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Hydrolysis of zeolites: new insights from biased ab initio molecular dynamics

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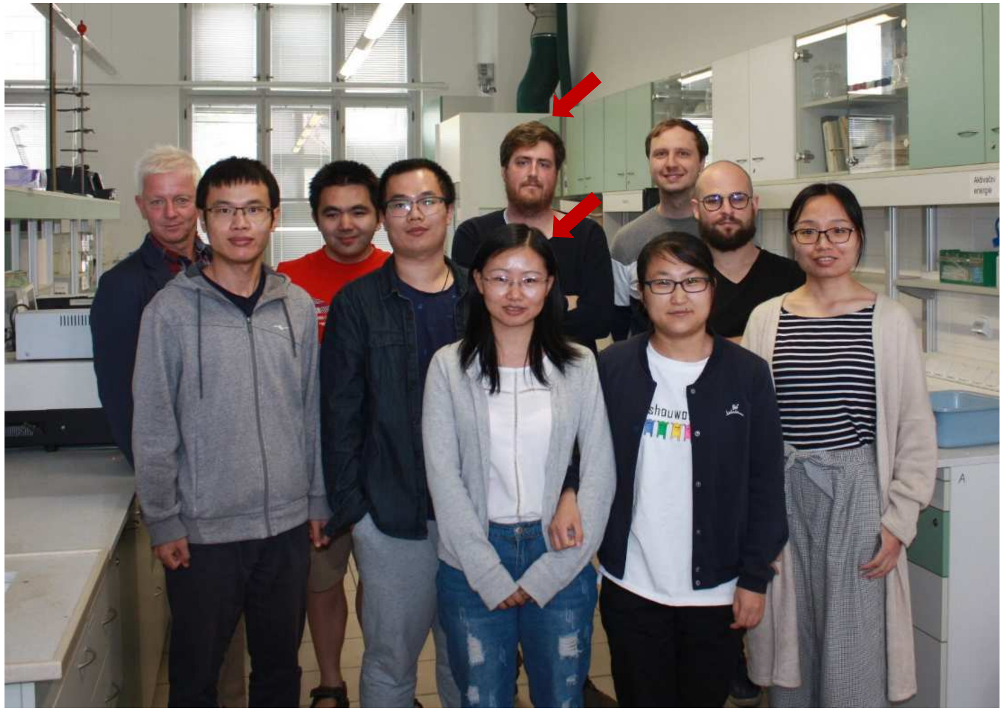
2nd Users Conference of IT4Innovations
Ostrava, Czechia
07/11/2018

Acknowledgements



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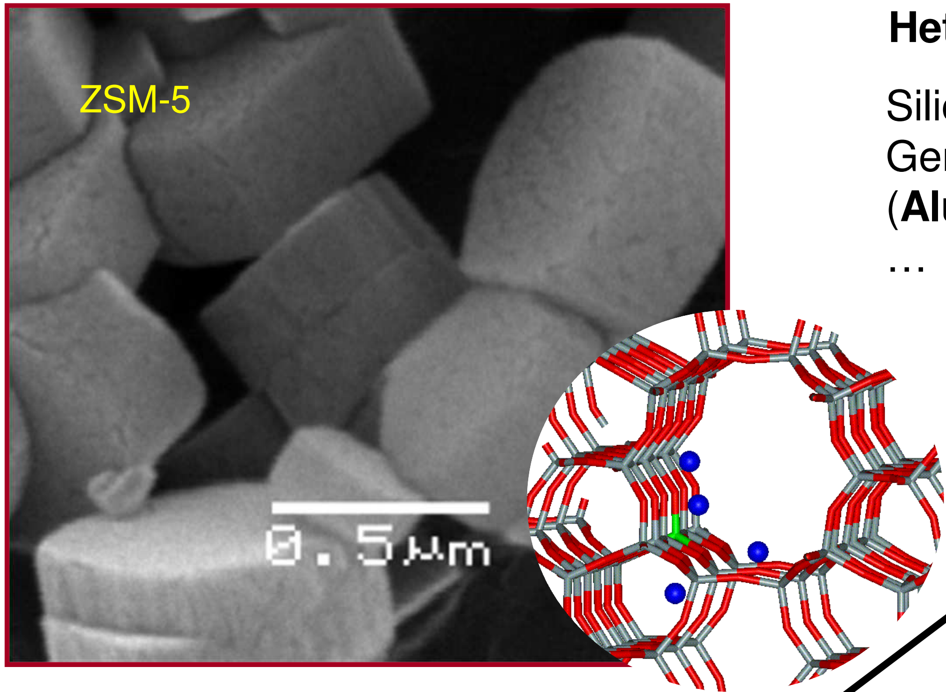
Grant No. 17-01440S

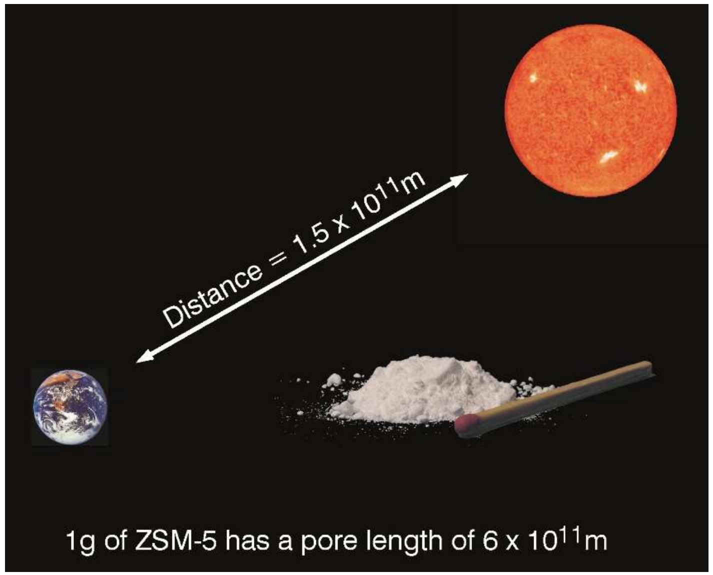
Microporous Structures - Zeolites



Heteroatom doped porous silicates (SiO_2)

Silicates
Germanosilicates
(**Aluminosilicates**/Borosilicates/Galliumsilicates)
…

