disilanol



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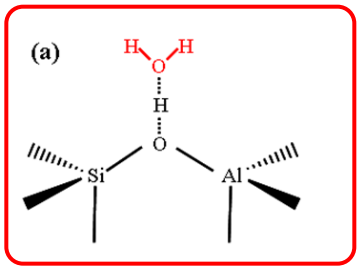
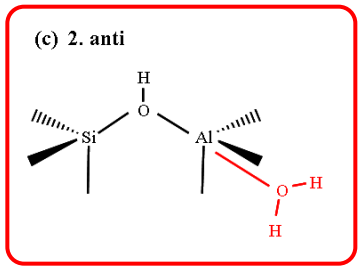
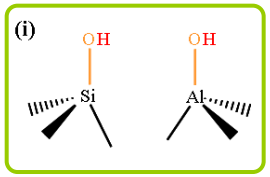


H_2O ads on BAS

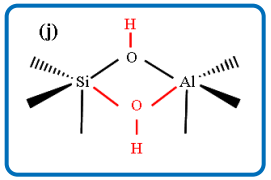


H_2O ads on Al in anti to BAS



hydrolysis Al-O

Malola et al., *Angew. Chem Int. Ed.*, **2011**



vicinal silanol on Al-O-Si

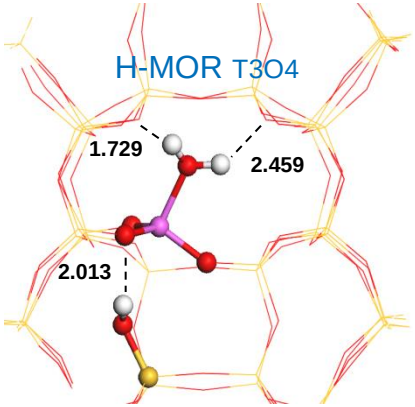
Interaction	Geometry	H-MOR		H-ZSM-5
		T1O3 (8 membered ring)	T4O4 (12 membered ring)	T10O2 (10 membered ring)
a) H_2O ads on BAS	H2O...HO	-105	-39	-48
c) H_2O ads on Al in anti to BAS	Al_V	-100	-67	-59
i) hydrolysis Al-O*	Si-OH HO-Al	-30	-38	13
j) vicinal silanol on Al-O-Si*	vicinal silanol	-43	-18	46

*stability depending on insertion site

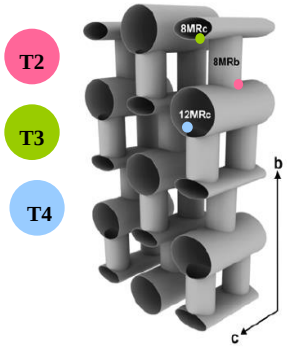
- water adsorption on Al in anti to BAS most exothermic reaction

1. Hydrolysis/adsorption reactions implicating one water molecule

- water adsorption on Al in anti position to BAS favored if
  - **1. sterical constraints:** unhindered anti attack on Al
    proton occluded in small cavities
  - **2. hydrogen bonding:** adsorbed H_2O and formed silanol
    stabilized by framework oxygen atoms
- elongation of the Al-O bond
- for certain T sites Al-O bond break



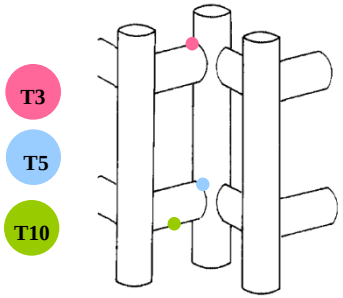
Mordenite



Al_{IV}
- T2O8 (rAl-OH = 2.27 Å)
- T3O4 (rAl-OH = 2.91 Å)

Al_V
- T4O4 (rAl-OH = 2.12 Å)

