UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Zeolite catalysed conversion of alcohols to hydrocarbons: from molecular to industrial scale

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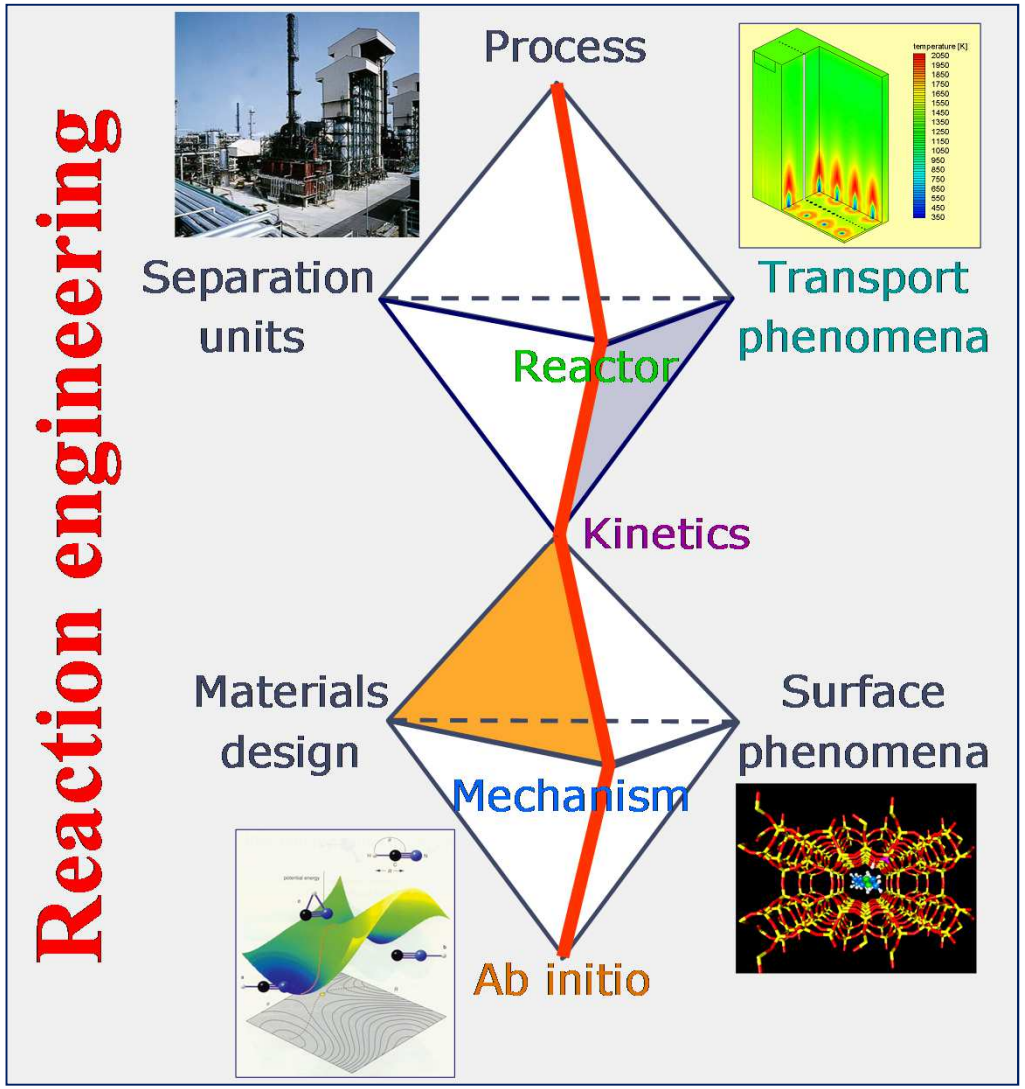
Laboratory for Chemical Technology

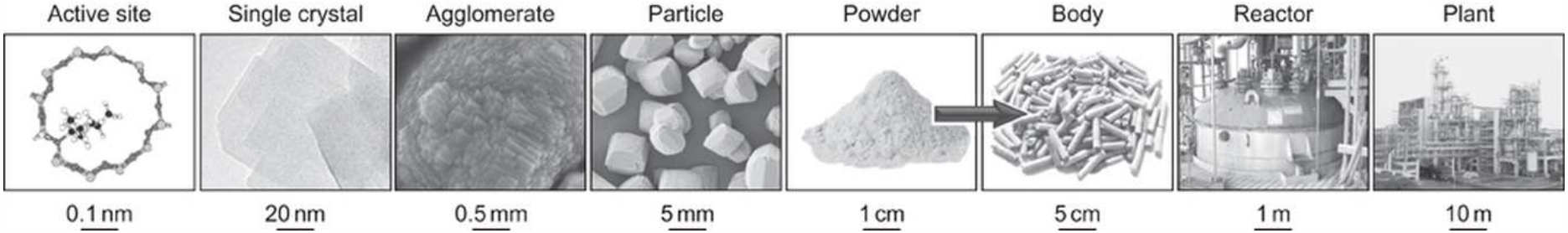
from atom (nm) to full process (m)



Process level

Molecular level

Heterogeneous Catalysis: a Multiscale process



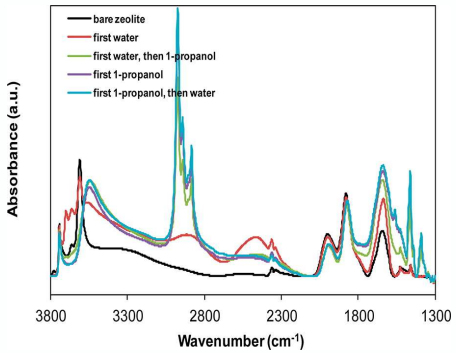
Ultra high vacuum
0.01-1 kPa

Low-moderate pressure
5-30 kPa

Moderate –high pressure
500-30000 kPa

spectroscopic studies

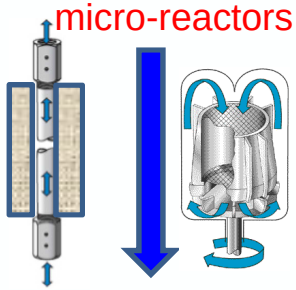
Reactive intermediates in reaction mechanism



Temporal Analysis of Products

Sub millisecond time resolution experiments for insight into reaction mechanism

Bench scale micro-reactors



Reaction kinetics study for obtaining reaction rate coefficients

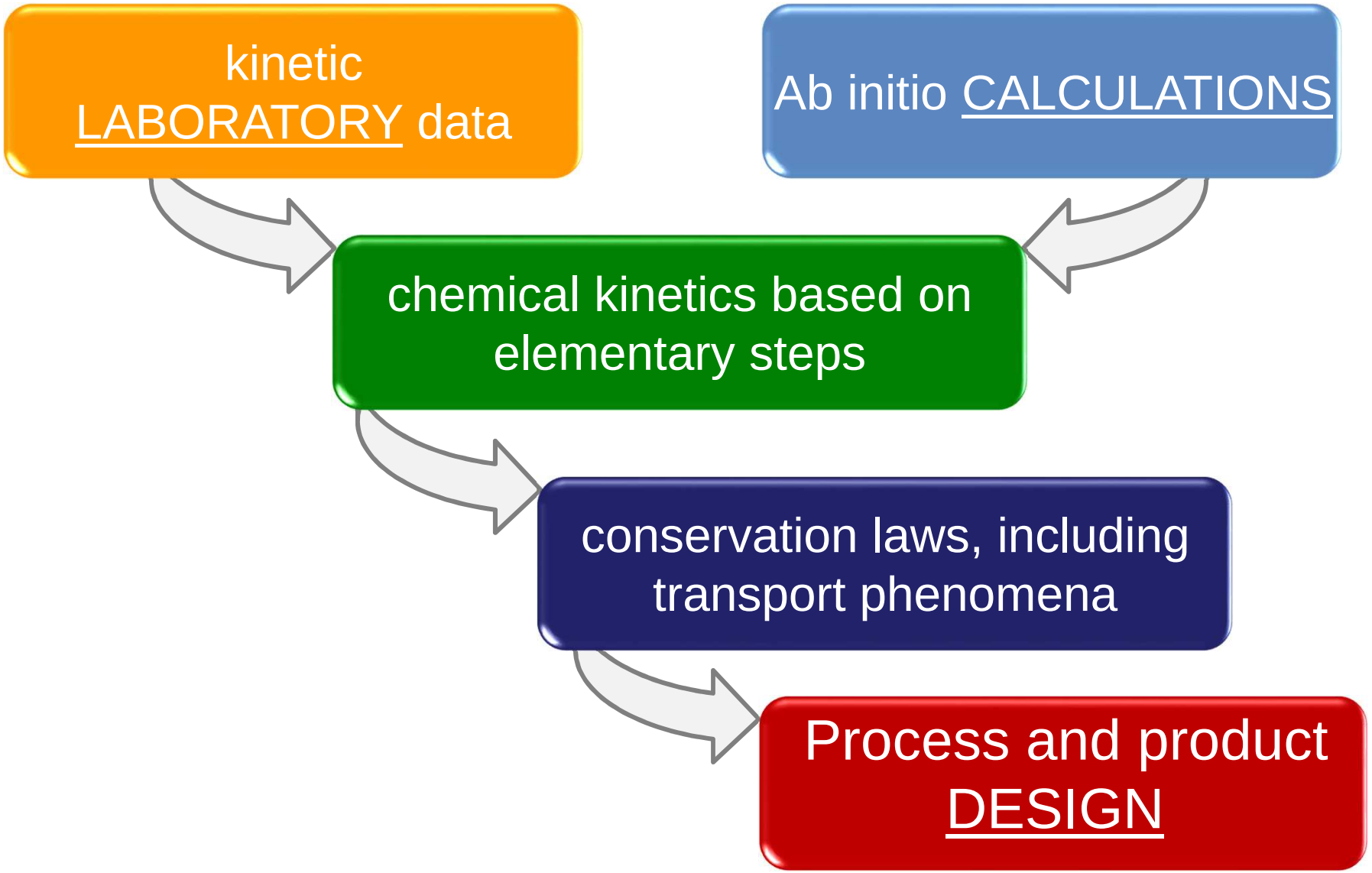
Pilot plants

Demonstration

Industrial reactor

Commercial scale production

Multi-scale modeling: la voie royale



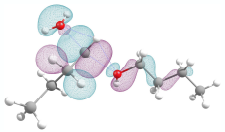
M.-F. Reyniers & G.B. Marin, Annu. Rev. Chem. Biomol. Eng. 5 (2014) 563