Large surface area (~ 500 m^2/g)
Dense network of microporous channels



Applications: adsorbent, catalysts, supports, ion-exchangers

Pros: thermal stability, low cost, microporosity

Cons: slow diffusion, only 235 topologies synthesized till now

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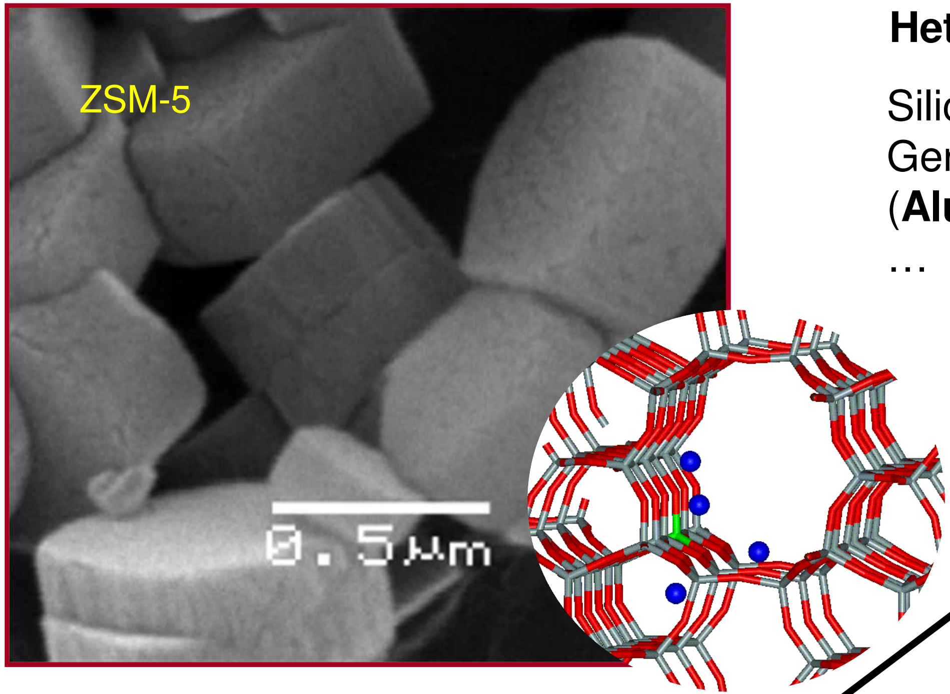

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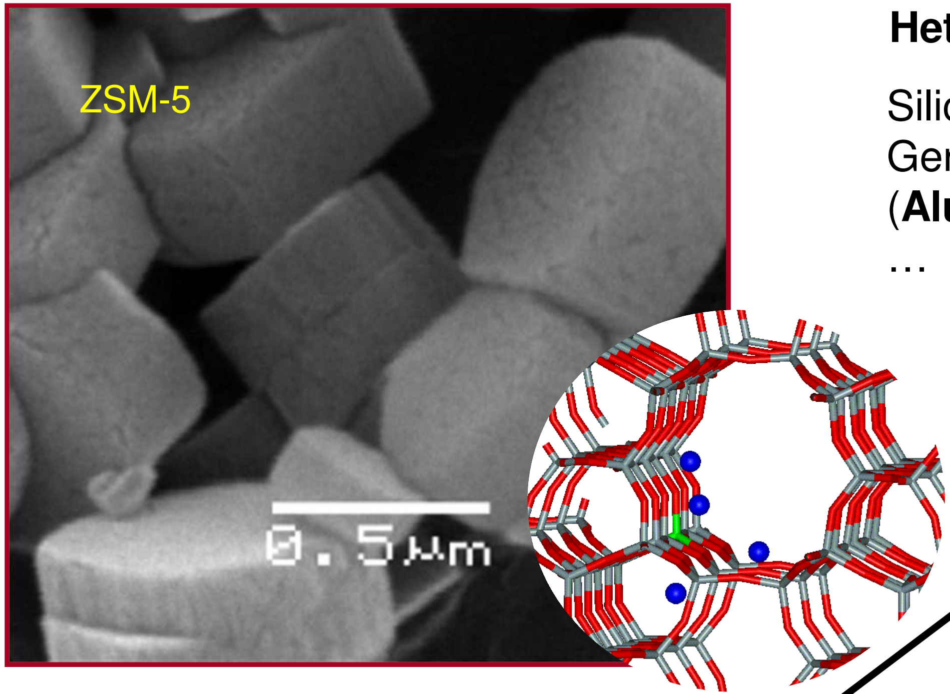

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Hierarchical zeolites:
combining micro and mesoporosity

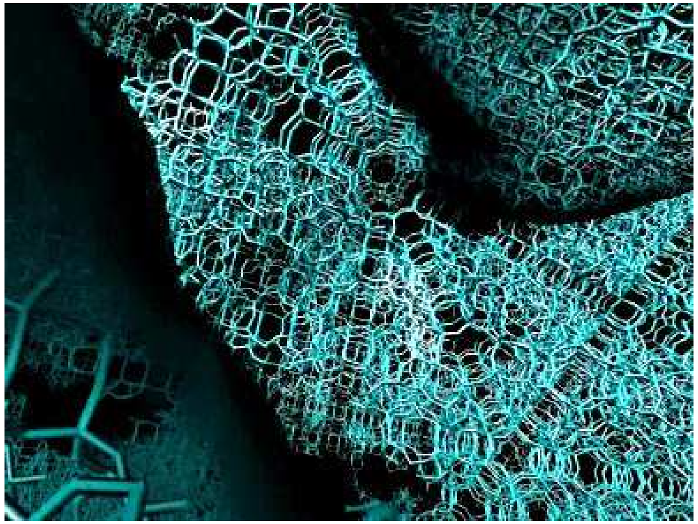
Why Zeolite Hydrolysis?

- Zeolites considered as stable catalysts up to high temperatures
- Zeolites instabilities sometimes reported in literature, e.g., biomass conversion (water content, acidity, T)
- Instability of zeolites in water under specific conditions is used on purpose to improve properties

