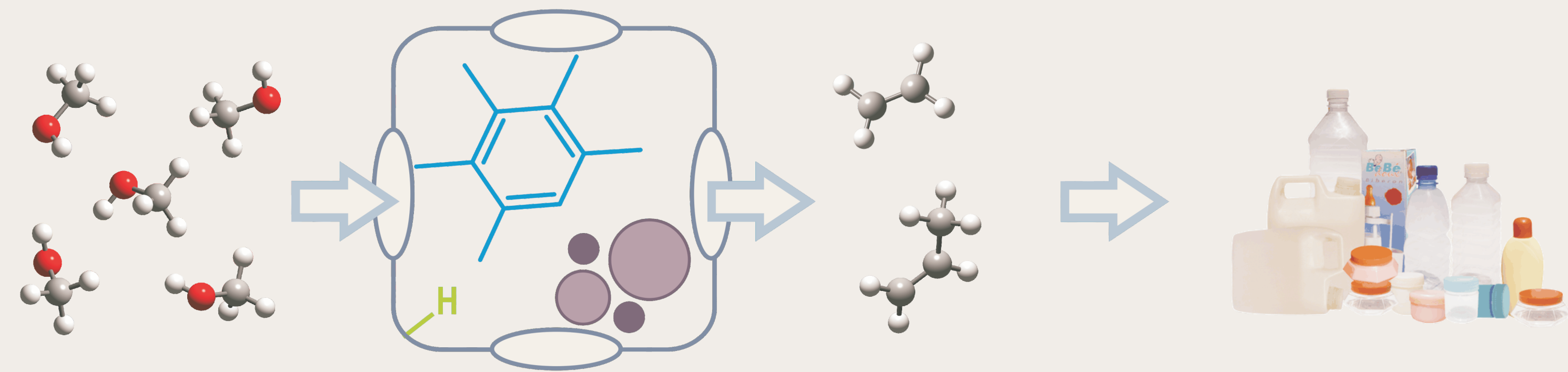


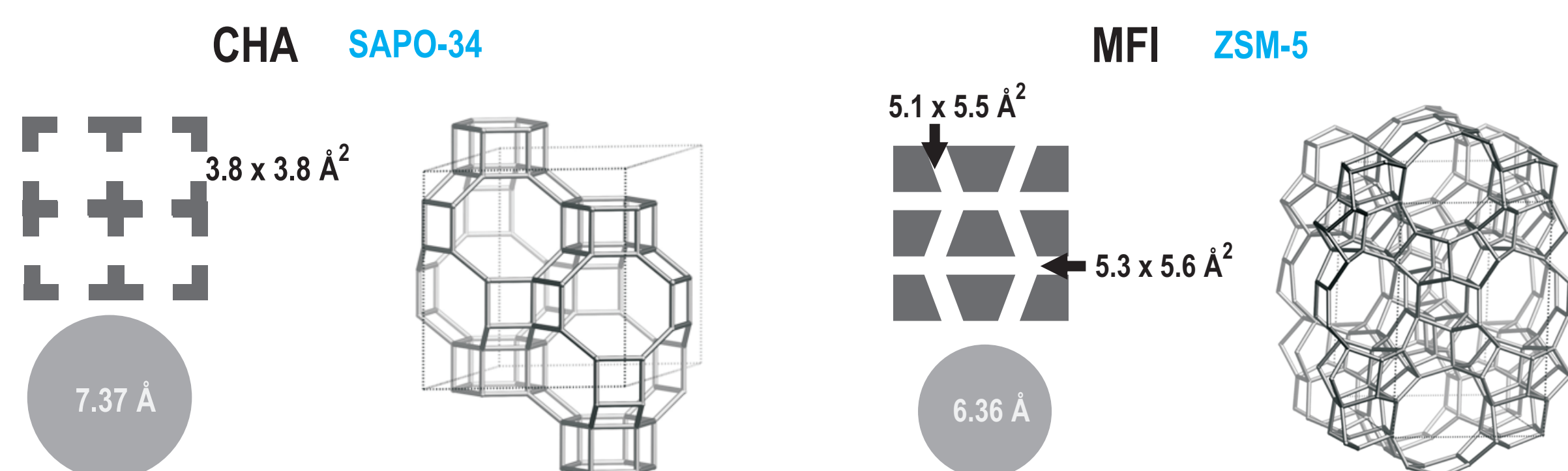
## Methanol to Olefins (MTO)