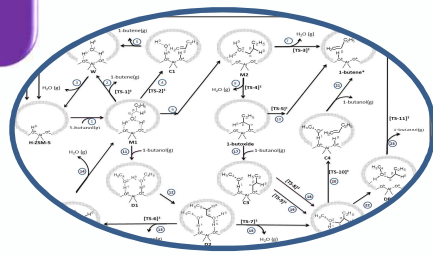
First-principles based kinetic modeling

VASP 5.3
PAW method
GGA: PBE-D2

Geometry optimization
electronic energy (0 K)

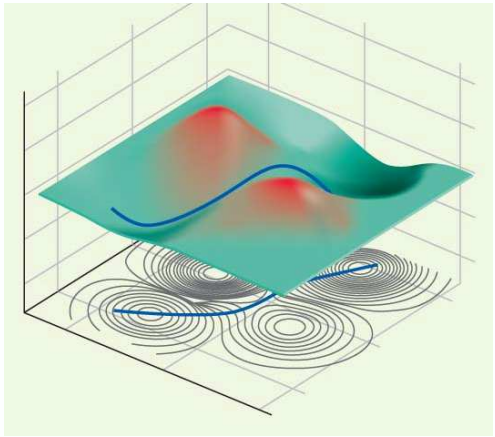
Vibrational analysis
frequencies





Reaction network

Statistical thermodynamics
H(T), S(T), G(T)



Thermo & Kinetics
K, k_+, k_-

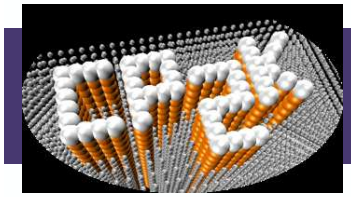
Isothermal

F_{in} → Plug flow reactor → F_{out}

Reactor Model

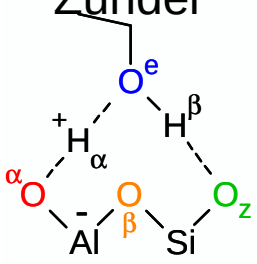
- Conversion and Selectivity
- Reaction path analysis

- Guidelines process conditions
- Guidelines catalyst design/screening



Ab Initio Molecular Dynamics

Zundel



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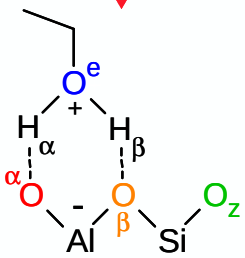
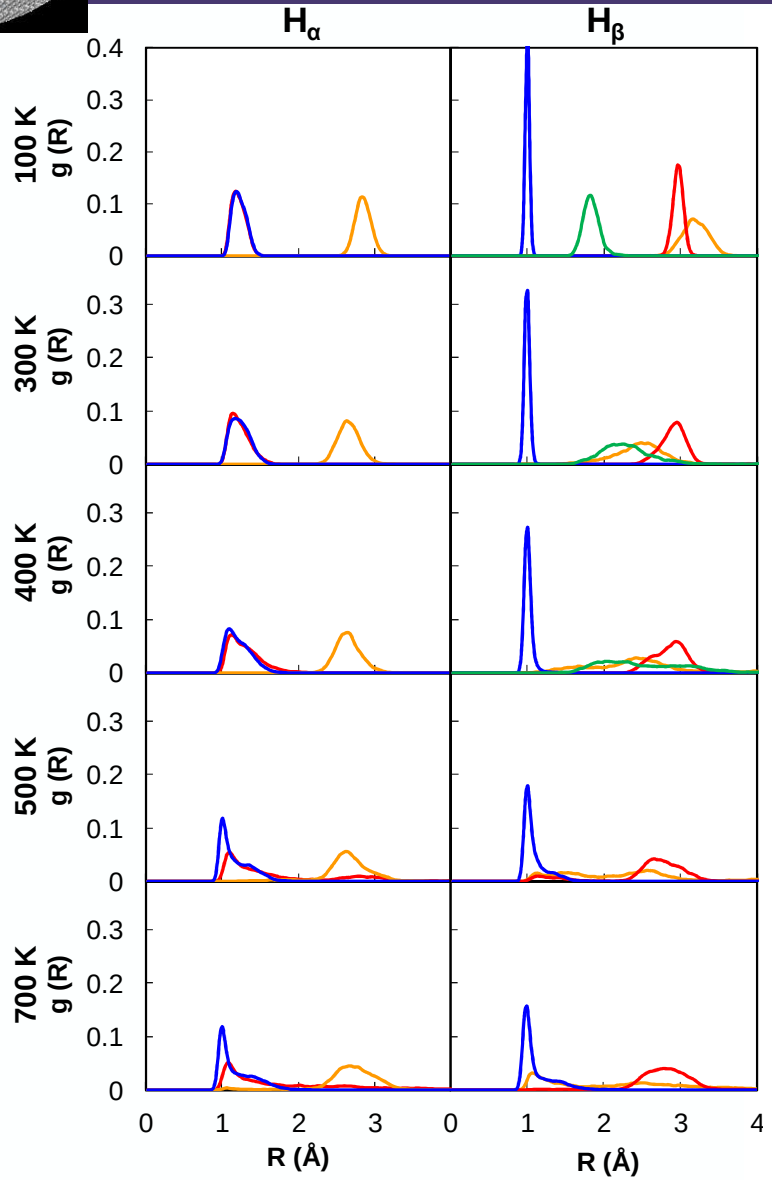


Eigen



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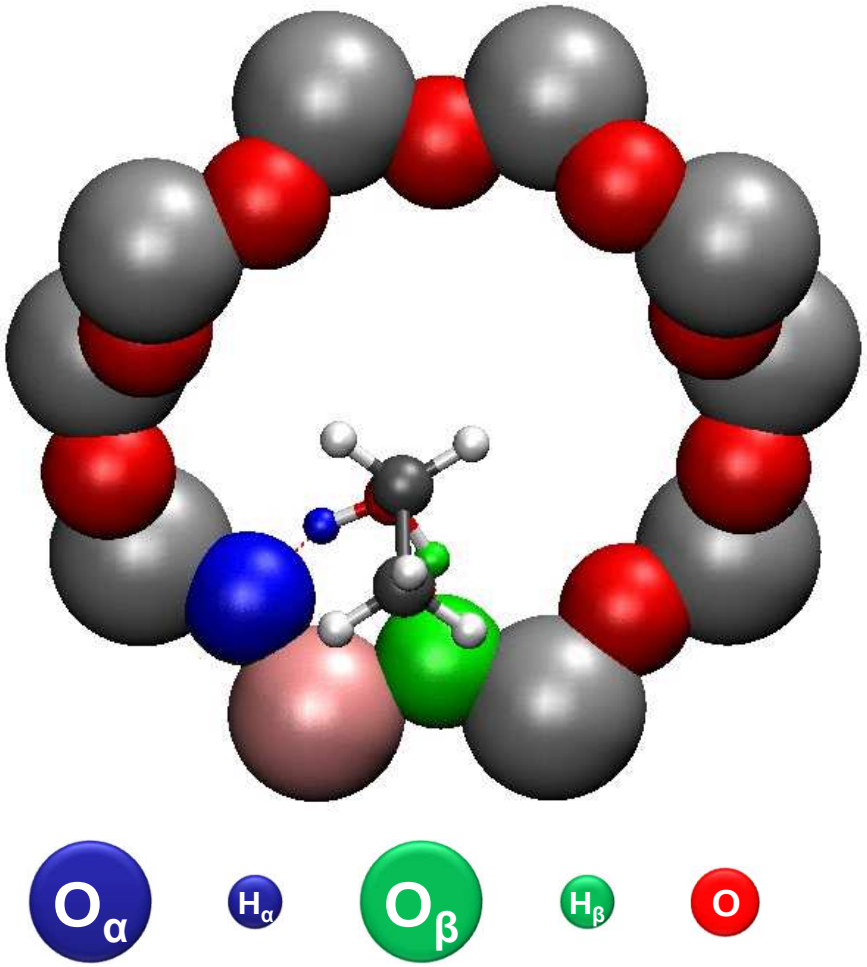
NVT, 300 K