ZSM-5

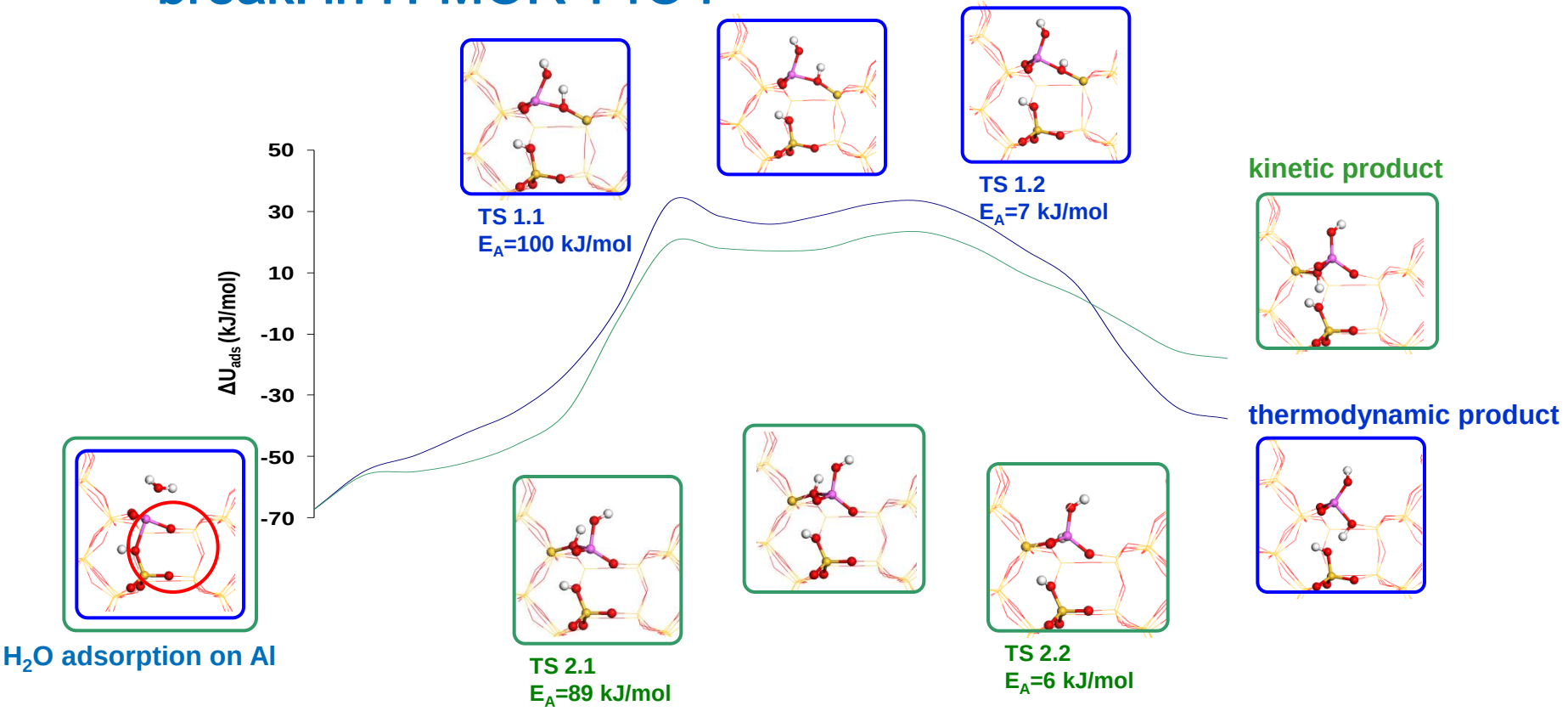


A_{IV}
- T3O4 (rAl-OH = 2.28 Å)

strongly weakened Al...OH bond:
- T5O2 (rAl-OH = 2.18 Å)
- T10O2 (rAl-OH = 2.19 Å)

1. Hydrolysis/adsorption reactions implicating one water molecule

- mechanism of the first water splitting and Al-O bond break: in H-MOR T4O4



1. Hydrolysis/adsorption reactions implicating one water molecule

- mechanism of the first water splitting and Al-O bond break: in H-MOR T4O4

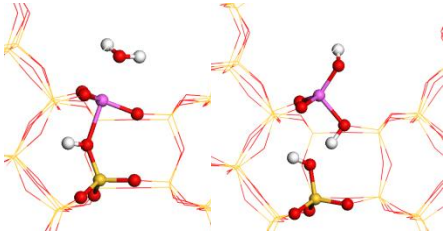
- water adsorption/splitting:
  - thermodynamic and kinetic products depend on which oxygen atom water splitting took place
    - no descriptor found predicting preferred splitting site
  - first water adsorption determines extraction direction of EFAL in cavity: e.g. 12MR (see full mechanism)

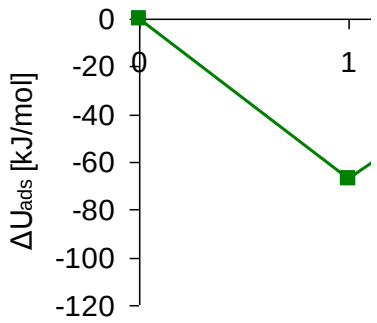
2. Mechanistic approach for the Dealumination/Desilication

- simple Dealumination: e.g. pathway in H-MOR at T4O4

1 H_2O adsorption

1 H_2O bond break Al-O





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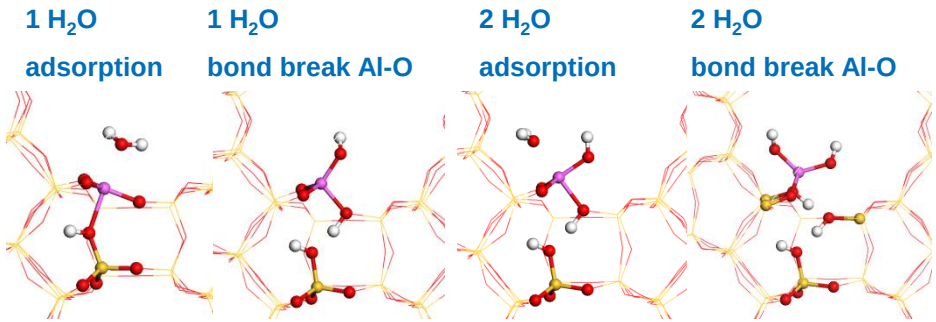