Al-zeolites: FCC catalyst

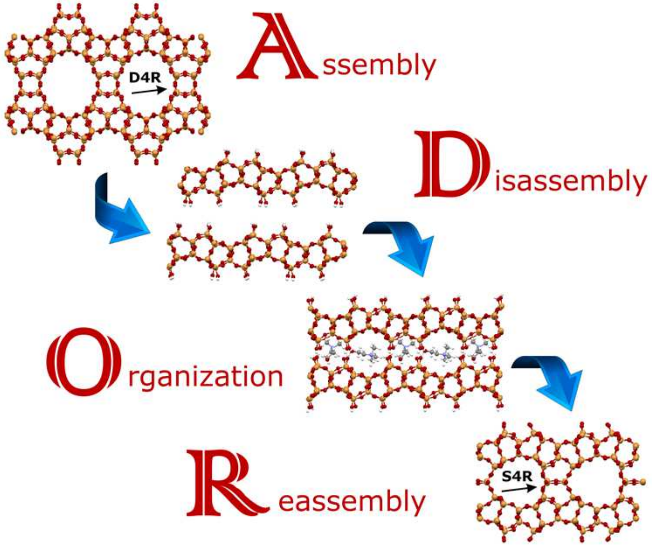
www.Technip.com

Si-zeolites: Hierarchical zeolites



Veronica Belusa: www.chemistryviews.org

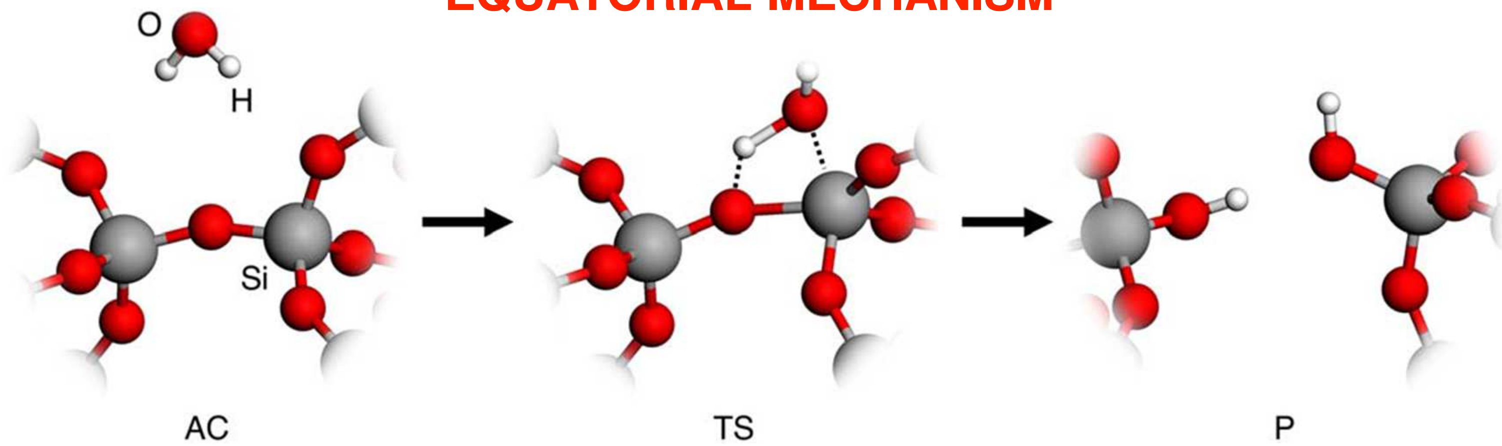
Ge-zeolites: ADOR



Čejka *et al. Nature Chem.* (2013, 2015, 2016)

State of the Art – CMS on (Alumino)silicates Hydrolysis

EQUATORIAL MECHANISM



O-down adsorption

1,2-dissociation

Hühn *et al.*, 10.1002/jcc.24892

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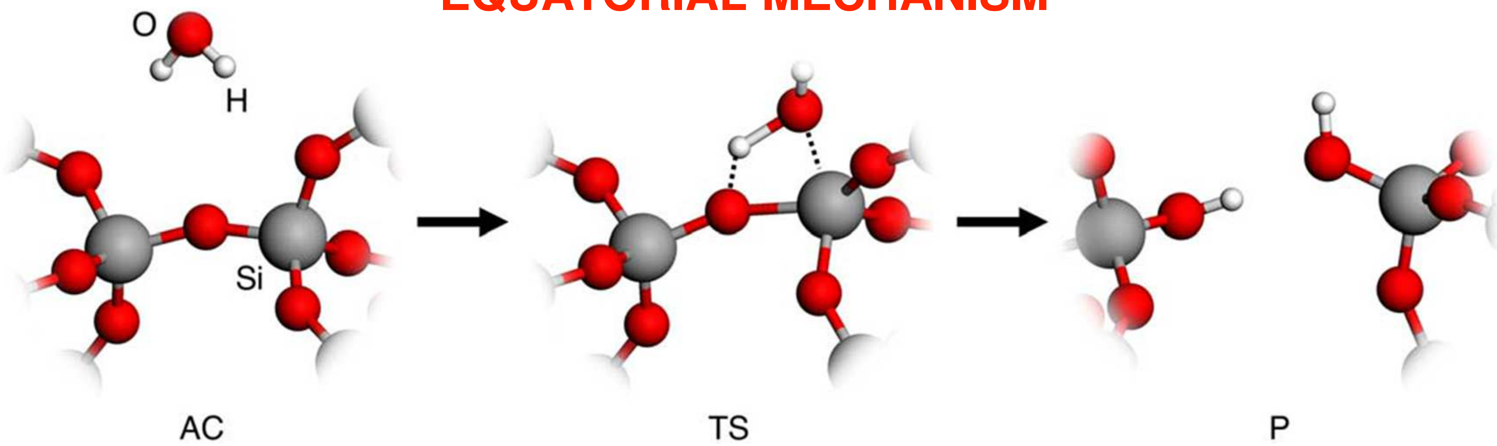