Alexopoulos et al. J. Phys. Chem. C (2016) 7172-7182

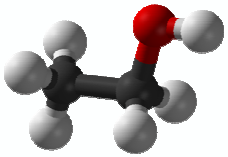
Acid catalyzed ethanol conversion

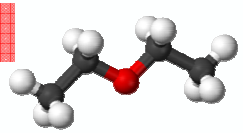
DEE

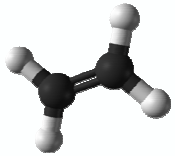
Ethanol

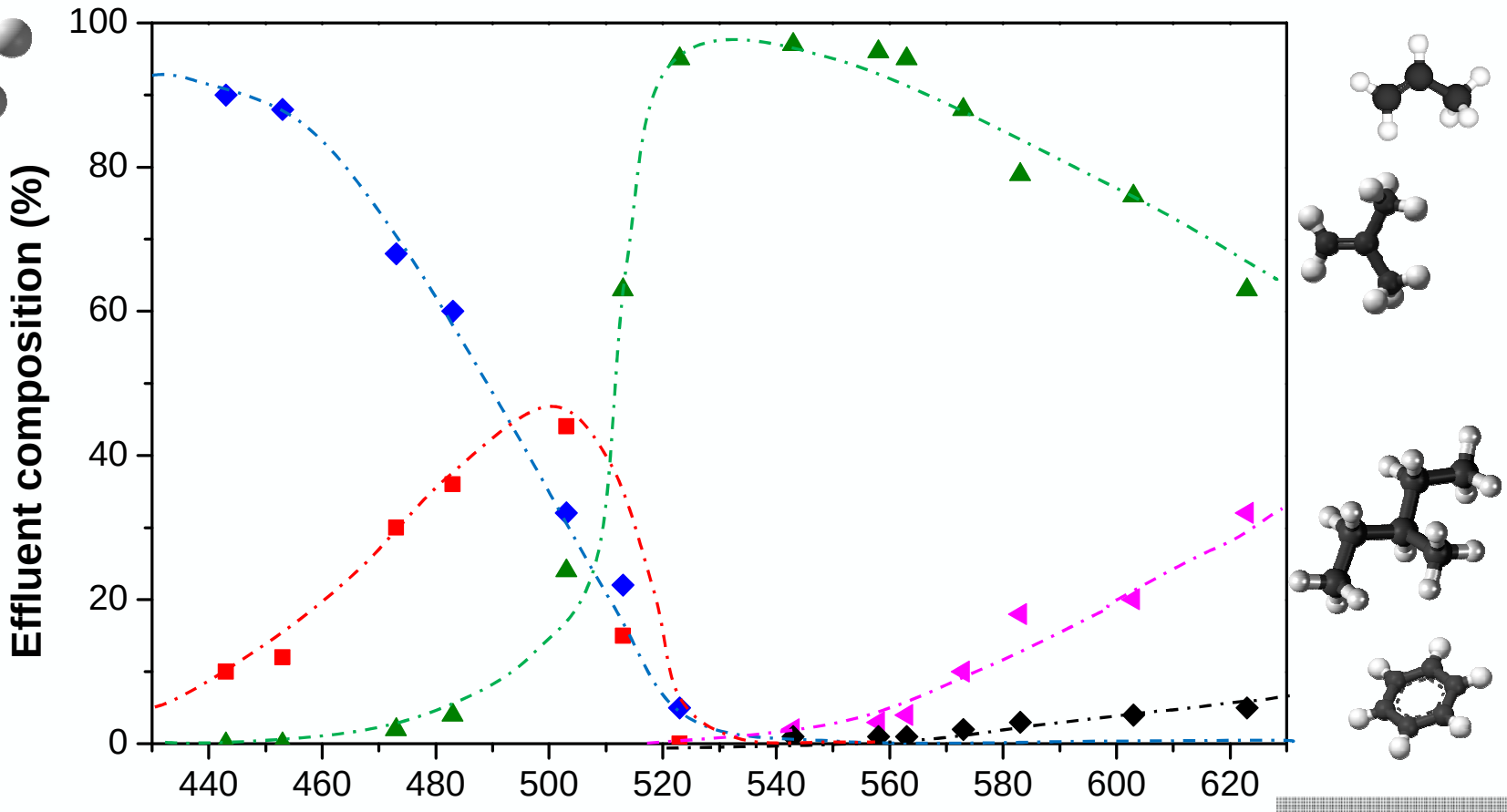
Ethylene

Light olefins









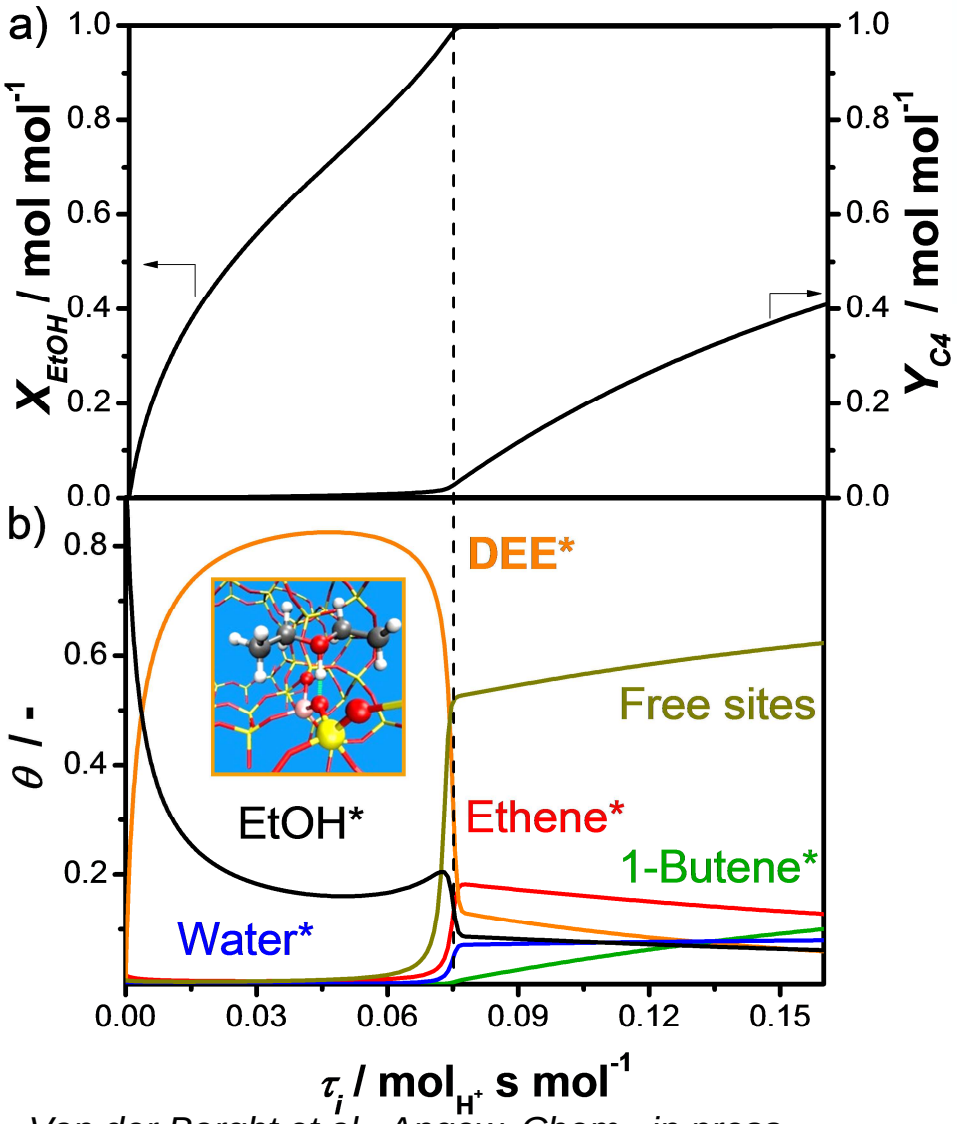
C_{5+} hydrocarbons

H-ZSM-5

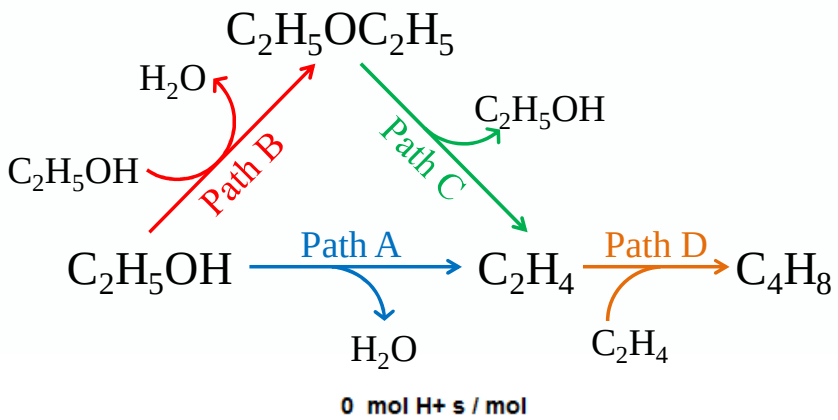
$p_{EtOH,0}$= 20 kPa : $W/F_{EtOH,0}$ = 8 kg s mol^{-1}