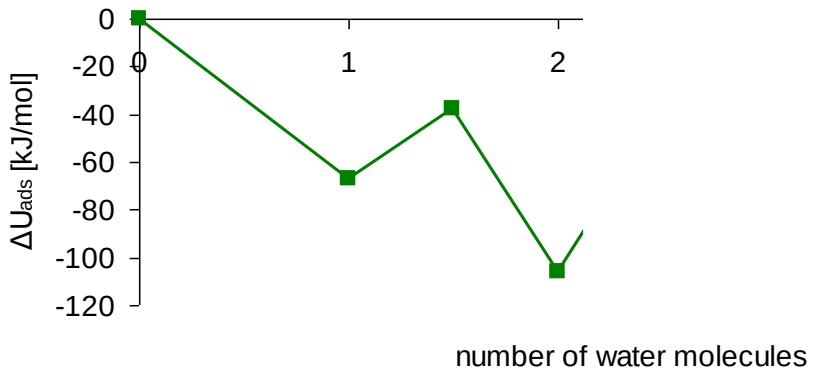

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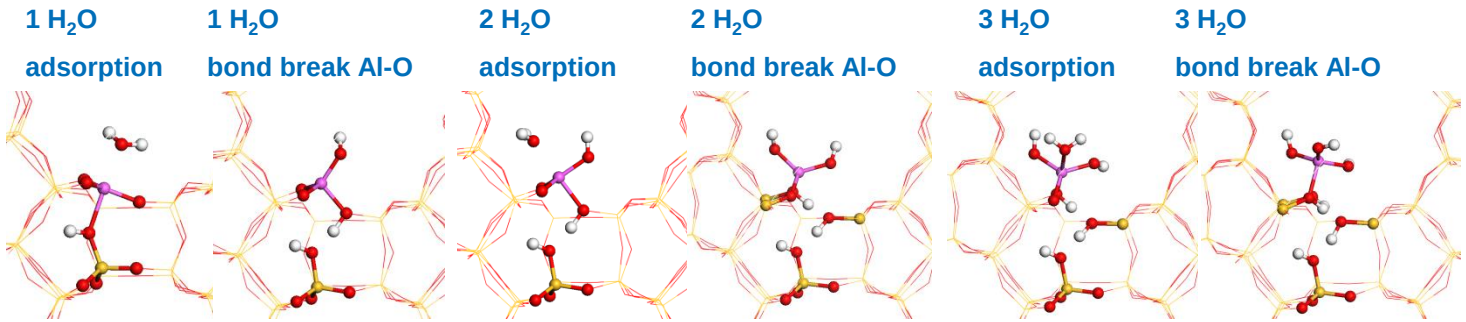

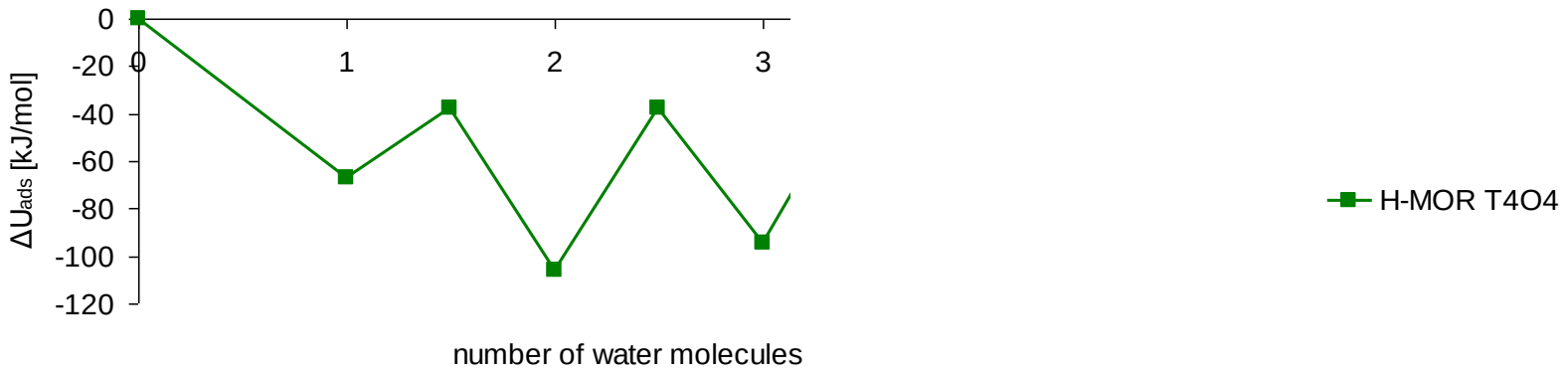

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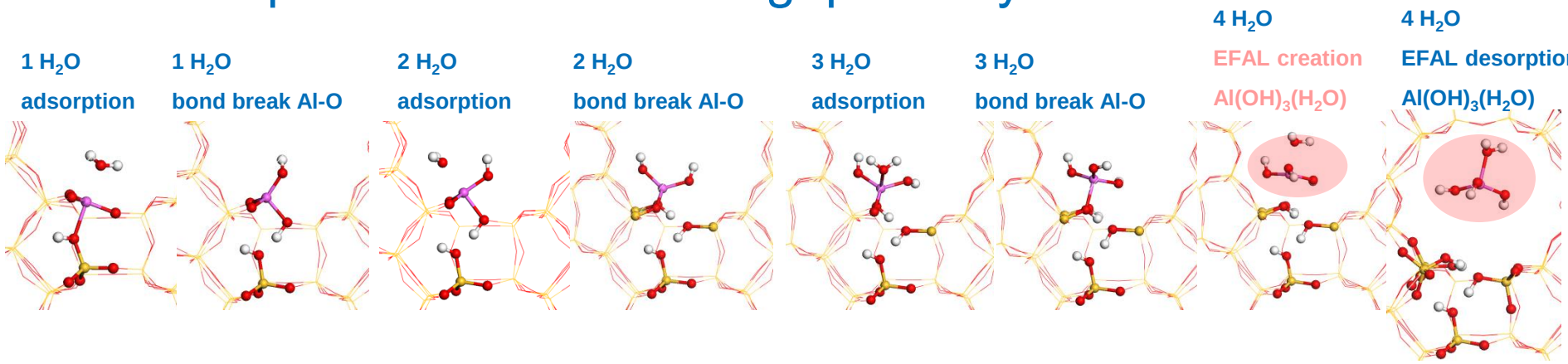