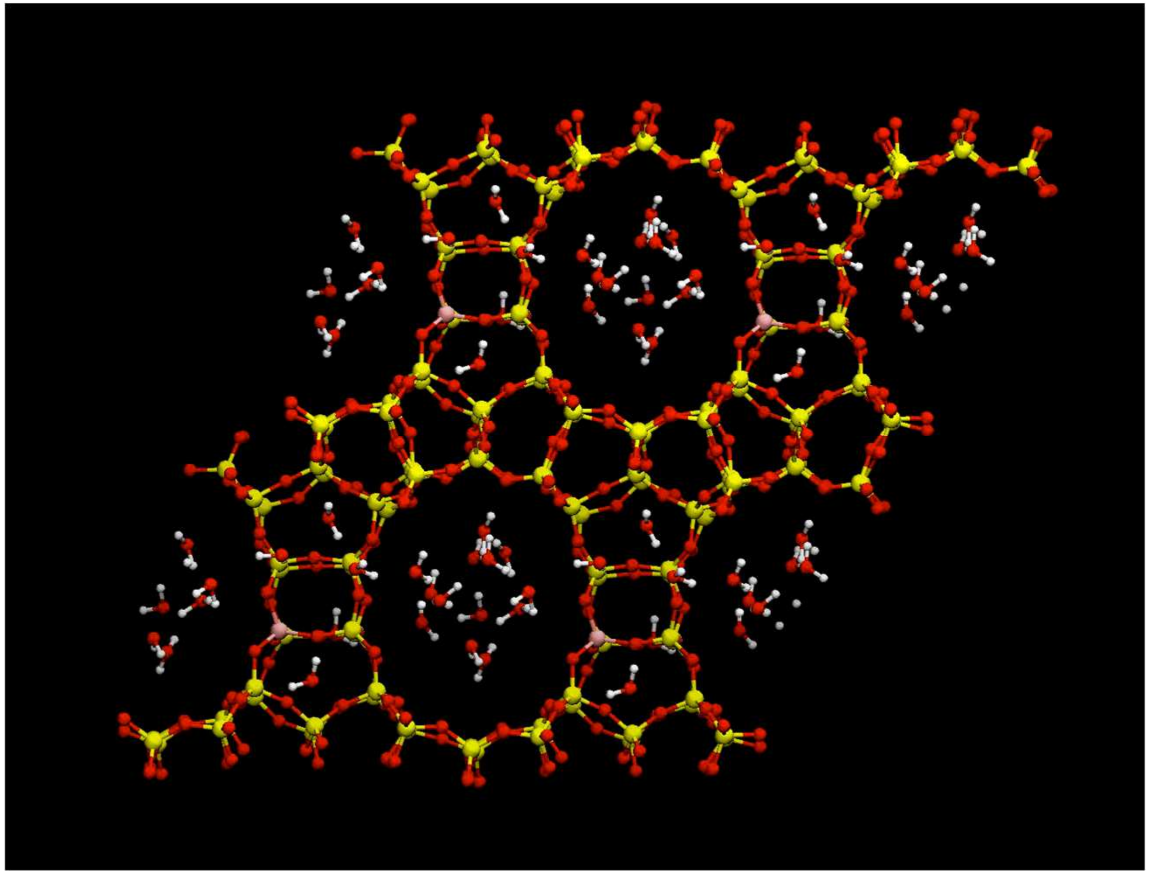
O-down adsorption 1,2-dissociation

Bond hydrolysis	**Activation barrier (kJ/mol)**	**System**	**Method/Set-up**
Si-O	160-210	Clusters	DFT (MP2/CC corrections), low H_2O, approximate inclusion of T effects (RRHO)
Ge-O	-	-	
Al-O	70-120	Various zeolites	

- Lack of investigations into Si-O hydrolysis in zeolites
- Completely absent in the case of Ge-O
- Al-O research limited to low T, low H_2O, few mechanisms

Si - Hühn *et al.* (10.1002/jcc.24892*)*, Pelmenschikov *et al.* (10.1021/jp011820g)
Al - Silaghi *et al.* *(*10.1016/j.jcat.2016.04.021, 10.1021/cs501474u)

More Realistic Model – solvation & temperature

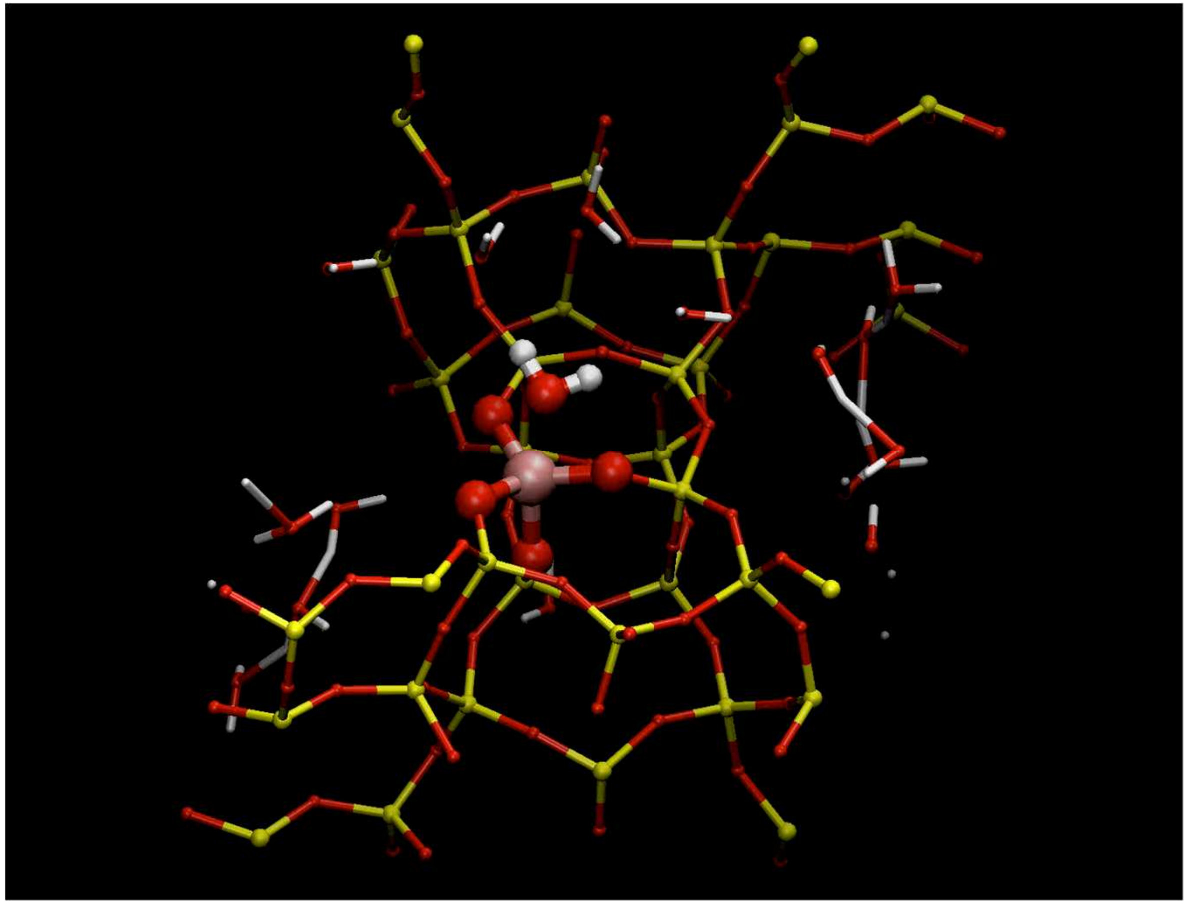


- UTL/CHA zeolites with Ge/Si/Al
- Neat water, 300-370K, explicit solvation up to 1g/cm^3

- *Ab initio* molecular dynamics
  - propagation of classical Newtonian equations of motions for classical nuclei in *ab initio* potential
  - NVT ensemble -> Helmholtz free energies

- Potential for classical nuclei from dispersion-corrected density functional theory
  - using Vienna ab initio simulation package (VASP)
  - approx. 100k core hours per reaction on Salomon (~150 ps)

How to study reactions using molecular dynamics?