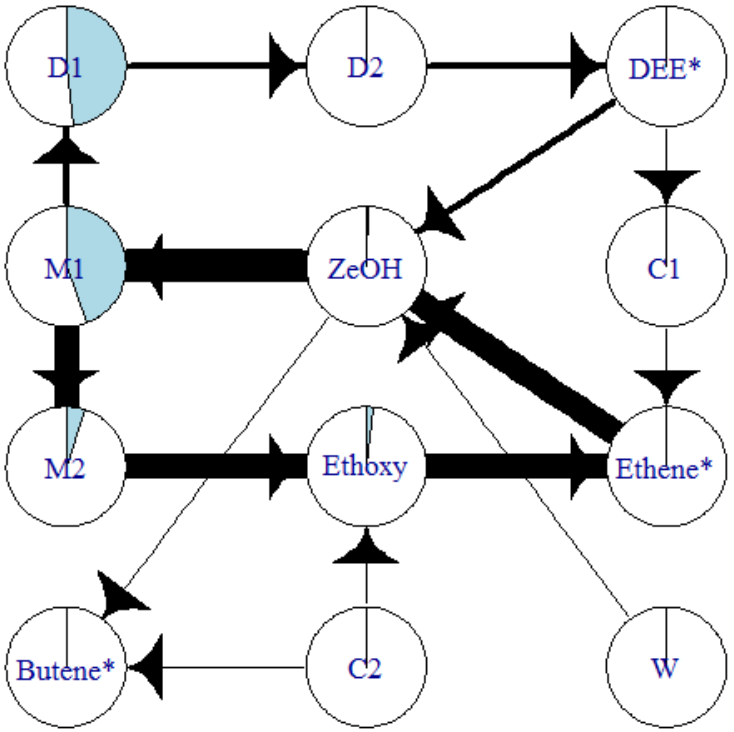
Ethanol conversion to higher HC

H-ZSM-5, T = 573 K, $p_{EtOH.0}$ = 30 kPa



Van der Borght et al., Angew. Chem., in press



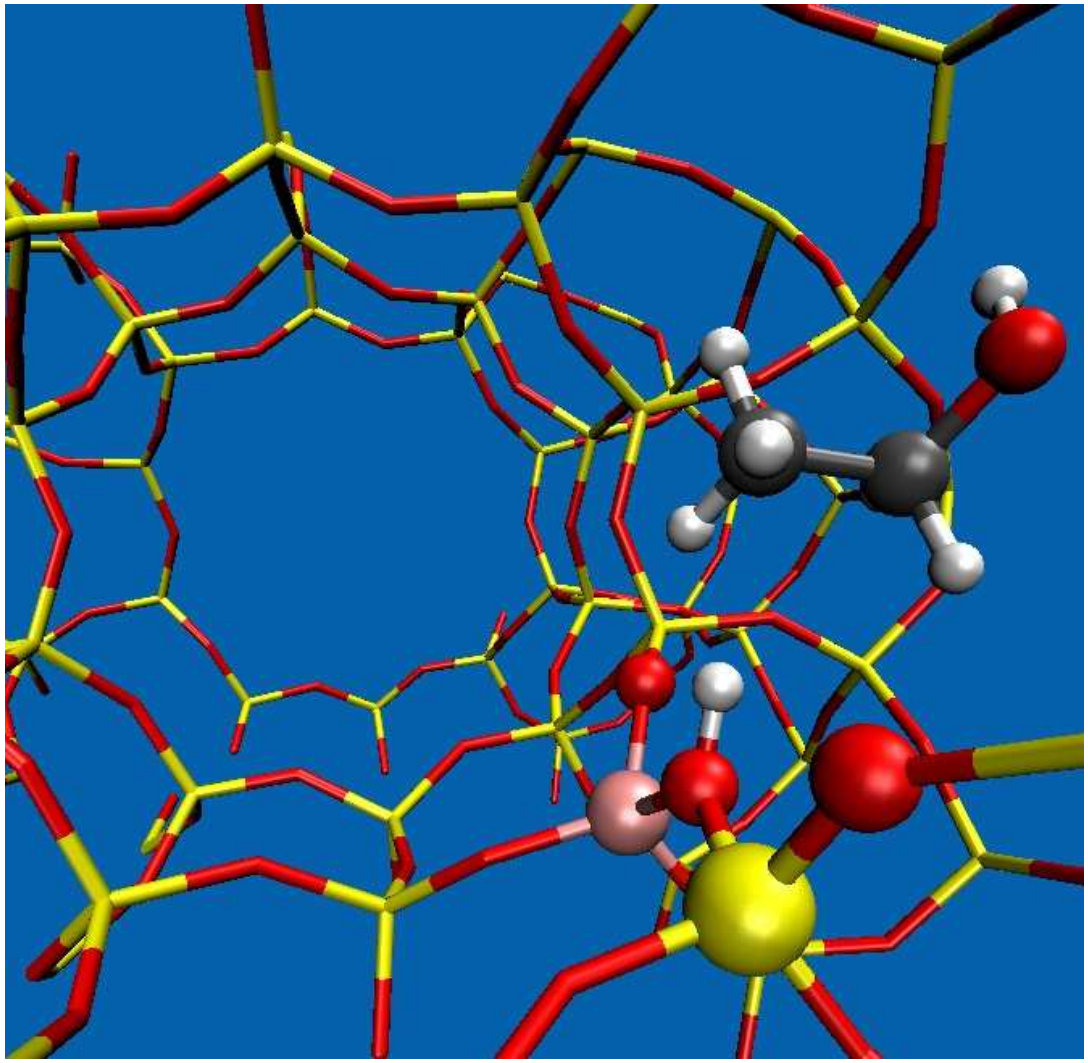


Overview

- Introduction
- Dehydration of bioalcohols on zeolites
  - First principles kinetic model development
  - Experimental validation
  - Reaction-path analysis
  - Effect of zeolite
  - Industrial reactor scale
- Conclusions

Alcohol adsorption in zeolites

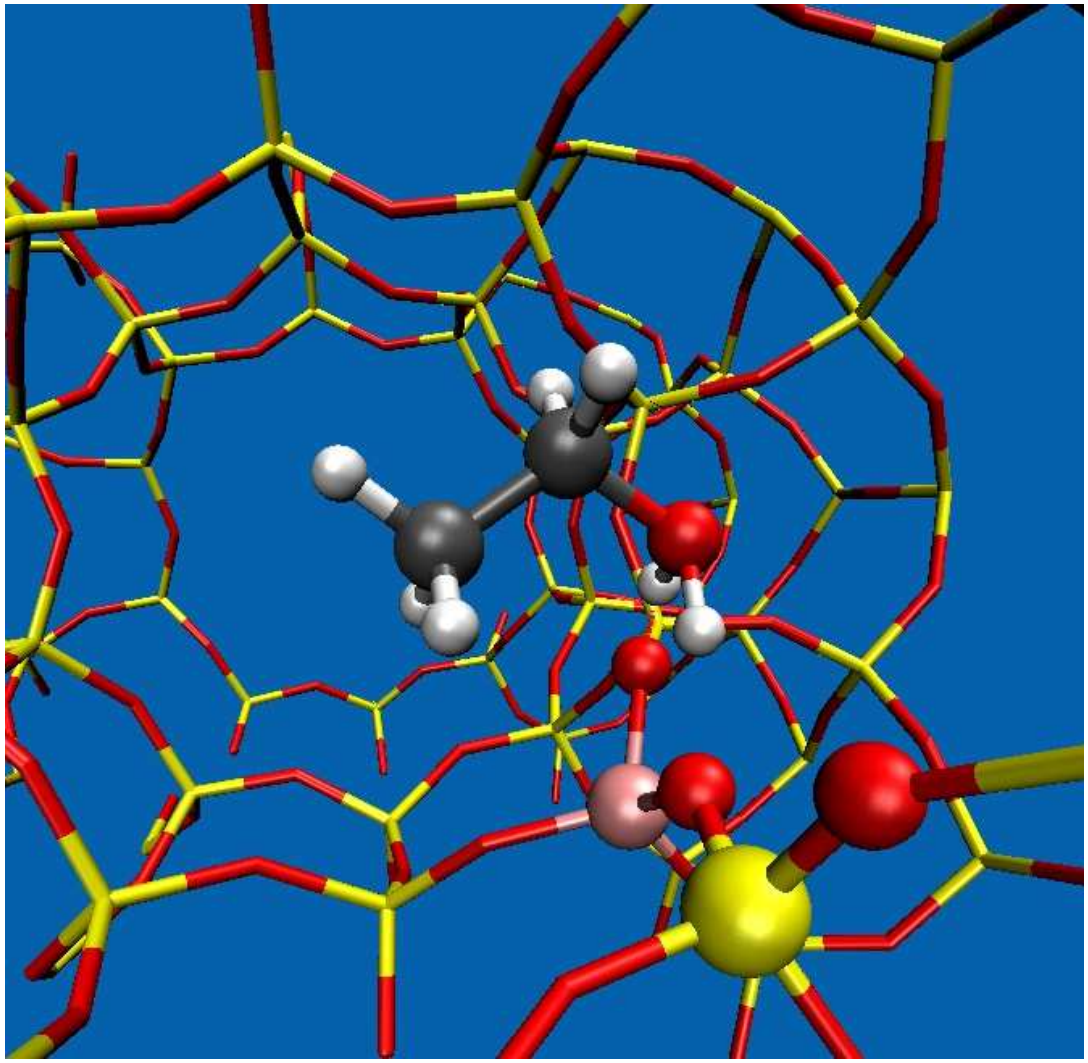
Ethanol physisorption in H-ZSM-5



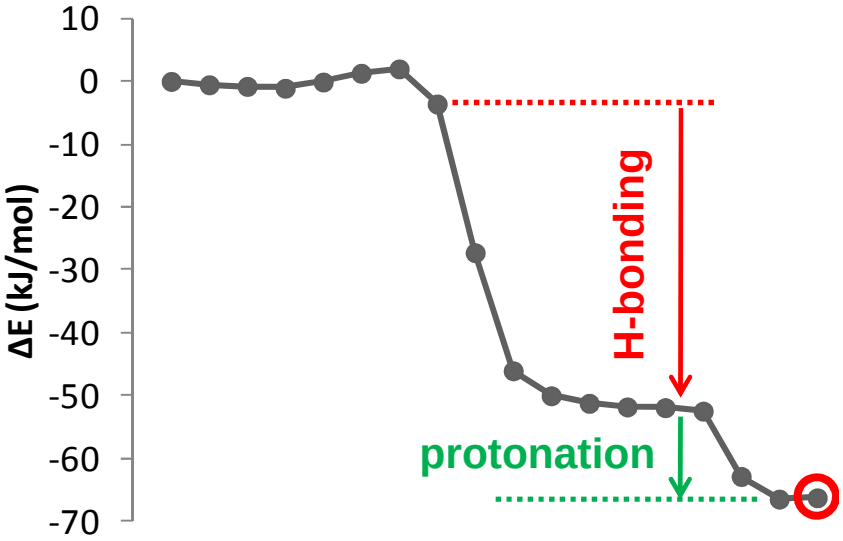
- van der Waals:
  - dipole-dipole
  - dipole-induced dipole
  - dispersive
- H-bonding
- electrostatic interactions

H-bonding and protonation: chemisorption

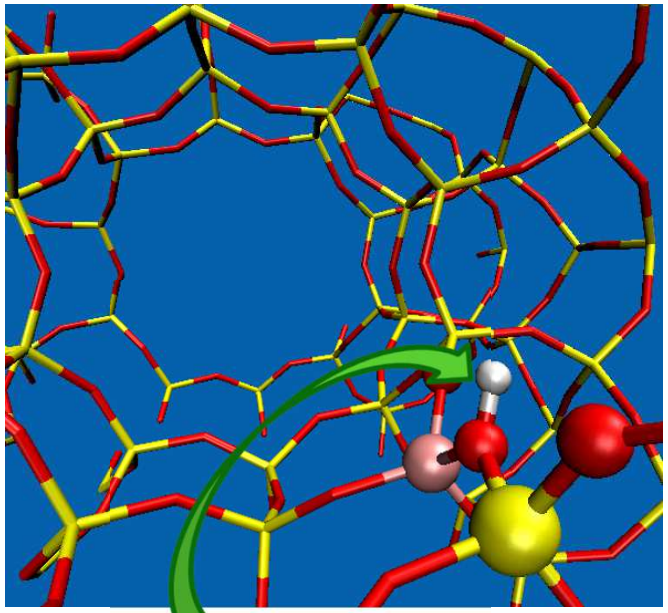
Ethanol adsorption and protonation in H-ZSM-5