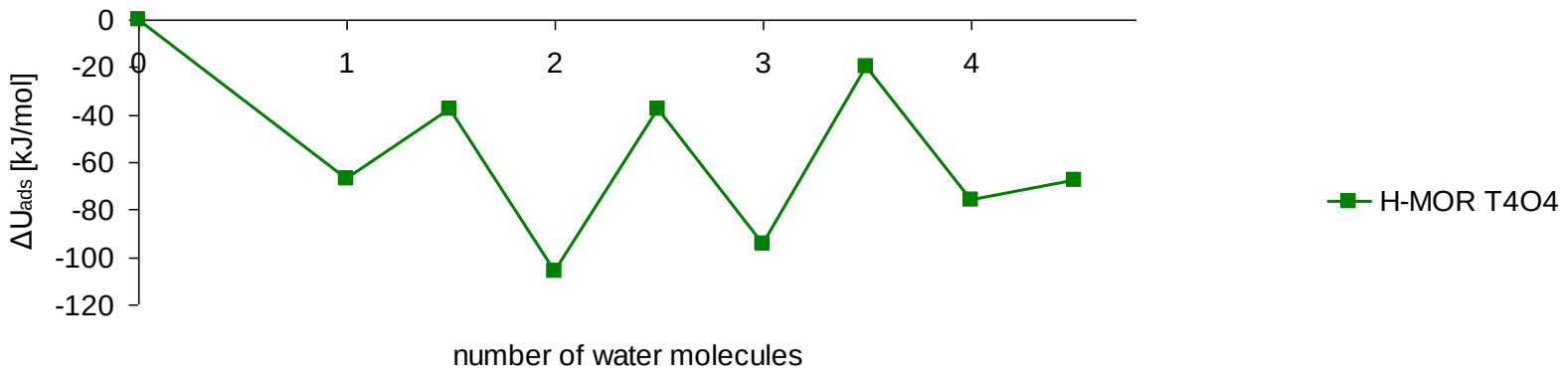

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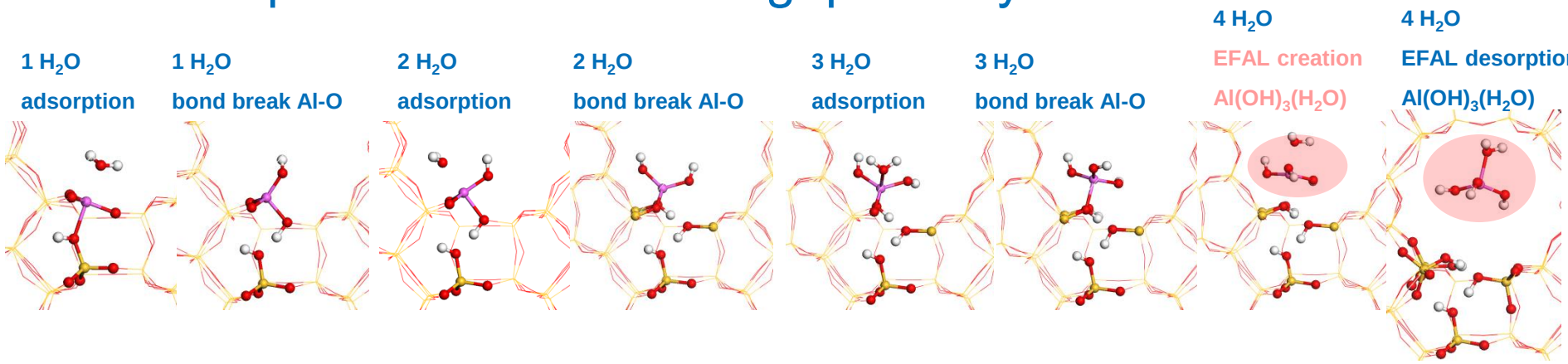
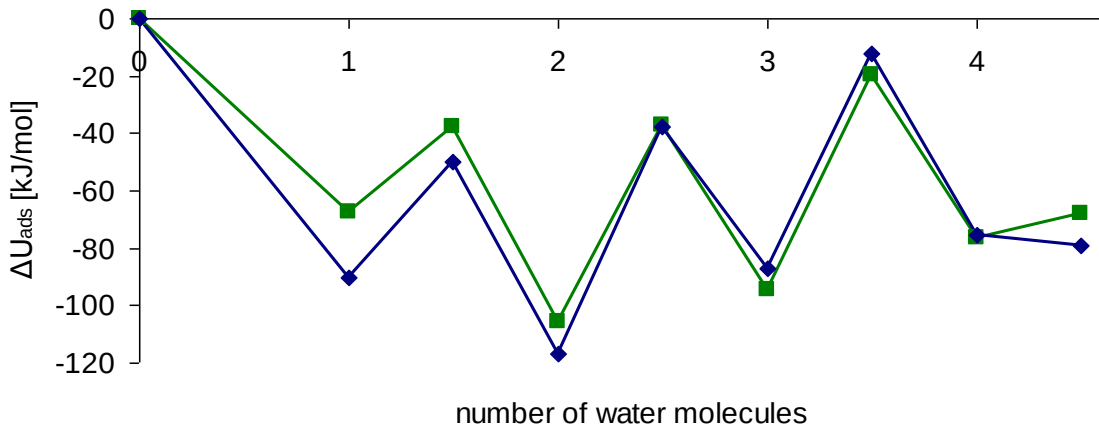
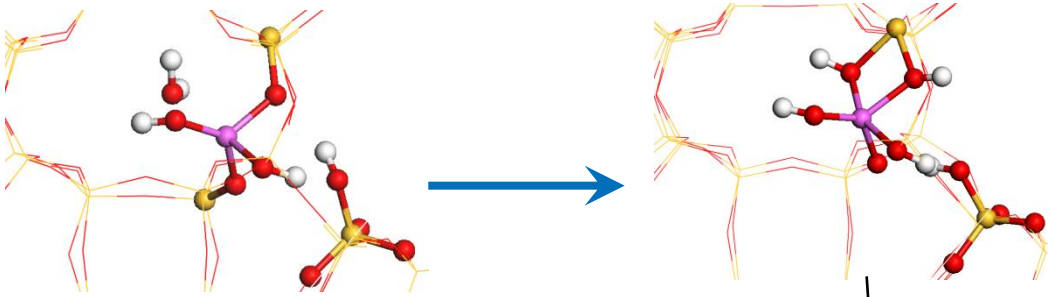