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- Reactions are activated processes
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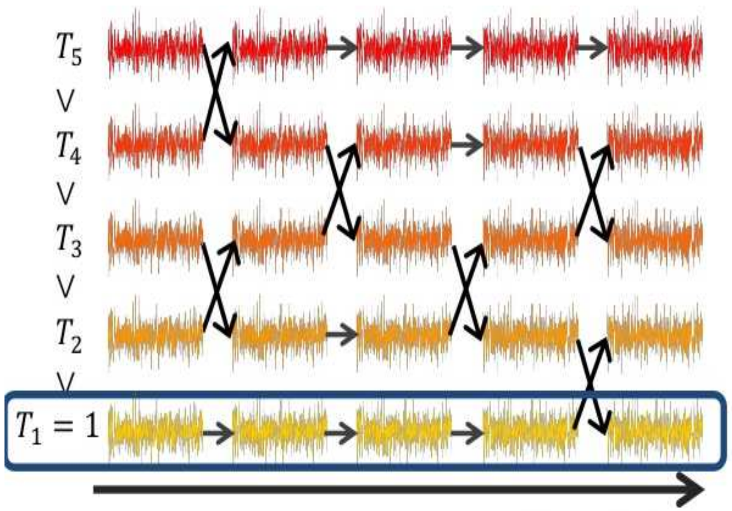


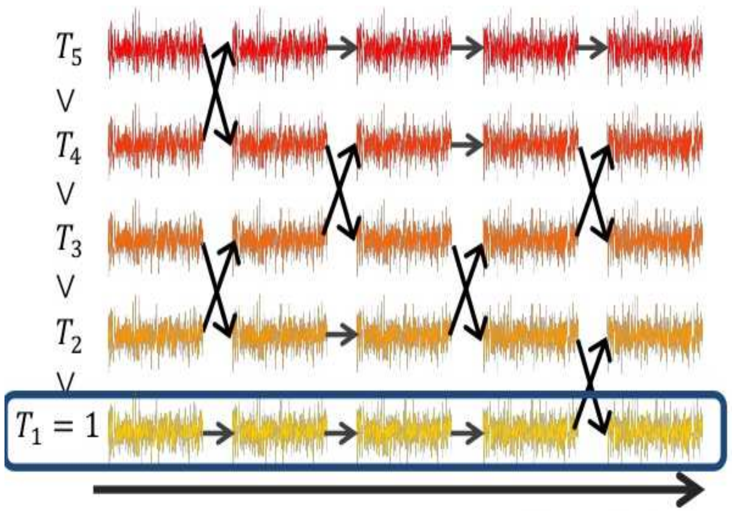
Parallel tempering / replica exchange

- ✓ Big exploratory potential
- × Only useful for smaller barriers

How to bias MD?

along all degrees of freedom
(using temperature, pressure, …)

along selected degrees of freedom
(reaction coordinate, order parameter, collective variable)



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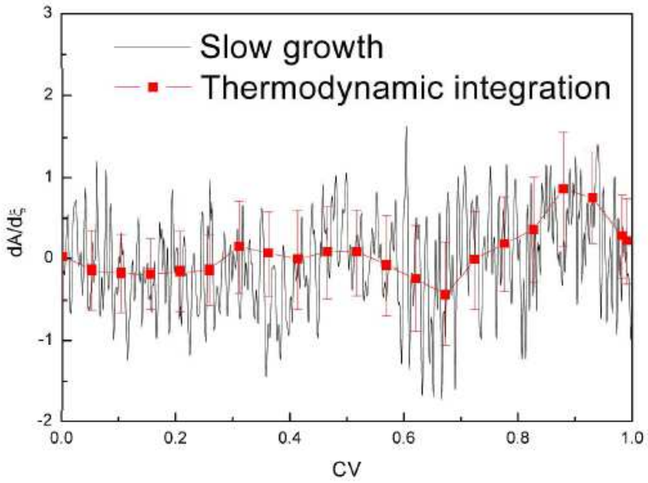
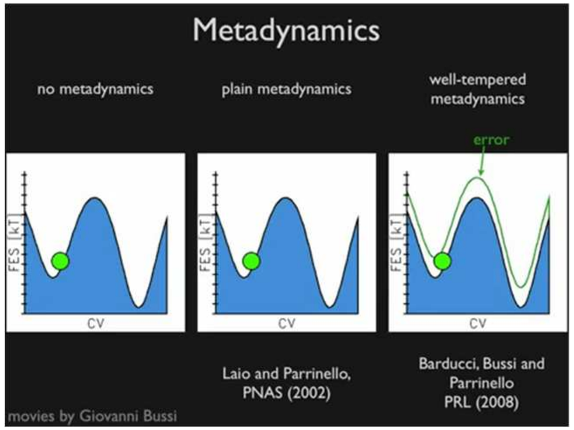


Thermodynamic Integration



Metadynamics

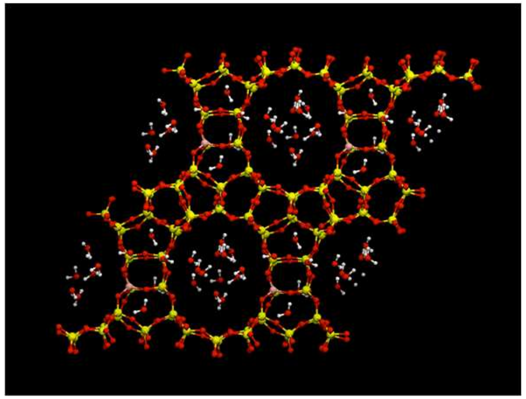
- ✓ Big exploratory potential
- × Only useful for smaller barriers

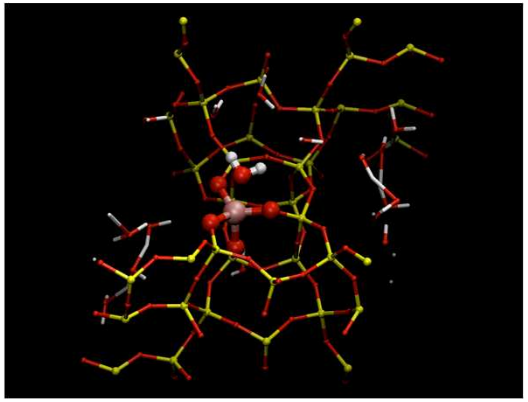
- ✓ Quantitative description of free energy surface
- ✓ Highly-activated processes accessible
- × Less exploratory
- × Choosing correct CV is non-trivial