Catalyzed by

Zeolite framework  
Zeolitic acid sites  
**Hydrocarbon pool (HP)** [1,2]



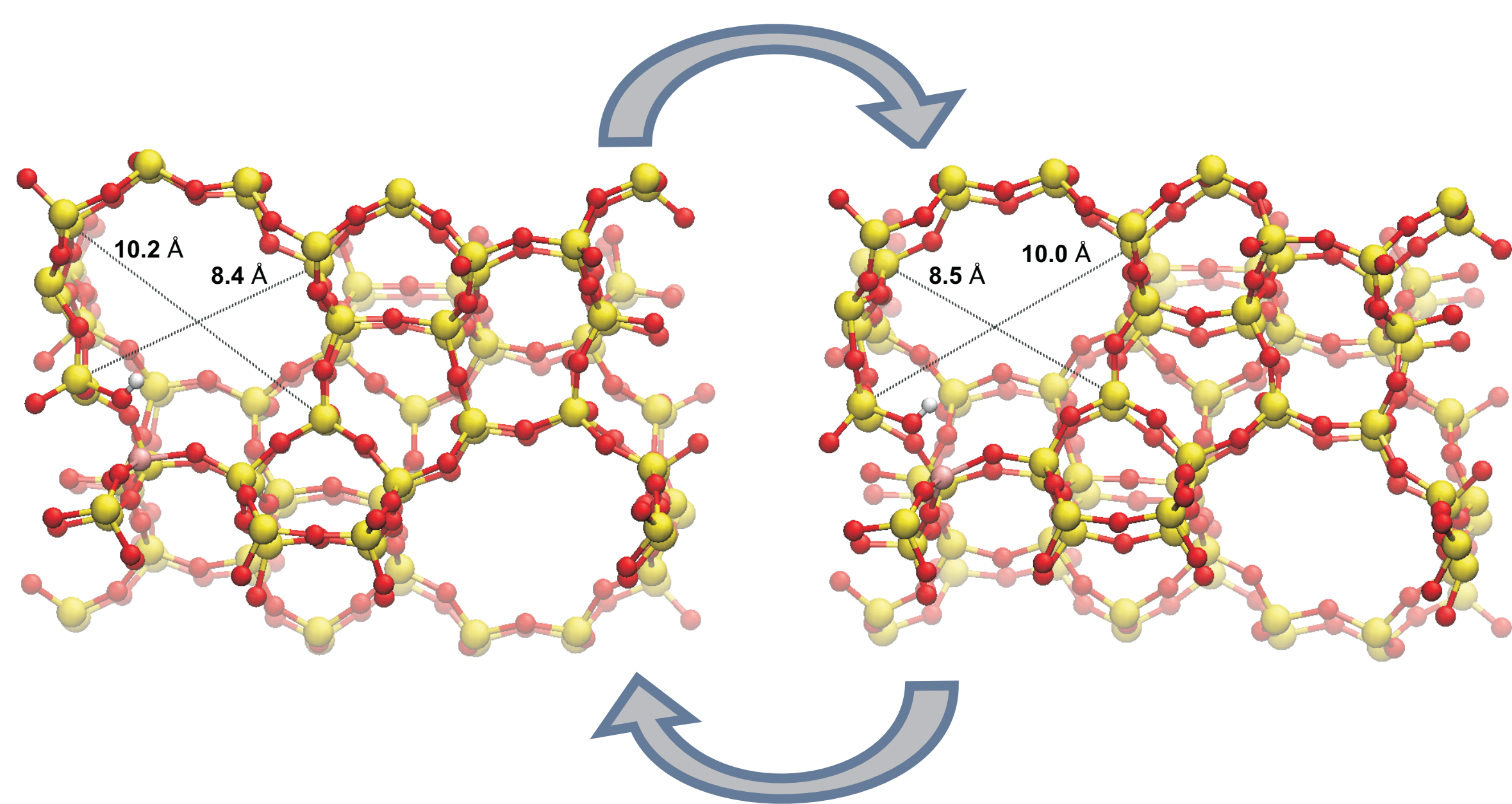
### Typical MTO catalysts:



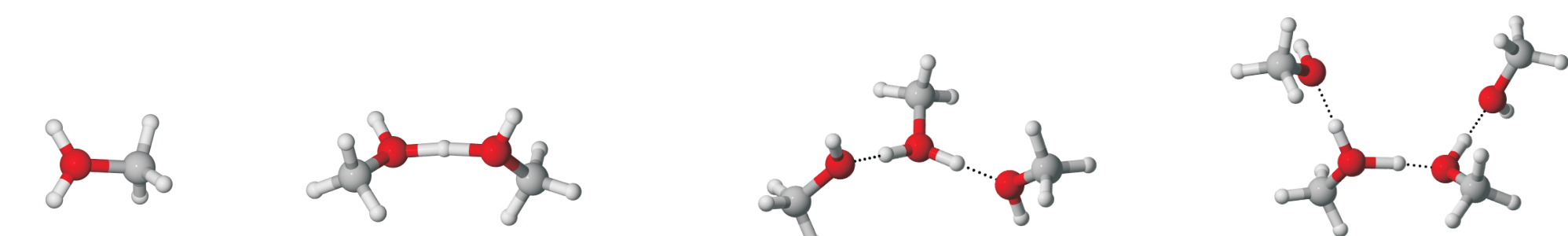
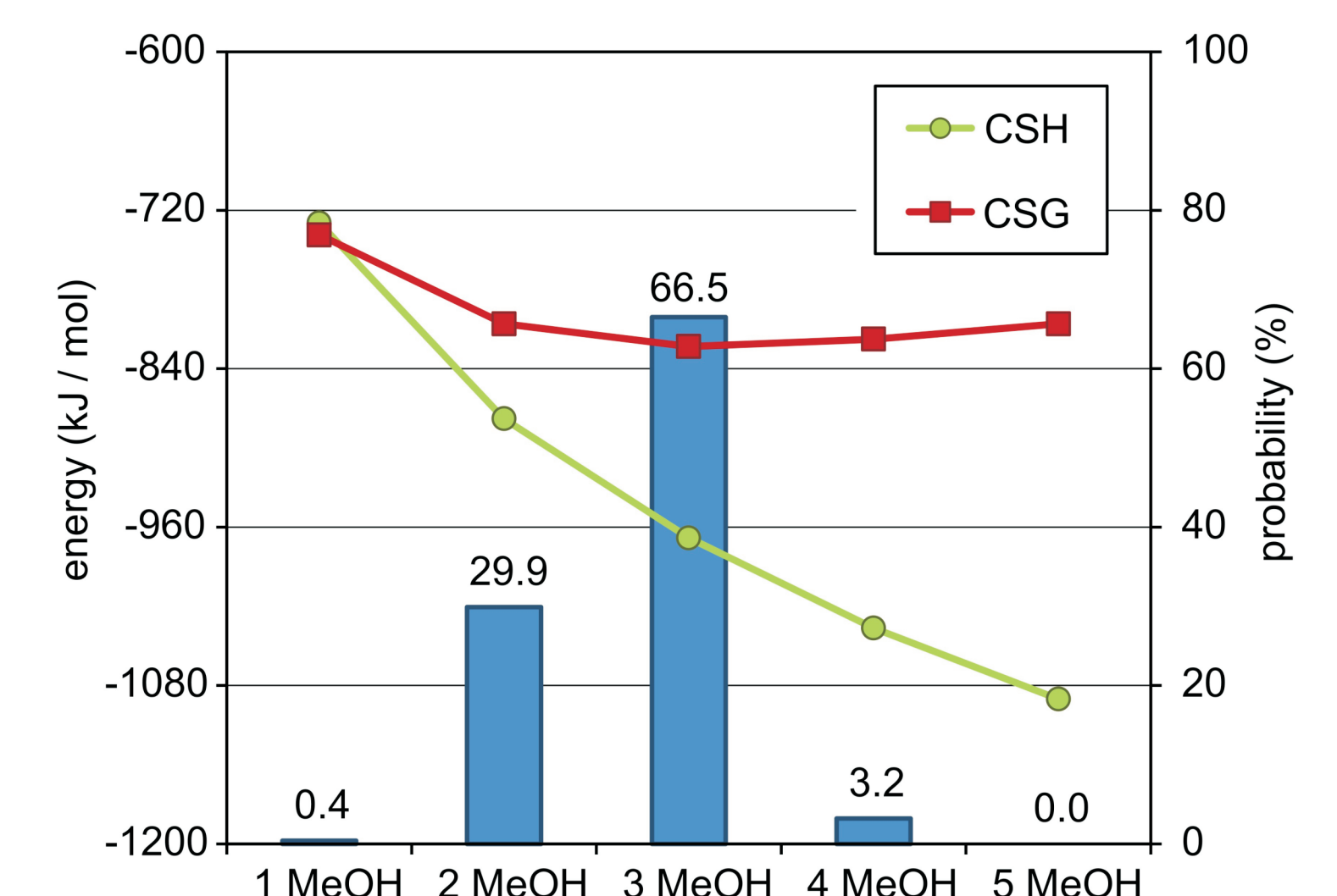