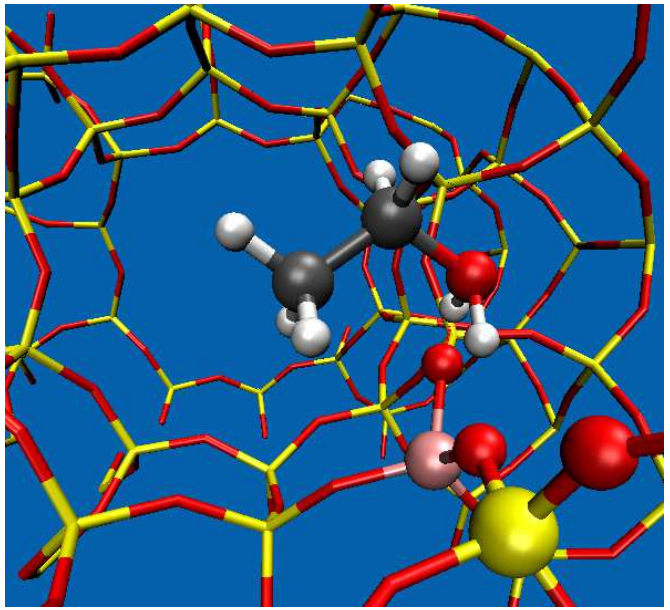


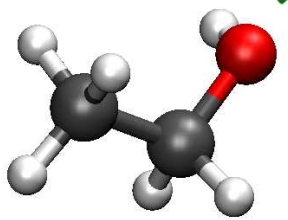
Nudged Elastic Band calculation with PBE-D2 functional



Alcohol adsorption & reaction in zeolites





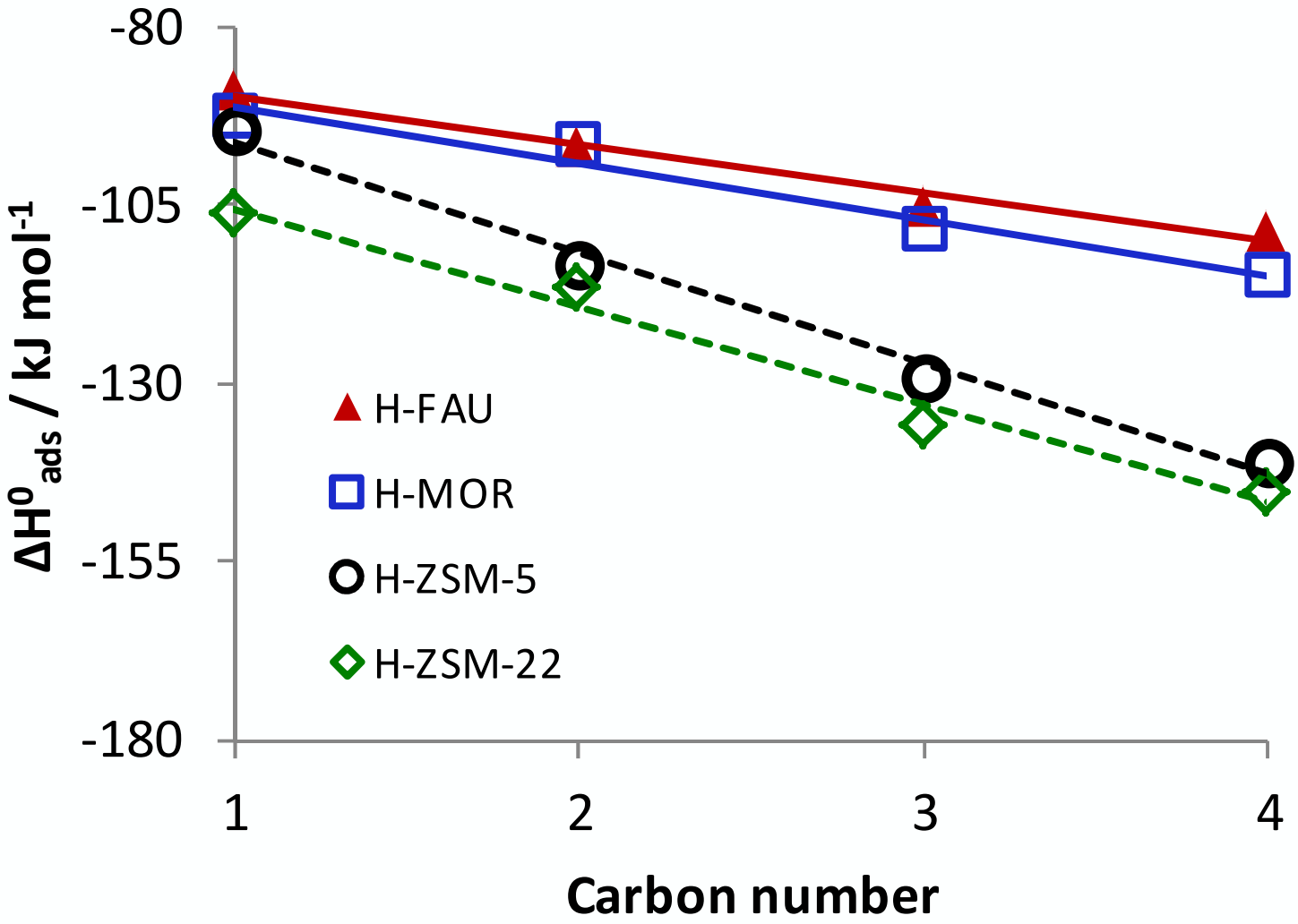


$$r = k\,\theta_{ads,alcohol} = k\,K_{ads}\,p_{alcohol}$$

$$K_{\text{ads}} = \exp\left(-\frac{\Delta G^{0}_{ads}}{RT}\right) = \exp\left(-\frac{\Delta H^{0}_{\text{ads}} - T\Delta S^{0}_{\text{ads}}}{RT}\right)$$

$$k = \frac{k_b T}{h}\exp\left(\frac{\Delta S^{0,\#}}{R}\right)\exp\left(-\frac{\Delta H^{0,\#}}{RT}\right) = \frac{k_b T}{h}\exp\left(-\frac{\Delta G^{0,\#}}{RT}\right)$$

Chemisorption: effect of chain length



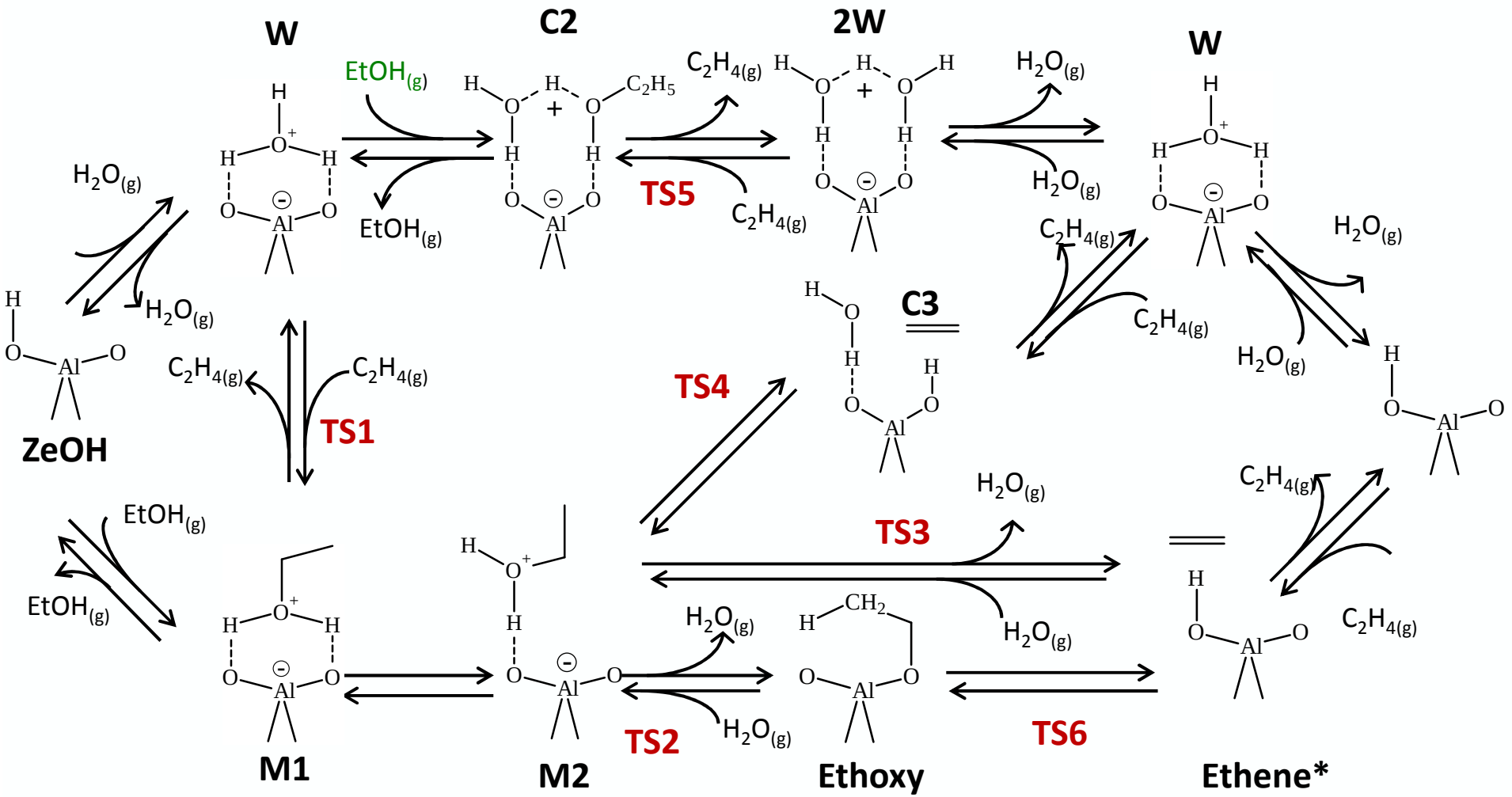
Nguyen et al., J. Catal. (2015) 322,91-103