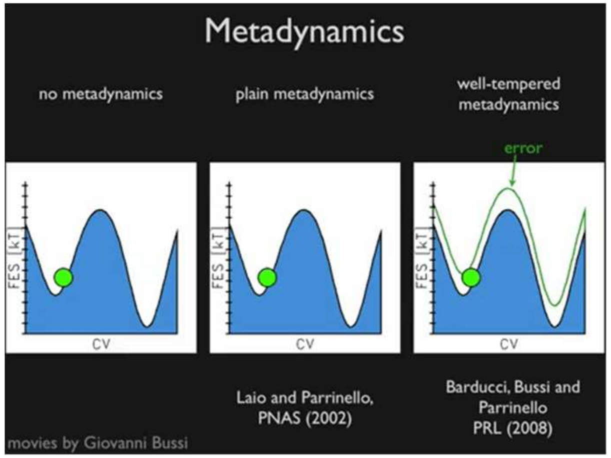
Cheng *et al.* (10.1021/acs.jpclett.5b02247)

http://goo.gl/jbLgB

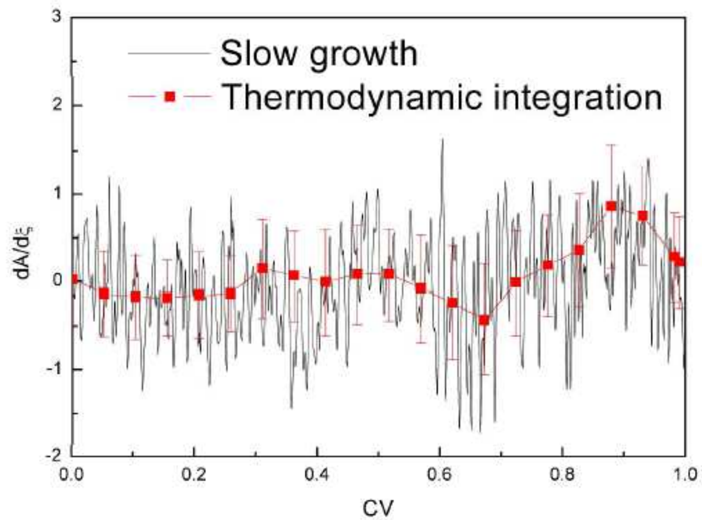
Back to zeolite hydrolysis...but now using biased AIMD