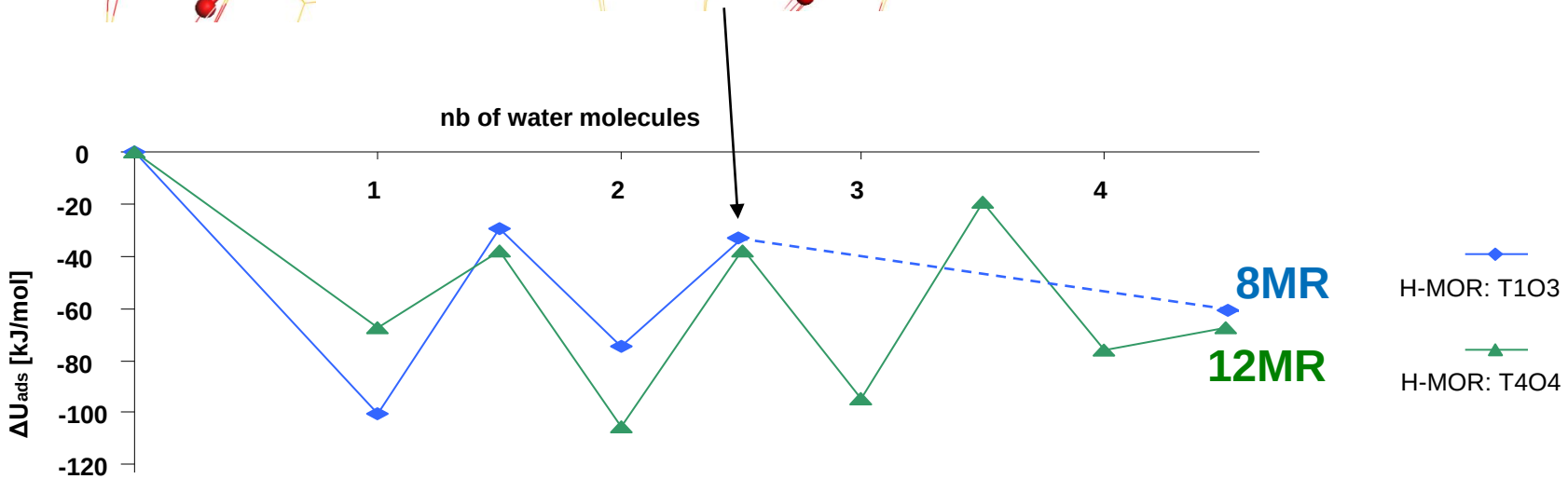


2. Mechanistic approach for the Dealumination/Desilication

- T1O3 in H-MOR: local sterical effects (curvature) of 8MRc

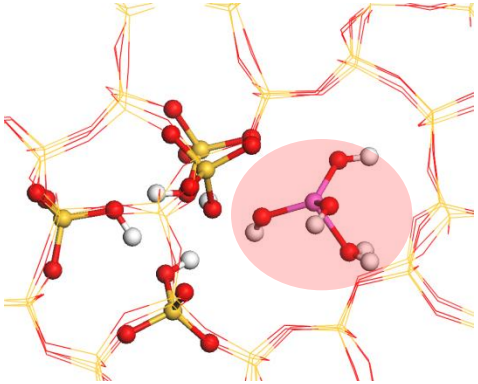


vicinal disilanol:
further dealumination is blocked

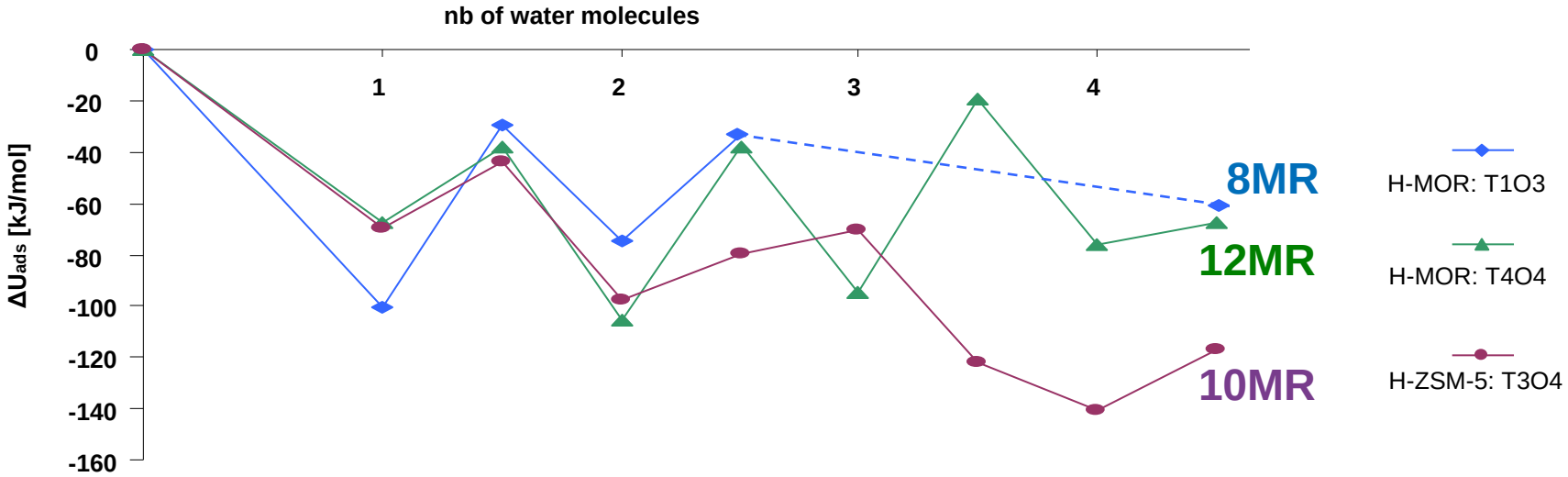


2. Mechanistic approach for the Dealumination/Desilication

- T3O4 in H-ZSM-5: EFAL $Al(OH)_3(H_2O)$ in 10MR

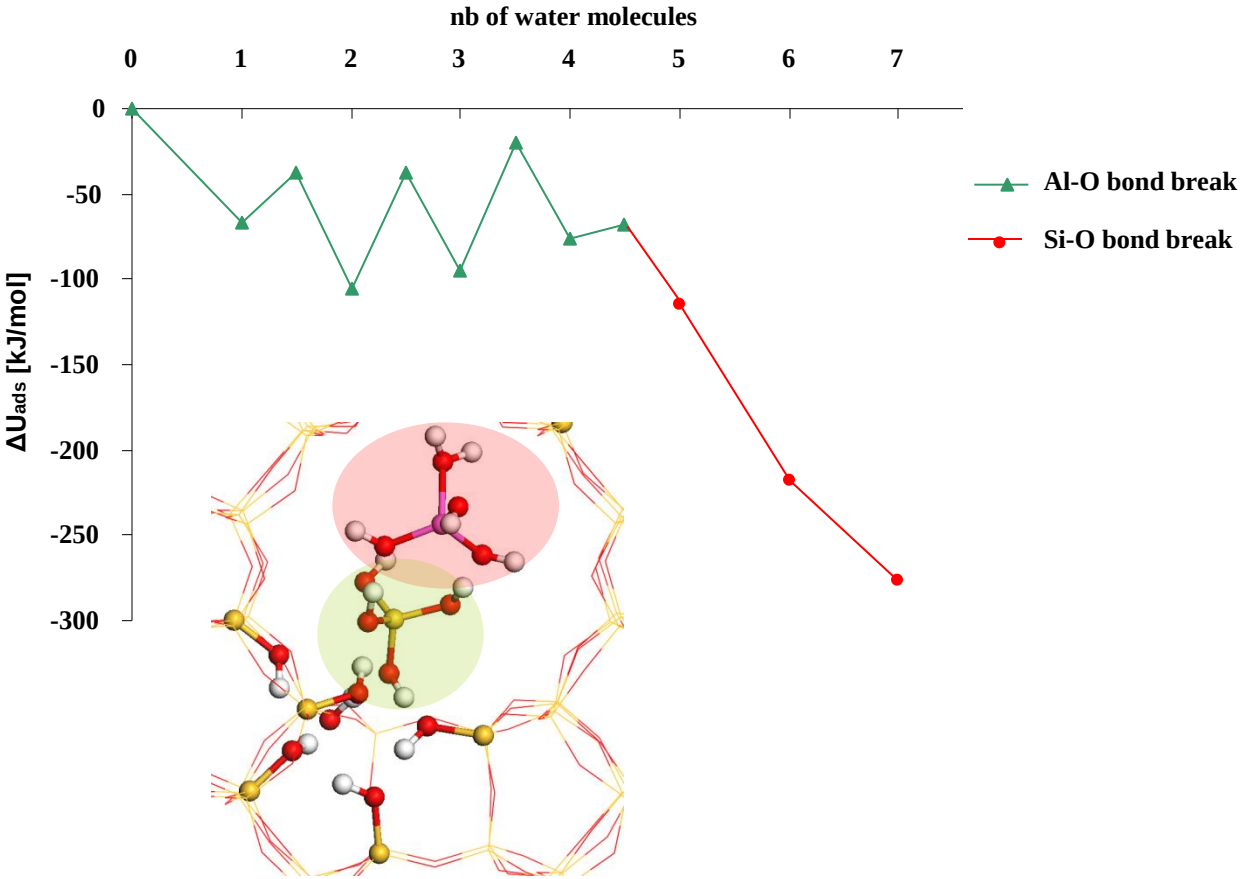


stabilizing effect of the 10MR

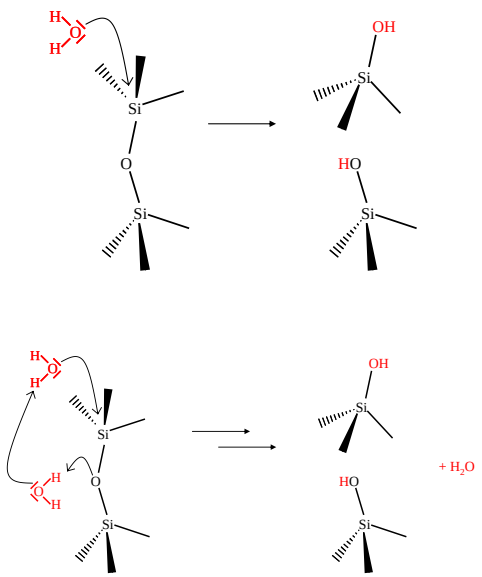