Overview

- Introduction
- Dehydration of bioalcohols on zeolites
  - First principles kinetic model development
    - ➢ Ethanol dehydration

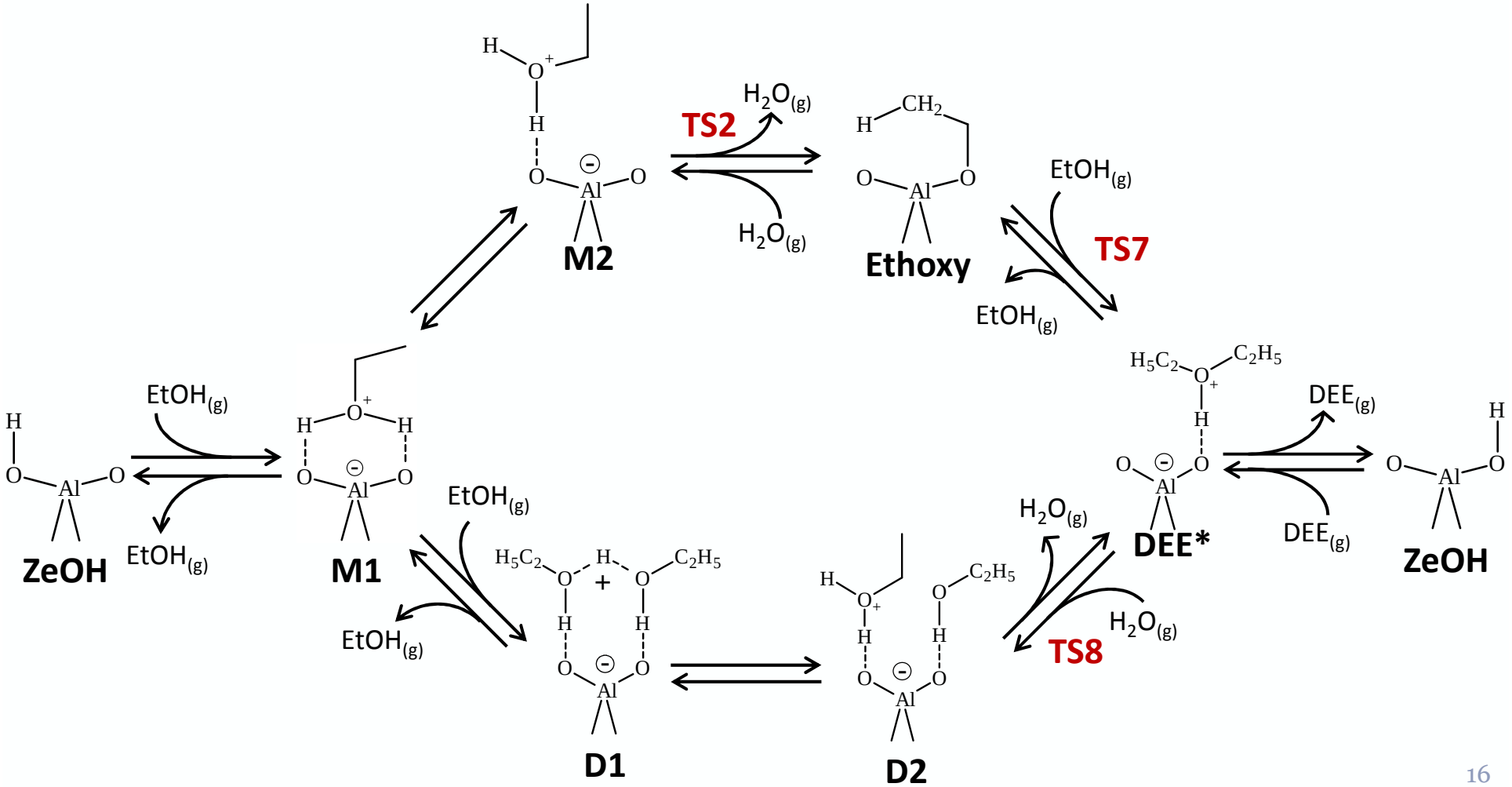
Ethanol to Ethene: H-ZSM-5

A: $EtOH_{(g)} \rightarrow C_2H_{4(g)} + H_2O_{(g)}$

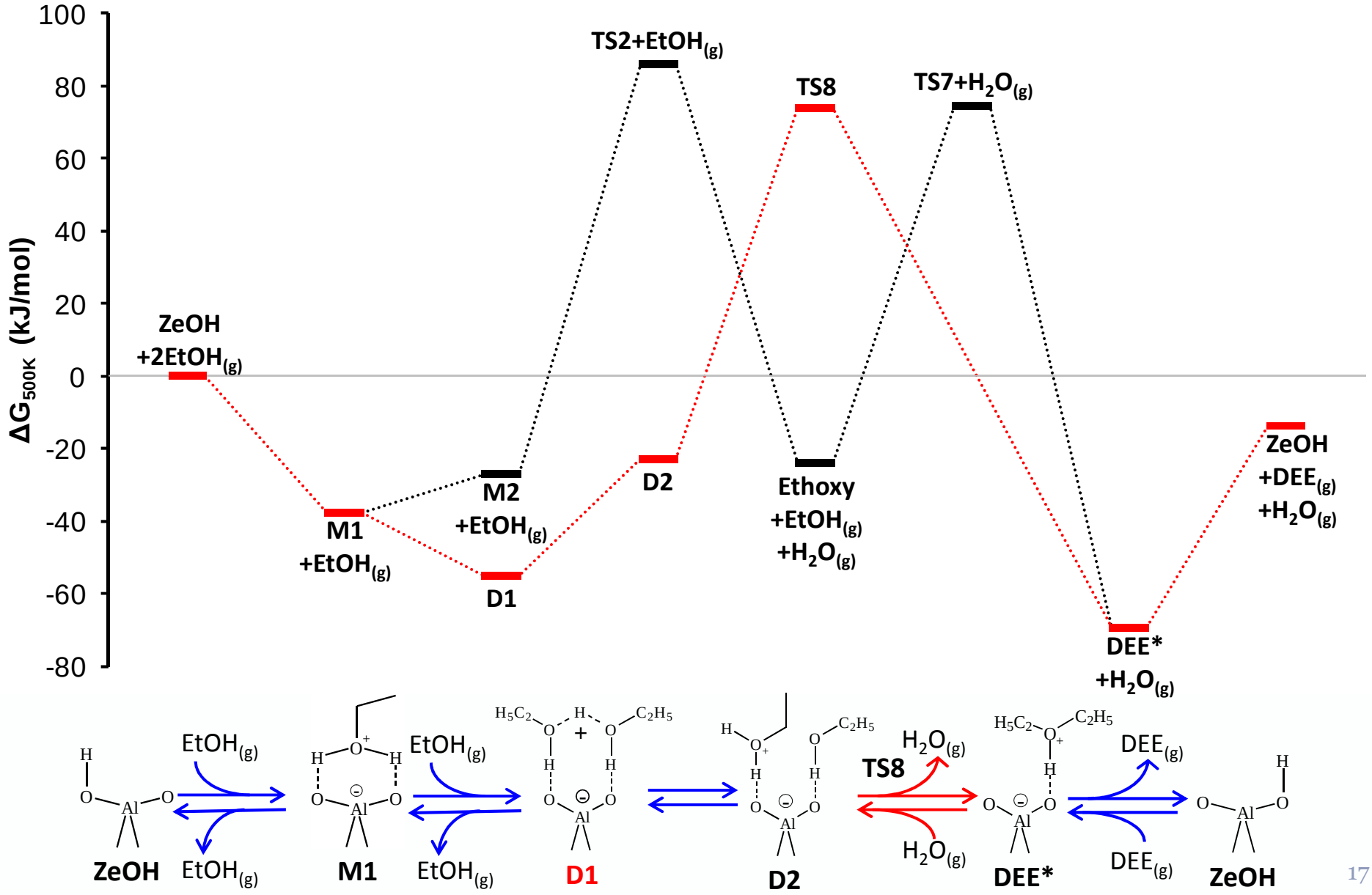


Ethanol to Diethyl ether: H-ZSM-5

B: $2EtOH_{(g)} \rightarrow DEE_{(g)} + H_2O_{(g)}$