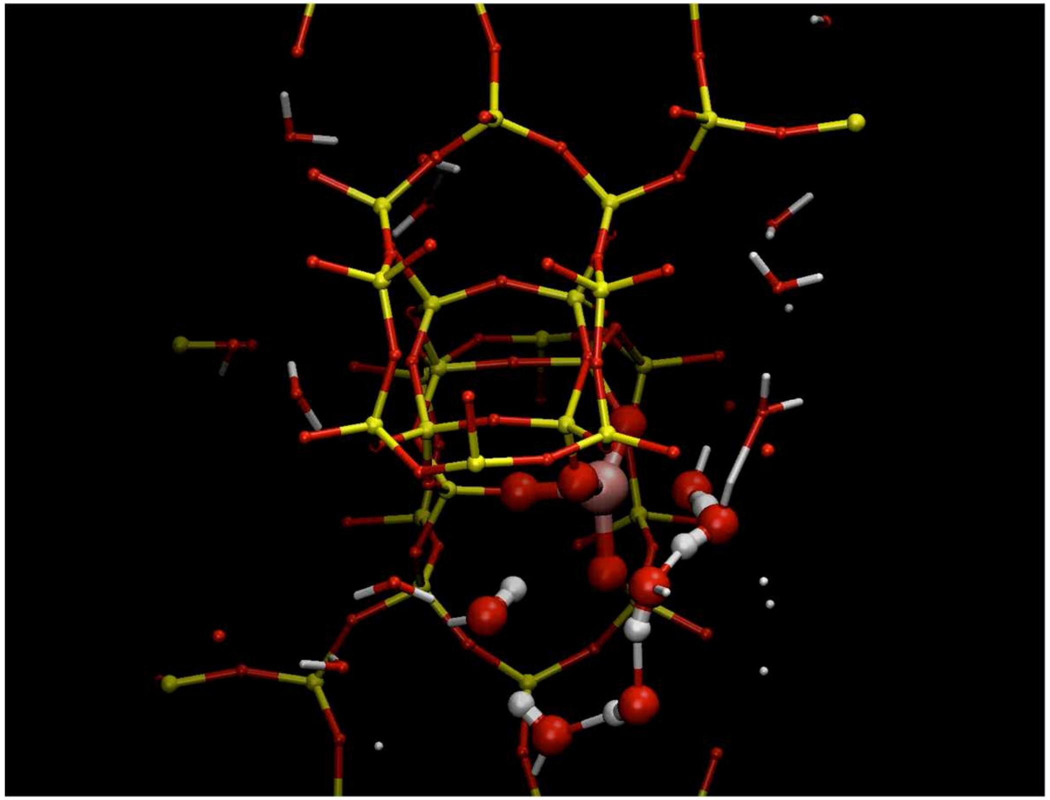


Metadynamics (MTD) - exploratory



Thermodynamic integration (TI) - quantitative

New hydrolysis mechanism for Si/low-Ge zeolites



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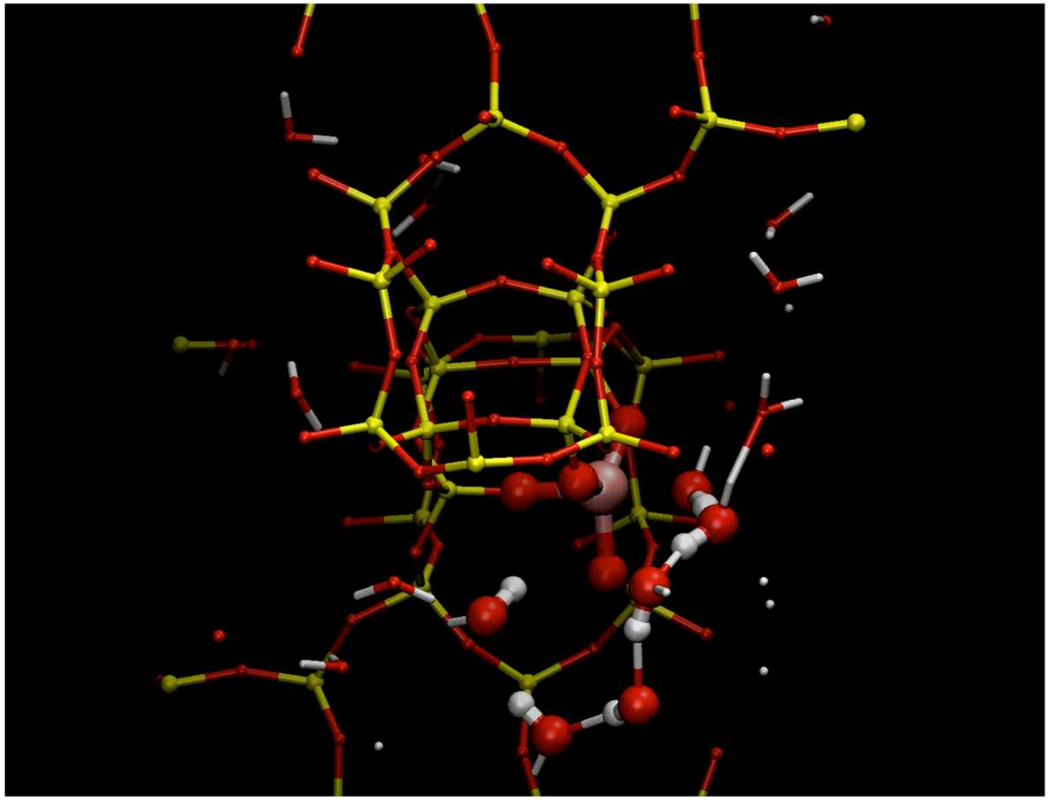
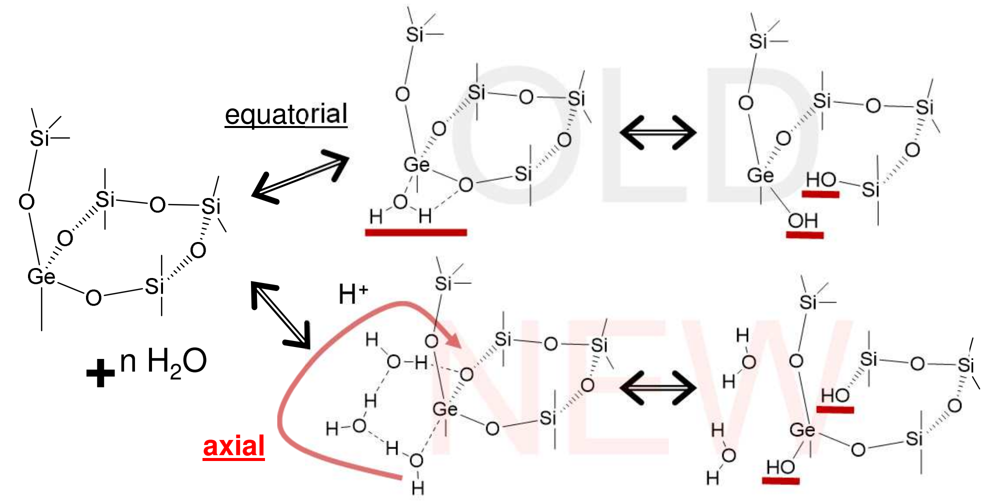
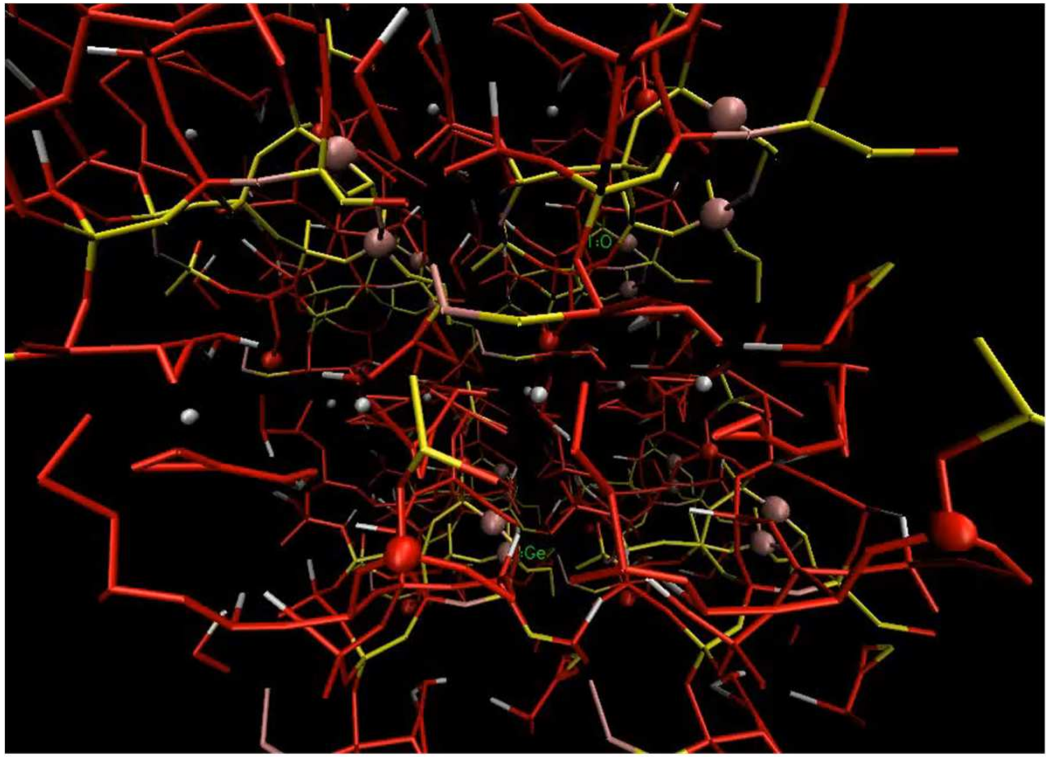




Lower barriers and less endergonic reactions for AXIAL mechanism

Support from experiment: ^{17}O NMR – isotopic exchange from water into framework at RT (Si-^{17}O-Si)
(St Andrews – R. E. Morris + S. Ashbrook)