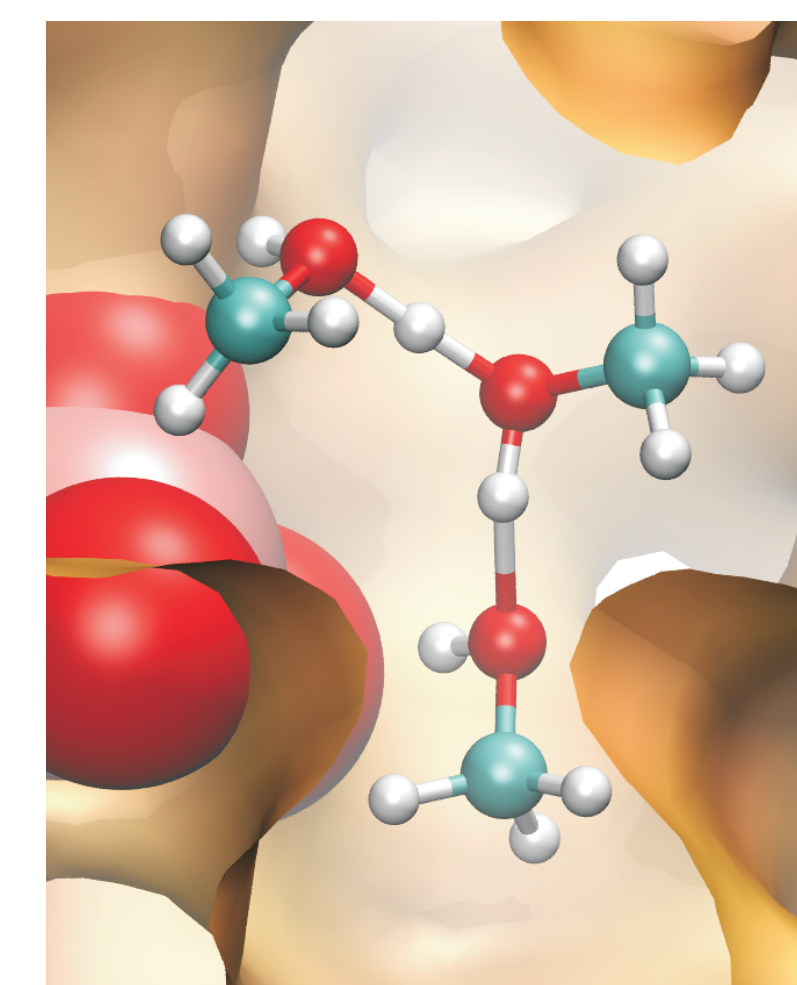
### Methodology:

- ✦ Ab initio molecular dynamics / metadynamics [3]
- ✦ Periodic calculations in CP2K
- ✦ revPBE, GPW basis set, D3-corrections
- ✦ NPT/NVT at 670 K

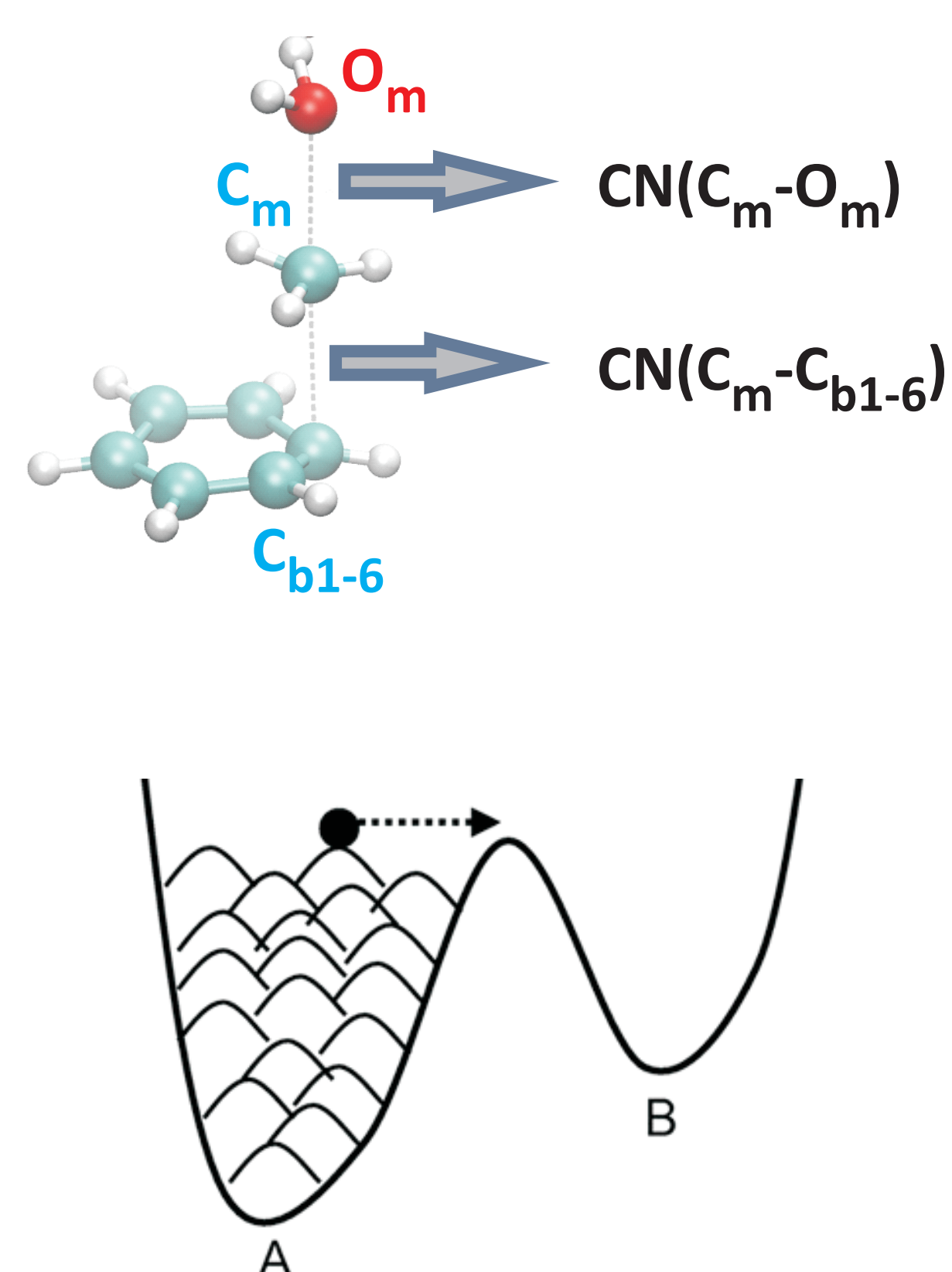
## Framework flexibility



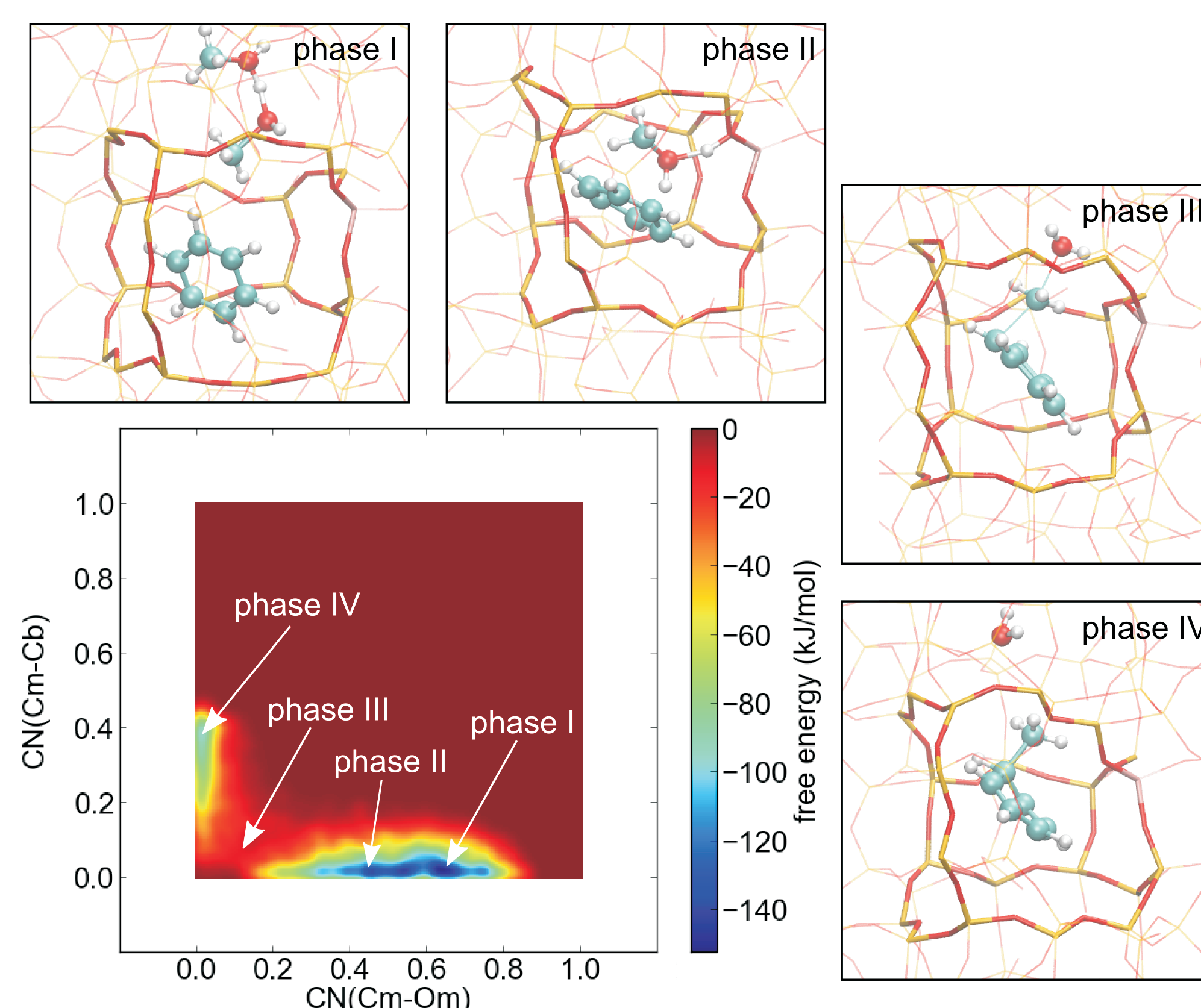
## Methanol forms protonated clusters



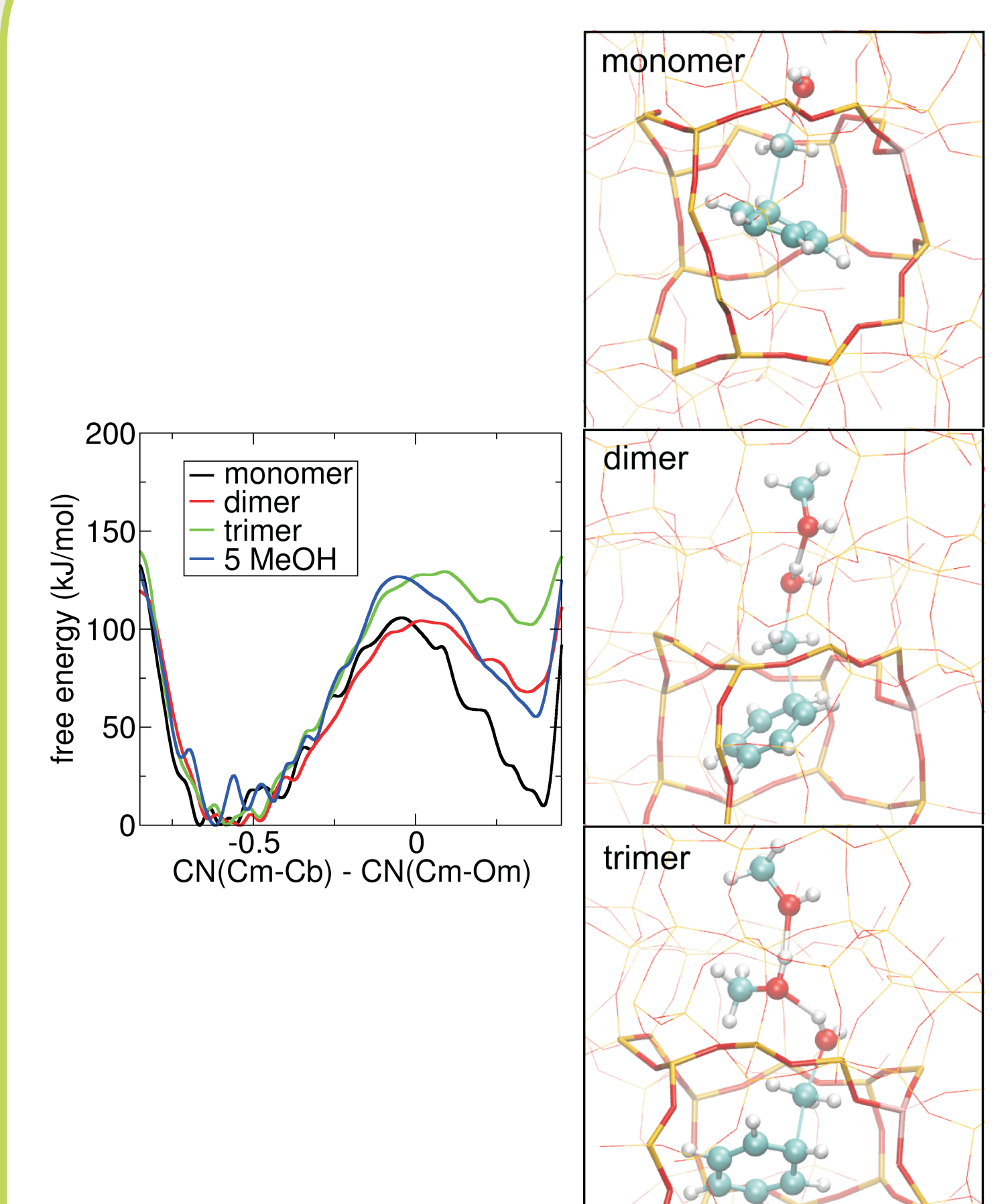
## Metadynamics: collective variables



## Reaction pathway



## Reactivity of methanol clusters



## References

- [1] Hemelsoet, K.; Van der Mynsbrugge, J.; De Wispelaere, K.; Waroquier, M.; Van Speybroeck, V. *ChemPhysChem* **2013**, *14*, 1526 – 1545.
- [2] Olsbye, U.; Svelle, S.; Bjorgen, M.; Beato, P.; Janssens, T. V. W.; Joensen, F.; Bordiga, S.; Lillerud, K. P. *Angew. Chem.-Int. Ed.* **2012**, *51*, 5810-5831.
- [3] Laio A. and Parrinello M. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 12562-12566.

## Summary

- ☑ Stable protonated methanol dimers and trimers are formed in the channel intersections of H-ZSM-5.
- ☑ The stabilization of a proton in methanol increases until methanol trimers are formed.
- ☑ Methanol clusters are less reactive than a single methanol molecule.