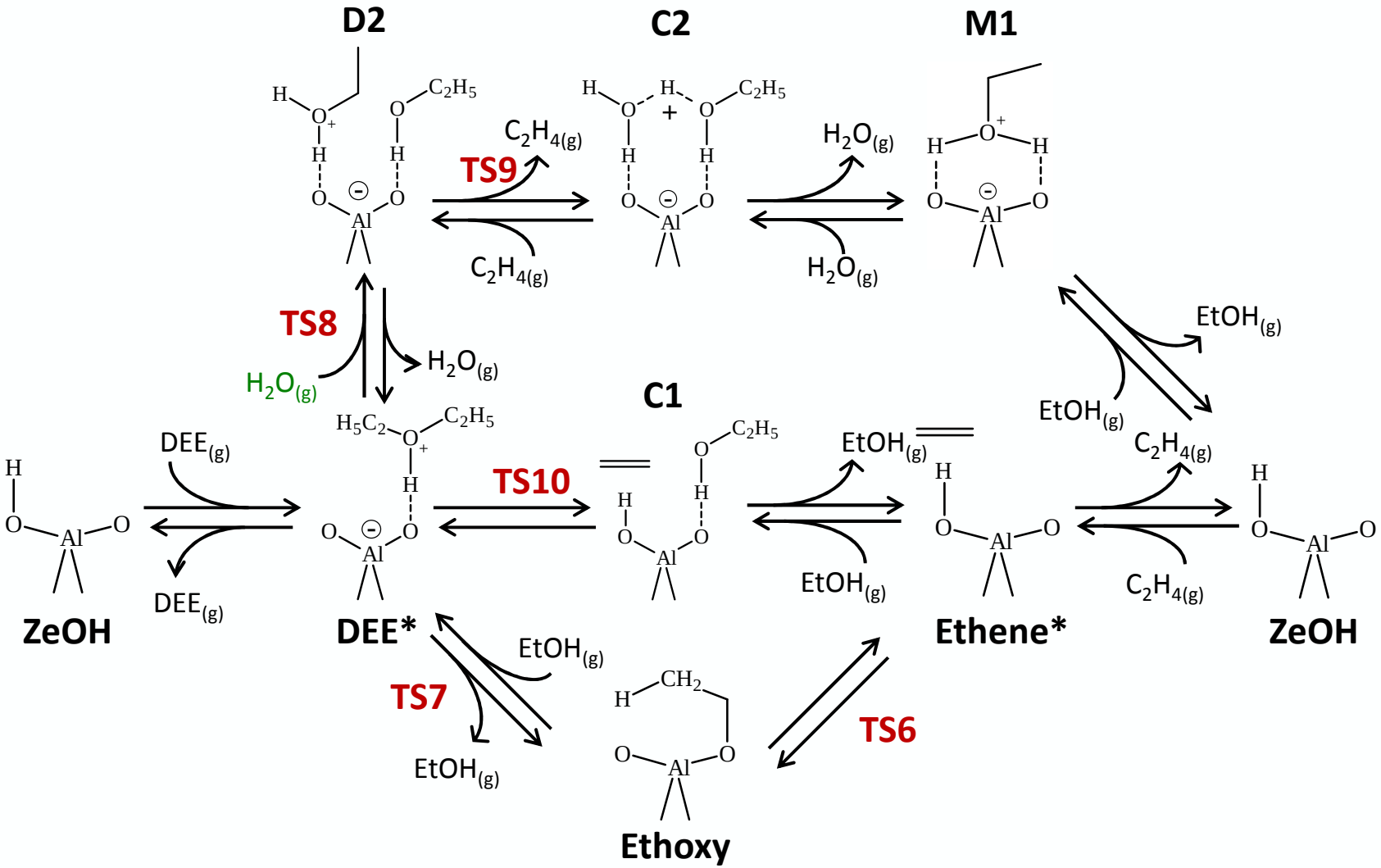


Ethanol to Diethyl ether: H-ZSM-5



Diethyl ether to Ethene:H-ZSM-5

C: $DEE_{(g)} \rightarrow EtOH_{(g)} + C_2H_{4(g)}$



Overview

- Introduction
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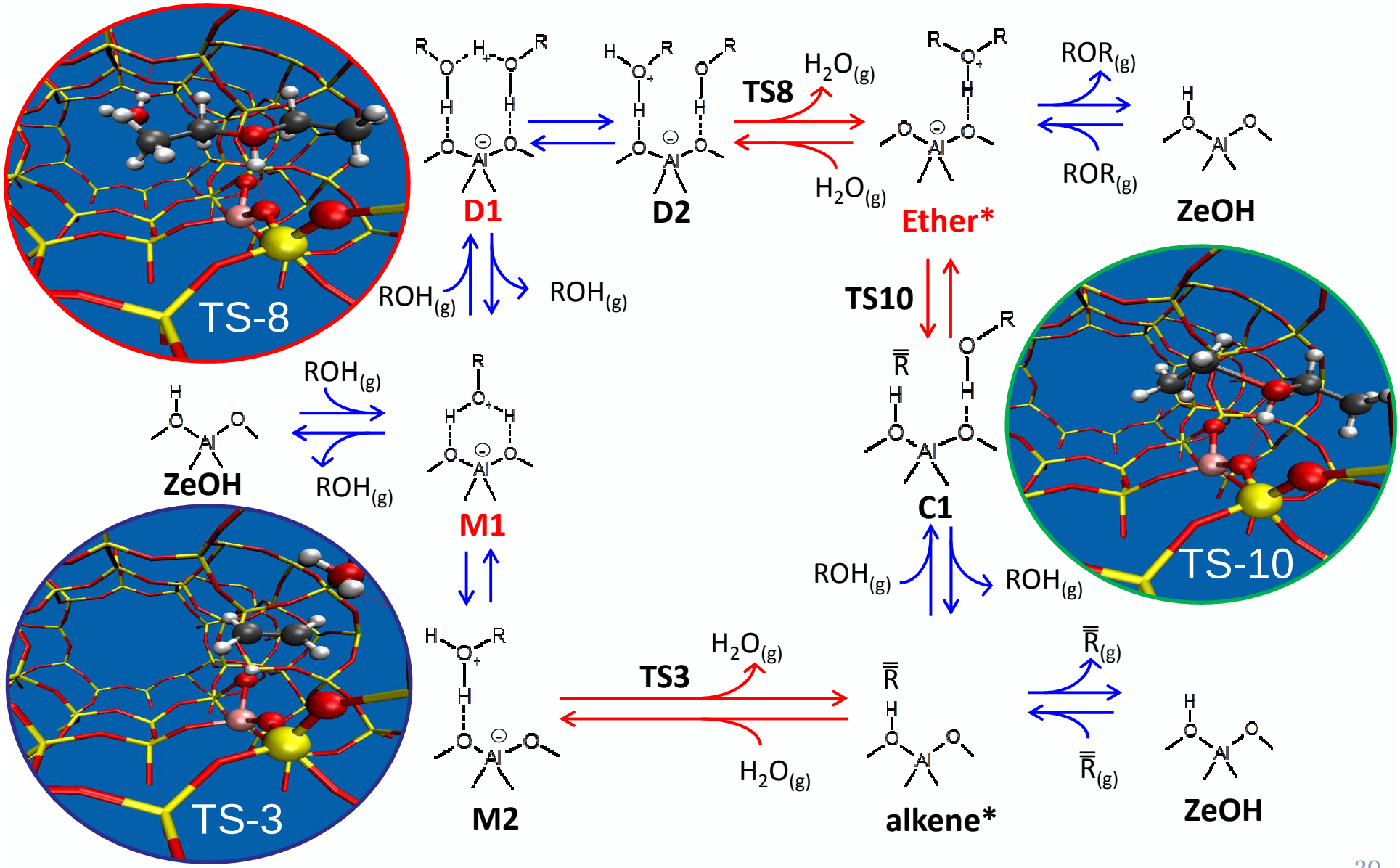
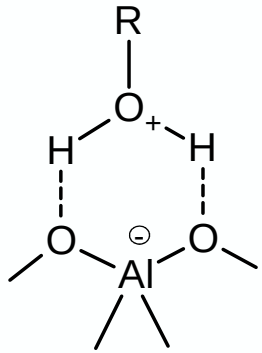
    - ➢ Butanol dehydration: idem