2. Mechanistic approach for the Dealumination/Desilication

- Dealumination (at T4O4)/Desilication (at T2) in H-MOR



Si-O hydrolysis



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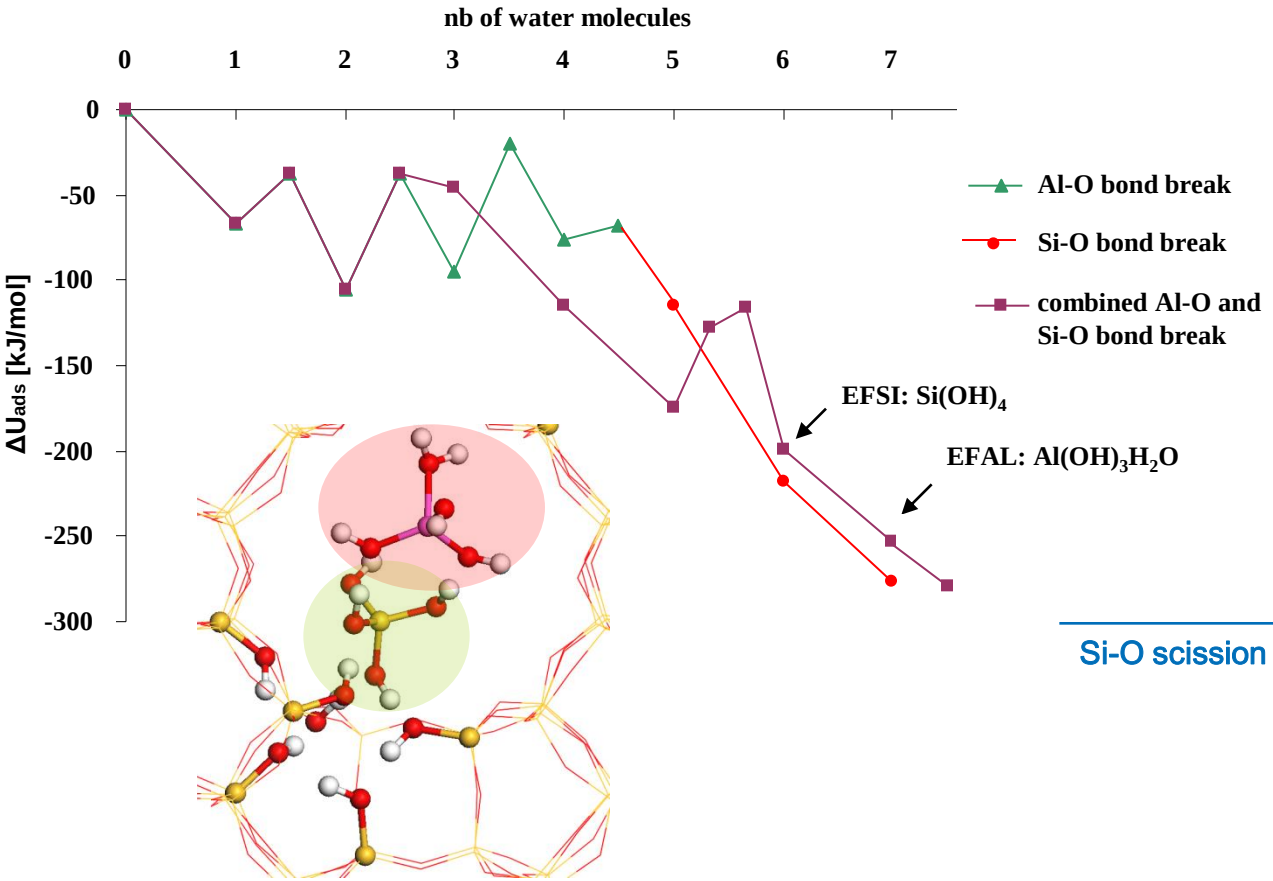

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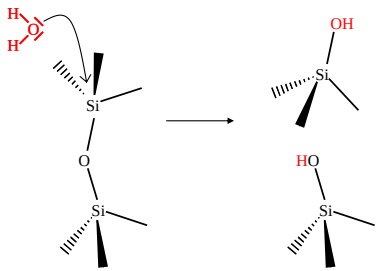
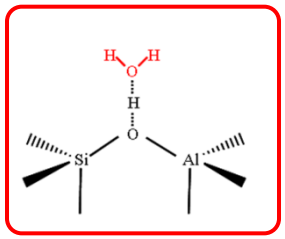
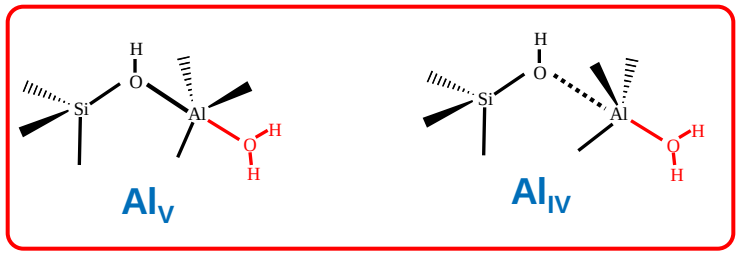
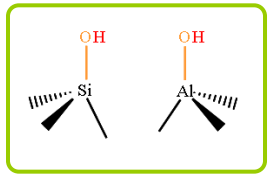


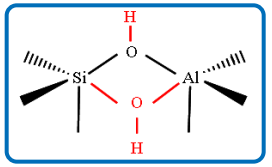
	Si framework (no defect site)	defect sites
Si-O scission	-10 to 98 kJ/mol	-100 to -60 kJ/mol

Summary







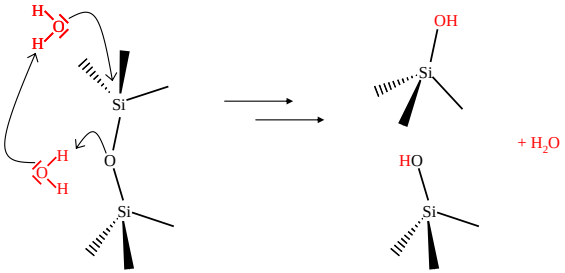


- adsorption of water on Al in anti position to BAS most exothermic reaction
- first water adsorption predicts extraction direction of EFAL
- EFAL stability depends on pore size
  - **highest stability in 10MR of H-ZSM 5**
- thermodynamical preference of a combined (consecutive/simultaneous) dealumination/desilication →Marcilly's Mechanism Marcilly, Pétrole et Techniques, **1986**
- desilication preferentially takes place at defect sites