New hydrolysis mechanism for high-Ge zeolites



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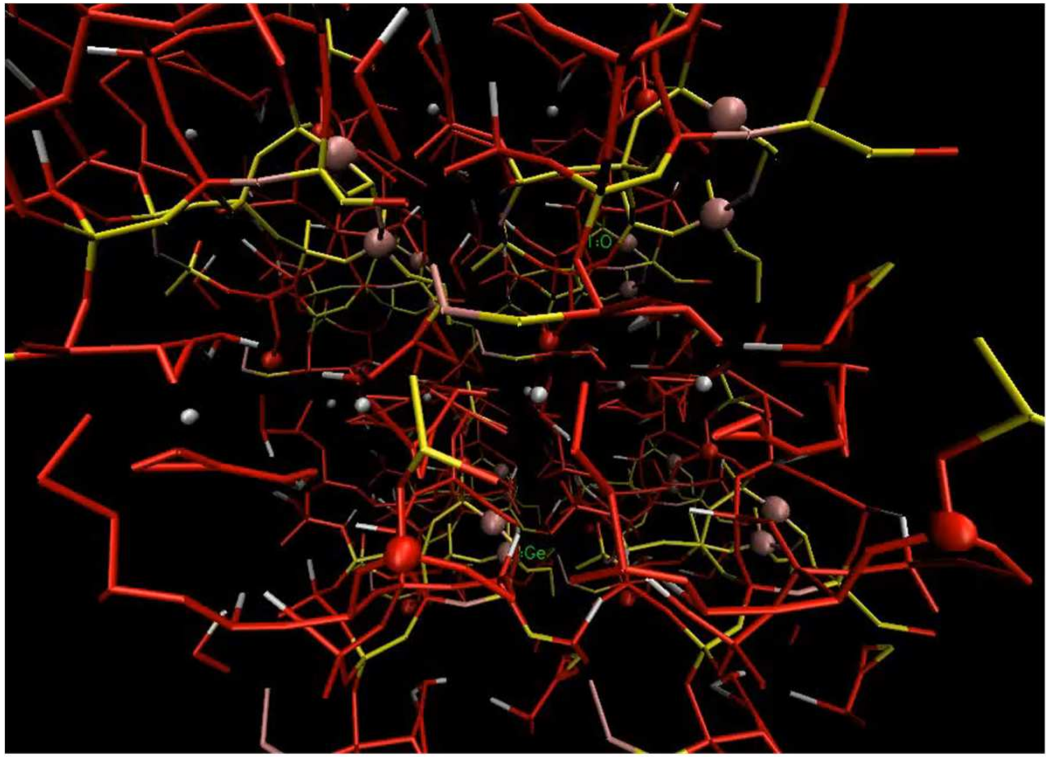

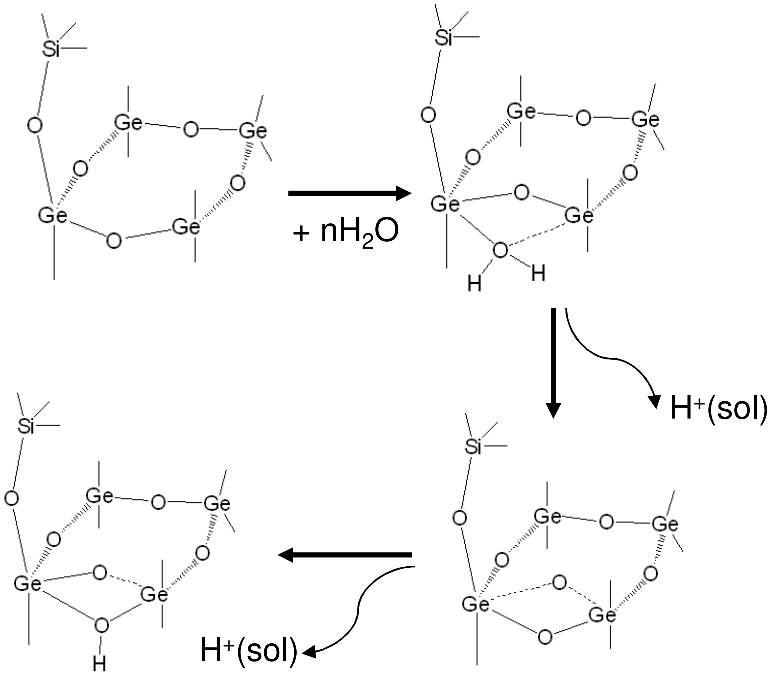

Almost no barrier and exorgonic reaction for high-Ge mechanism

Support for experiment: fast dissolution (few seconds) of high-Ge samples in RT in full solvation regime (ADOR), water adsorption isotherms experiments

Conclusions

- The role of proper water solvation is significant – dynamical treatment is essential
  - new mechanisms for Si/Ge zeolites
  - lower barriers and more favourable reaction energies
  - corroborating existing experimental data (ADOR) and even motivating new investigations (NMR)

- Biased AIMD
  - ✓ chemical reactions in realistic conditions (solvent, temperature, pressure …)
  - ✓ exploratory aspect (mechanism, products, reaction networks)
  - × costly with some pitfalls (choice of CV, statistical convergence issues, …)

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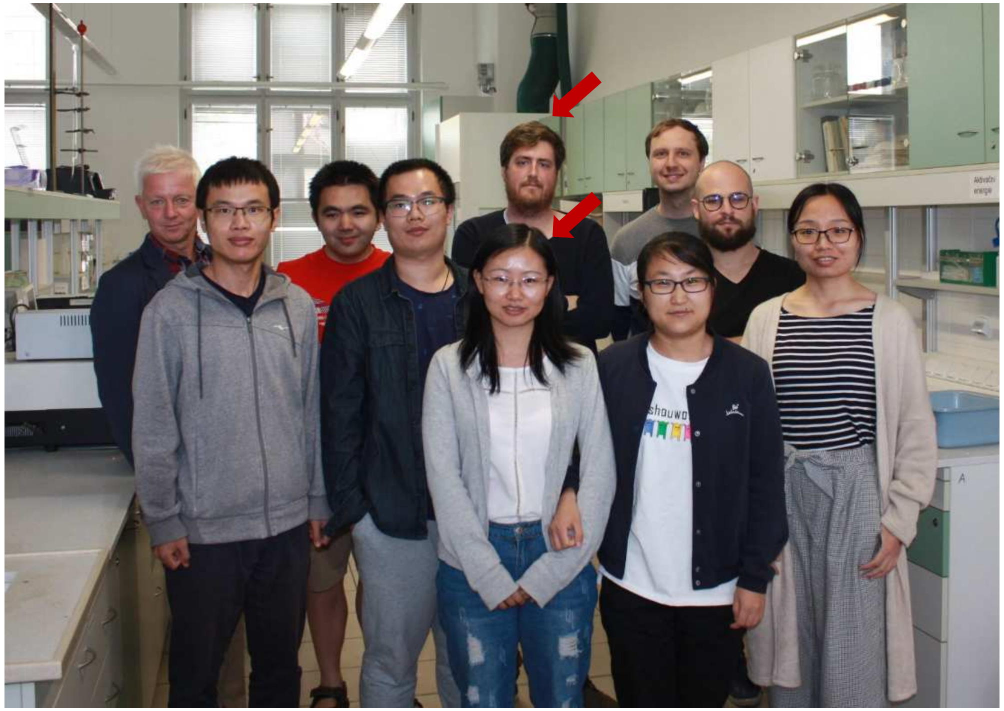

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