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

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- **Hierarchical Zeolites**
  - Introduction of Mesopores
    - Dealumination: steaming and acid treatment
    - → extra-framework Al (EFAL)
    - Desilication: aqueous basic treatment
    - → extra-framework Si (EFSI)
Mechanism and Formation of Mesopores

**Dealumination**

- **Marcilly’s Mechanism**
  - steamed ZSM-5 displays formation of vast areas of mesopores
  - sinusoidal channels more susceptible to dealumination
  - extraction of EFAL hindered within straight channels

- Marcilly, Pétrole et Techniques, 1986
- Ban et al., J. Phys. Chem., 2010
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

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

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

- **Mordenite**: 4 T sites  
  Si/Al = 47

![Diagram of ZSM-5 and Mordenite structures](image)

**Equations**

- **ZSM-5**: \( \text{AlSi}_{95}\text{O}_{192}\text{H} \)
- **Mordenite**: \( \text{AlSi}_{47}\text{O}_{96}\text{H} \)

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

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


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

- **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


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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)

\[
\Delta E_{\text{tot}} = E_{\text{PBE+D}} + \Delta MP2 = E_{\text{PBE+D}}^S + E_{\text{MP2,CBS}}^{T6} - E_{\text{PBE+D}}^{T6}
\]

**H-MOR:** T4O4

**MP2** high level


**PBE+D** low level


<table>
<thead>
<tr>
<th>pbc PBE+D</th>
<th>pbc PBE+D; MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-56.9 kJ/mol</td>
<td>-57.1 kJ/mol</td>
</tr>
</tbody>
</table>

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6T cluster
Results

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

Bond overlap population analyses

Petracovschi et al, Rapport IFPEN 62062, Dec. 2011

→ Al-O bond break if $r(\text{Al-O}) > 2.20 \text{ Å}$
1. Hydrolysis/adsorption reactions implicating one water molecule

- Non-dissociative water adsorption
- Dissociative water adsorption (with hydrolysis)
- Vicinal disilanol
1. Hydrolysis/adsorption reactions implicating one water molecule

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

*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 $\text{H}_2\text{O}$ and formed silanol
     stabilized by framework oxygen atoms
- elongation of the Al-O bond
- for certain T sites Al-O bond break

**Mordenite**

- $\text{Al}_{IV}^-$
  - T2O8 (rAl-OH = 2.27 Å)
  - T3O4 (rAl-OH = 2.91 Å)
- $\text{Al}_{V}^-$
  - T4O4 (rAl-OH = 2.12 Å)

**ZSM-5**

- $\text{Al}_{IV}^-$
  - 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

- $\Delta U_{ads}$ (kJ/mol)

- $E_A$:
  - 100 kJ/mol
  - 7 kJ/mol
  - 89 kJ/mol
  - 6 kJ/mol

- H$_2$O adsorption on Al

- kinetic product

- thermodynamic product
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

![Diagram showing the adsorption of water molecules and bond break in aluminium-oxygen (Al-O) bonds.](image-url)

![Graph showing the change in adsorption energy (ΔUads) as a function of the number of water molecules.](image-url)
2. Mechanistic approach for the Dealumination/Desilication

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

1 H$_2$O adsorption
1 H$_2$O bond break Al-O
2 H$_2$O adsorption
2 H$_2$O bond break Al-O

\[ \Delta U_{\text{ads}} [\text{kJ/mol}] \]

- H-MOR T4O4

(number of water molecules)

(example pathway in H-MOR at T4O4)
2. Mechanistic approach for the Dealumination/Desilication

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

![Mechanistic approach diagram](Image)

![Graph](Image)
2. Mechanistic approach for the Dealumination/Desilication

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

1. $\text{H}_2\text{O}$ adsorption
2. $\text{H}_2\text{O}$ bond break Al-O
3. $\text{H}_2\text{O}$ adsorption
4. $\text{H}_2\text{O}$ bond break Al-O
5. 4 $\text{H}_2\text{O}$ EFAL creation $\text{Al(OH)}_3(\text{H}_2\text{O})$
6. 4 $\text{H}_2\text{O}$ EFAL desorption $\text{Al(OH)}_3(\text{H}_2\text{O})$

Graph:
- $\Delta U_{\text{ads}}$ [kJ/mol]
- Number of water molecules

- H-MOR T4O4
2. Mechanistic approach for the Dealumination/Desilication

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

```
1 H₂O adsorption
1 H₂O bond break Al-O
2 H₂O adsorption
2 H₂O bond break Al-O
3 H₂O adsorption
3 H₂O bond break Al-O
4 H₂O

EFAL creation
Al(OH)₃(H₂O)

EFAL desorption
Al(OH)₃(H₂O)
```

![Graph showing ΔU adsorption vs. number of water molecules for H-MOR T4O4 and H-MOR T2O8](image)

- **Graph**:
  - **ΔU ads [kJ/mol]**
  - **Number of water molecules**: 1, 2, 3, 4
  - **H-MOR T4O4**
  - **H-MOR T2O8**
2. Mechanistic approach for the Dealumination/Desilication

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

  - Vicinal disilanol: further dealumination is blocked

![Graph showing the relationship between number of water molecules and ΔU_ads (kJ/mol)]

- ΔU_ads [kJ/mol]
- nb of water molecules
- 0, 1, 2, 3, 4

- H-MOR: T1O3
- H-MOR: T4O4

- 8MR
- 12MR
2. Mechanistic approach for the Dealumination/Desilication

- T3O4 in H-ZSM-5: EFAL Al(OH)$_3$(H$_2$O) in 10MR

stabilizing effect of the 10MR
2. Mechanistic approach for the Dealumination/Desilication

- Dealumination (at T4O4)/Desilication (at T2) in H-MOR
2. Mechanistic approach for the Dealumination/Desilication

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

![Graph showing the number of water molecules versus ΔU_ads [kJ/mol]]

- Si-O hydrolysis

<table>
<thead>
<tr>
<th>Si-O scission</th>
<th>Si framework (no defect site)</th>
<th>defect sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10 to 98 kJ/mol</td>
<td>-100 to -60 kJ/mol</td>
<td></td>
</tr>
</tbody>
</table>
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
Innover les énergies

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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

H-FAU

H-MOR

H-ZSM-5

color code: $\Delta$Uads(LAS) – $\Delta$Uads(BAS) [kJ/mol]

- $> 100$
- 50-100
- 0-50
- $< 0$
Model System

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

EFAL: Al(OH)$_3$H$_2$O
QUEL ZEOLITE?