Perspectives

- reaction barriers for entire dealumination/desilication path:
  - **especially for first water dissociation**

- increasing water amount: local hydration



- decreasing Si/Al ratio

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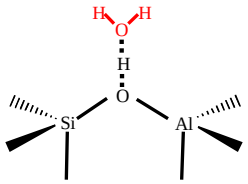
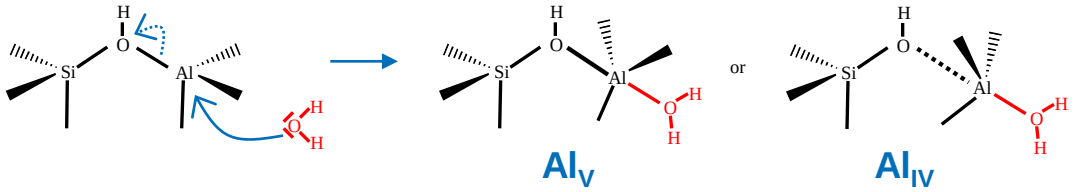
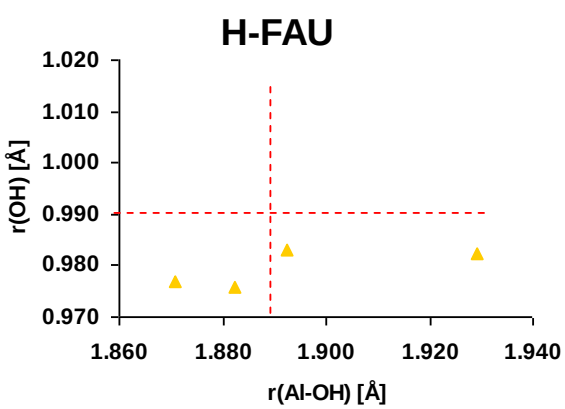
1. Water adsorption on BAS vs LAS

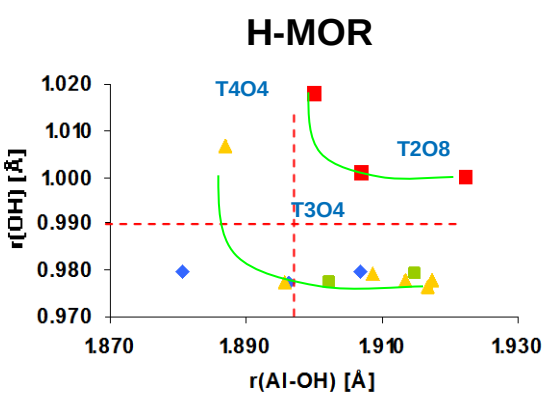
Adsorption on BAS

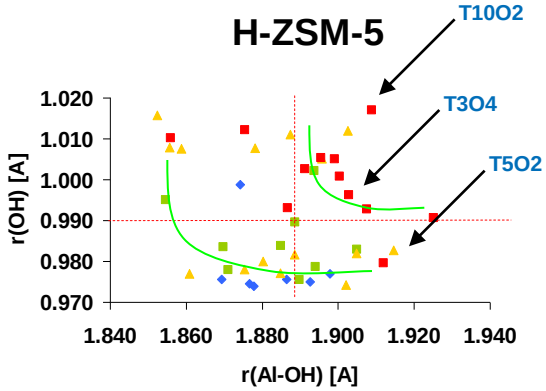


Anti attack of a water molecule on LAS: Rapport IFPEN 62062, Dec. 2011







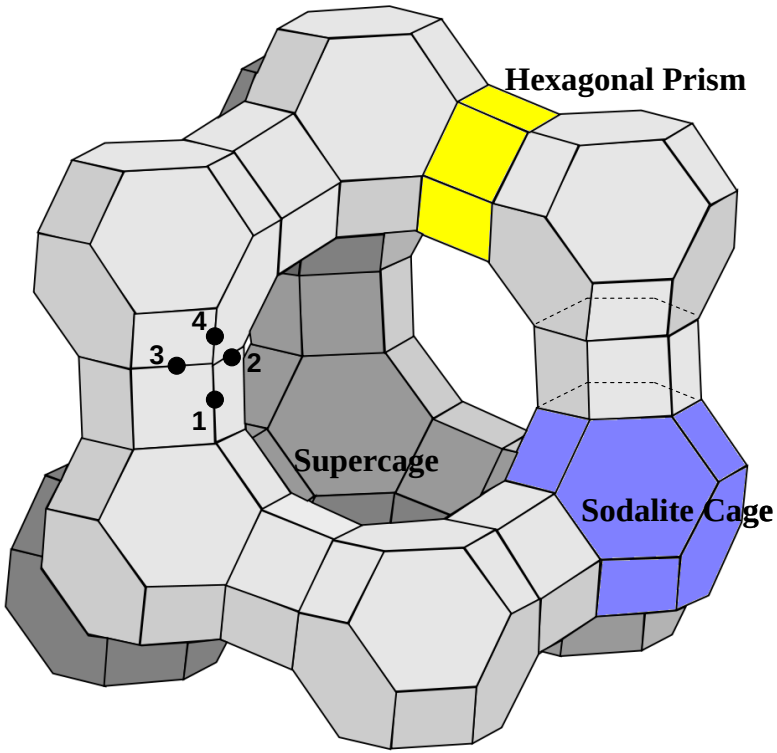


color code: ΔUads(LAS) – ΔUads(BAS) [kJ/mol]

- ◆ > 100
- ■ 50-100
- ▲ 0-50
- ■ < 0

Model System

- Faujasite: 1 T site; Si/Al ratio = 47



$AlSi_{47}O_{96}H$