UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

REACTION OF C1-C4 ALCOHOLS IN ZEOLITES

Cuong M. Nguyen, Marie-Françoise Reyniers and Guy B. Marin

Laboratory for Chemical Technology

Krijgslaan 281 (S5), 9000 Ghent, Belgium

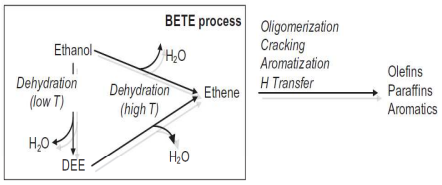
http://www.lct.UGent.be E-mail: CuongManh.Nguyen@UGent.be

ERIC European Research Institute of Catalysis

M2dcR2

BIOALCOHOLS TO BIOCHEMICALS

Bioalcohols can be converted to biochemicals and biofuels by means of zeolite-catalyzed processes:



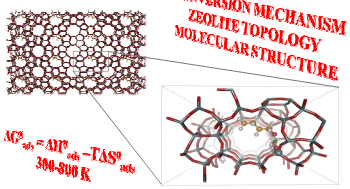
Insight into the detailed mechanism of the zeolite-catalyzed alcohol conversion is largely lacking and difficult to interpret from experiment only.

This poster presents molecular insight into the first alcohol-to-alkene reaction step.

SIMULATION METHODS

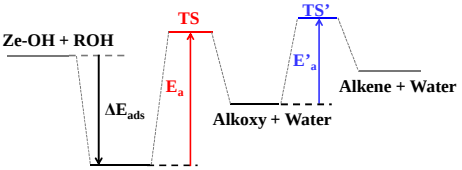
Periodic density functional theory calculations (DFT-D//DFT-D) of electronic energy and vibrational frequencies:

- alcohol-zeolite interactions are treated under periodic boundary condition, using the PBE functional.
- dispersion (D) correction is included to account for the van der Waals (vdW) interactions.



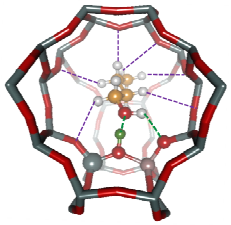
Statistical thermodynamics was used to obtain macroscopic parameters (ΔS^0, ΔH^0 and ΔG^0) at desired temperature.

ALCOHOL TO ALKENE



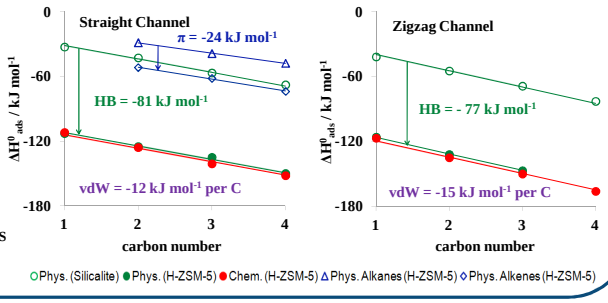
	H-FAU		H-MOR		H-ZSM-5		H-ZSM-22	
	E_a	E'_a	E_a	E'_a	E_a	E'_a	E_a	E'_a
Ethanol	157	92	155	87	146	95	129	95
1-Butanol	156	77	157	93	149	99	137	99
2-Butnol	119	65	-	-	-	-	-	-
T-Butanol	117	18	-	-	-	-	-	-

STABLIZING INTERACTIONS: HYDROGEN BOND vs. vdW

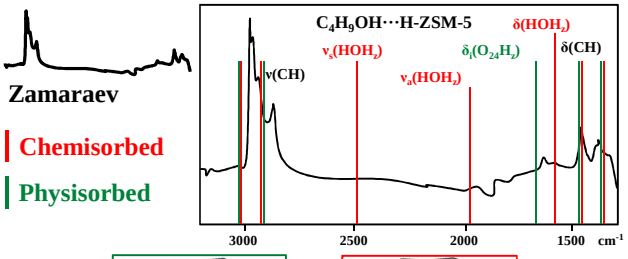


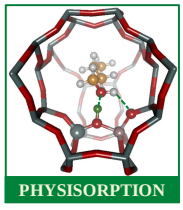
ΔH^0_{phys}: ROH > ALKENES > ALKANES

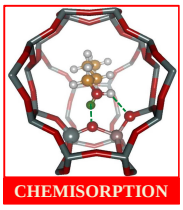
HB (ROH) > π (ALKENES)



VALIDATION I: IR SPECTRA



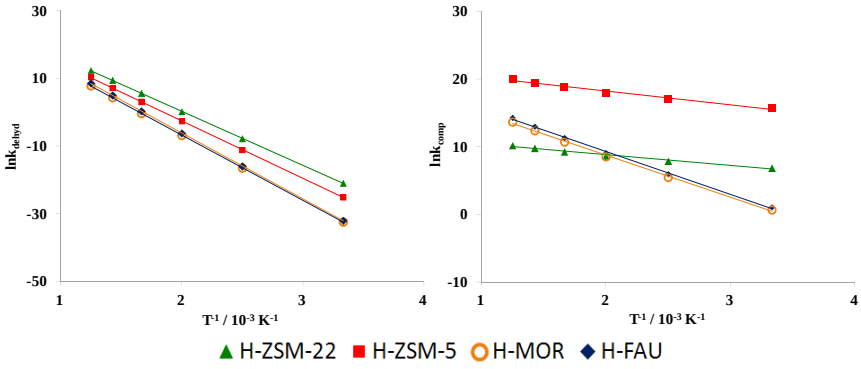




ETHANOL DEHYDRATION RATES

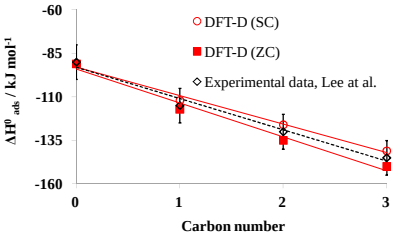
$$k_{dehyd} = \frac{k_b T}{h} \exp\left(-\frac{\Delta G^0_a}{RT}\right)$$

$$k_{comp} = k_{dehyd} K_{ads} = \frac{k_b T}{h} \exp\left(-\frac{\Delta G^0_a + \Delta G^0_{ads}}{RT}\right)$$



	H-FAU	H-MOR	H-ZSM-5	H-ZSM-5
k_{dehyd}/ s^{-1} (500 K)	1.9 10^{-3}	1.1 10^{-3}	7.1 10^{-2}	1.19
K_{ads}/ Pa^{-1}	4.6 10^6	4.8 10^6	9.4 10^8	4.8 10^3
k_{comp}/ s^{-1} Pa^{-1} (500 K)	8.9 10^3	5.1 10^3	6.7 10^7	5.7 10^3

VALIDATION II: ADSORPTION ENTHALPY



CONCLUSIONS

Periodic DFT-D//DFT-D is a comprehensive simulation package for ROH-Zeolite.

Lattice effects are electrostatic & vdW interactions to govern adsorption strength.

Alcohol to alkoxy is the rate-determining step of the alcohol-to-alkene conversion.

Activation energy (E_a): (i) decreases in going from large-pore to medium-pore zeolites.
(ii) decreases in going from primary to tertiary alcohol.

H-ZSM-5 is the most active zeolite for ethanol-to-ethene conversion step (300-800 K).

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