Dehydration : dominant mechanisms

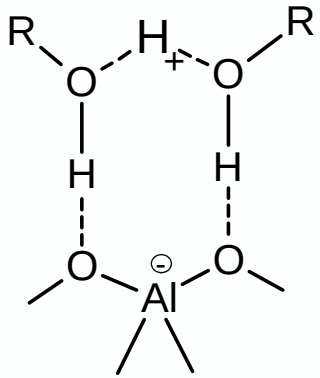


M. John et al., J. Catal. 330 (2015) 28

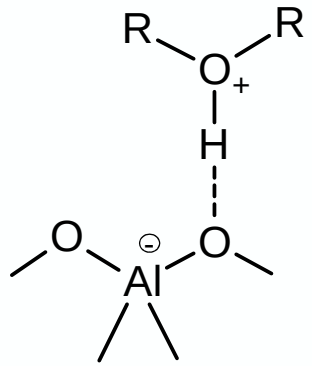
Dehydration: MARI's



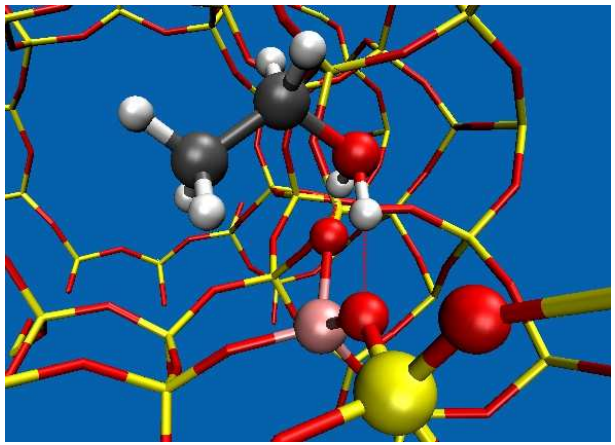
Monomer M1

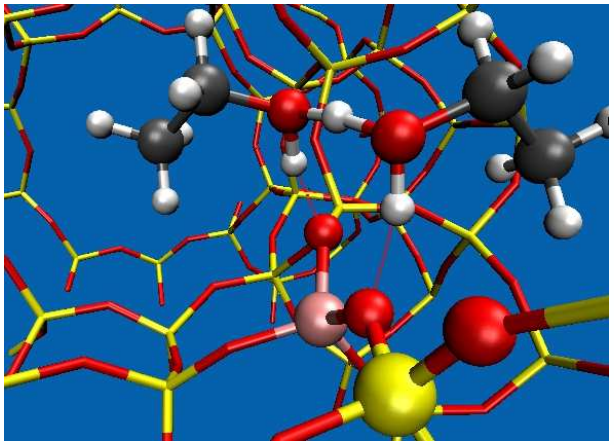


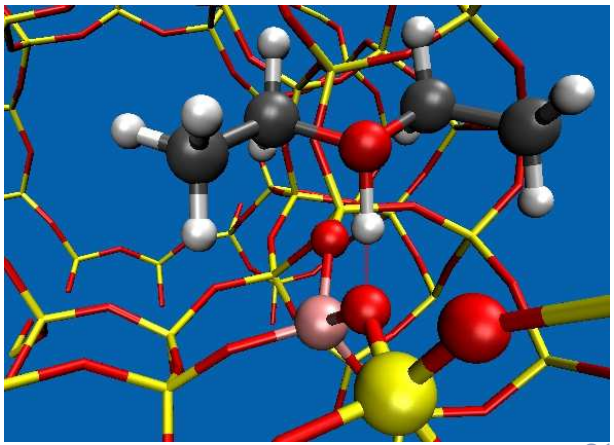
Dimer D1



Adsorbed ether
DRE*







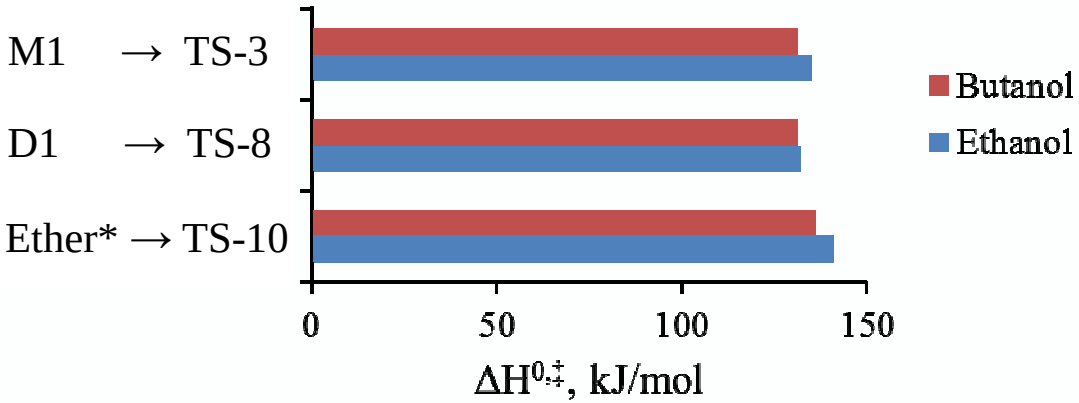
MARI's and Rate-Determining Steps

		A	B	C
(1)	$BuOH(g) + * \leftrightarrow M1$	1	1	0
(2)	**M1** $\leftrightarrow M2$	1	0	0
(3)	$M2 \leftrightarrow$ Butene* $+ H_2O_{(g)}$	**1**	0	0
(4)	Butene* $\leftrightarrow$ Butene$_{(g)}$ $+ *$	1	0	1
(5)	$M1 + BuOH_{(g)} \leftrightarrow D1$	0	1	0
(6)	**D1** $\leftrightarrow D2$	0	1	0
(7)	$D2 \leftrightarrow$ DBE* $+ H_2O_{(g)}$	0	**1**	0
(8)	DBE* $\leftrightarrow$ DBE$_{(g)}$ $+ *$	0	1	-1
(9)	**DBE*** $\leftrightarrow$ C1	0	0	**1**
(10)	C1 $\leftrightarrow$ Butene* $+$ $BuOH_{(g)}$	0	0	1
Path A	$BuOH_{(g)} \leftrightarrow$ Butene$_{(g)}$ $+H_2O_{(g)}$			
Path B	$BuOH_{(g)}+BuOH_{(g)} \leftrightarrow DBE_{(g)} +H_2O_{(g)}$			
Path C	$DBE_{(g)} \leftrightarrow$ Butene$_{(g)}$ $+BuOH_{(g)}$			

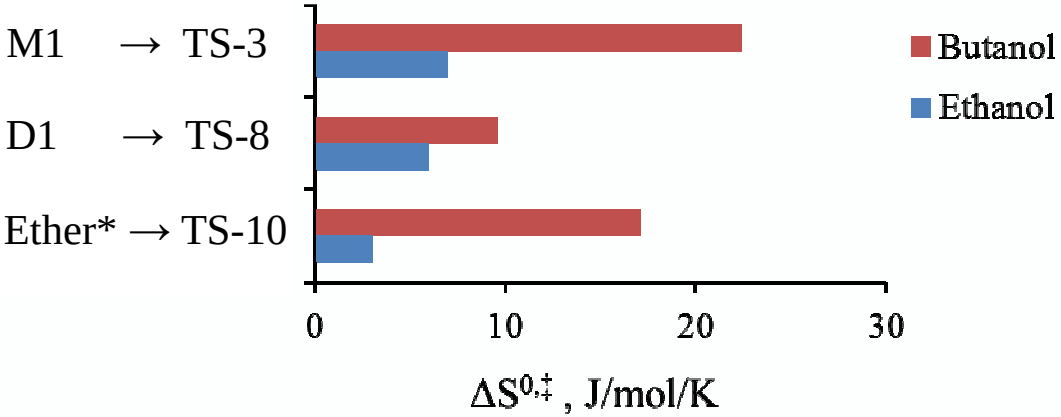
All reaction paths involving all the suggested mechanisms are included in the microkinetic model

$$TOF_{path} = \sum_{i}^{n} TOF_{mech}$$

Effect of alkyl chain length on Arrhenius parameters



	Surface species
M1	Chemisorbed alcohol monomer
D1	Chemisorbed alcohol dimer
Ether*	Adsorbed Ether (DEE/DBE)



Increase in alcohol chain length has marginal influence on activation enthalpy but leads to significant increase in activation entropy

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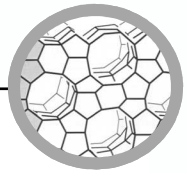
Experimental procedures and conditions

HZSM-5



Properties		
Si/Al	15	40
c_{H+}(mol kg^{-1})	0.77	0.36
BET (10^3 m^2 kg^{-1})	430	436
V_{micro}(10^{-5} m^3 kg^{-1})	1.1	1.1

Experimental conditions	
Temperature (K)	453 – 523
$p_{EtOH,in}$ (kPa)	8 – 50
$W/F_{EtOH,in}$ (kg s mol^{-1})	1.5 – 17.0

Reactor model equations

Reactor continuity equations for each gas-phase component i with PSSA for the surface species k:

$$R_k = \sum_j v_{jk} r_j = 0$$

with $e.g. r_j = k_j \theta_k p_i$

$$\theta_{H^+} + \sum_k \theta_k = 1$$

$$\frac{dF_i}{dW} = C_t R_i = C_t \sum_j v_{ji} r_j$$

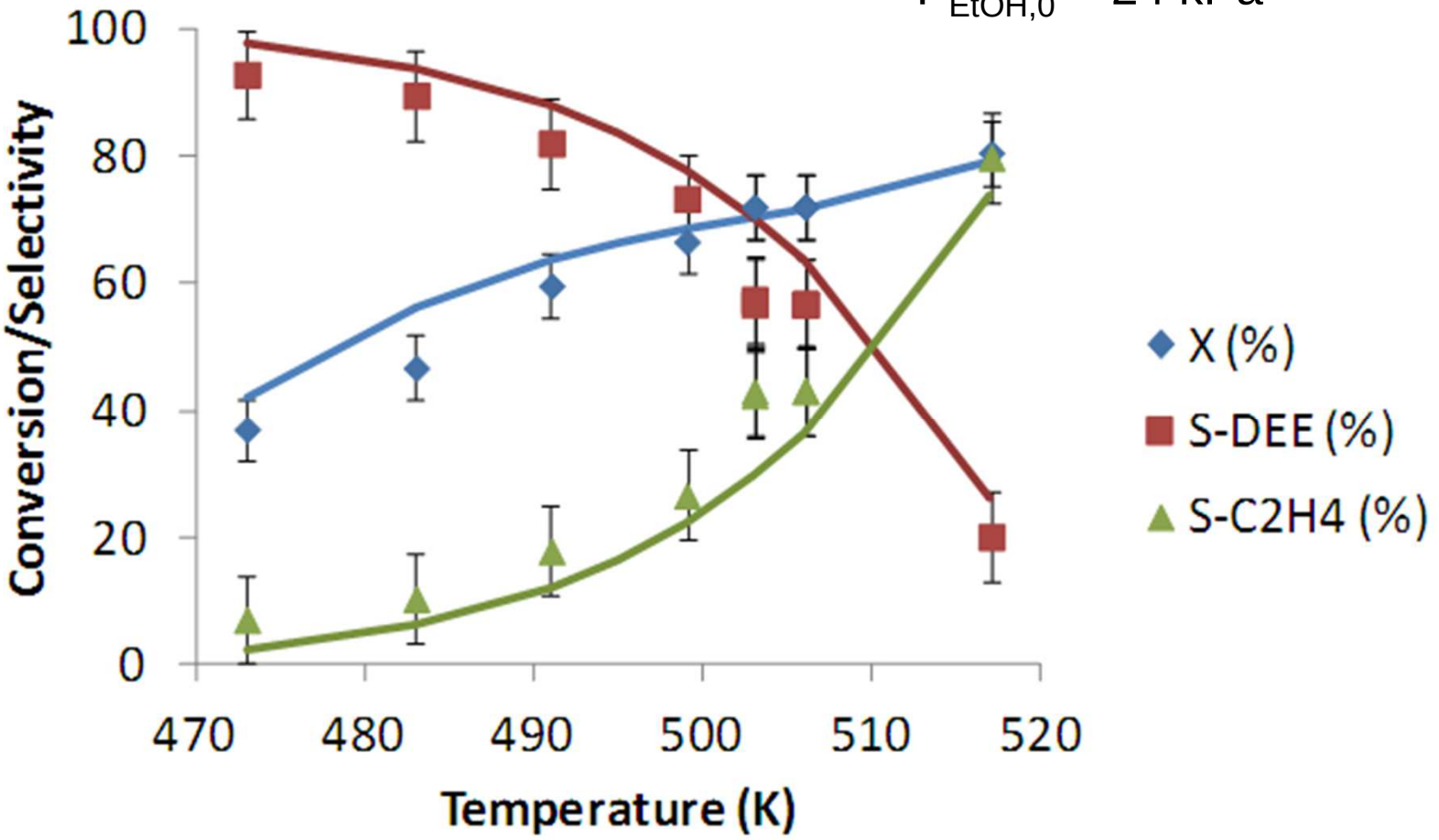
$F_i = F_{i,0}$ at $W = 0$

- F_i molar flow rate of component *i* (mol s^{-1})
- W catalyst mass (kg)
- C_t acid site concentration (mol H^+ kg^{-1})
- R_i net production frequency of component i (molecules $site^{-1}$ s^{-1} = mol $mol_{H^+}^{-1}$ s^{-1})
- r_j turnover frequency of elementary step j (molecules $site^{-1}$ s^{-1} = mol $mol_{H^+}^{-1}$ s^{-1})
- k_j rate coefficient of elementary step j
- θ coverage of surface species k
- p_i partial pressure of gas phase component *i*
- v_{ji} stoichiometric coefficient of component *i* in the elementary step *j*

Conversion and selectivities

$W_{cat}/F_{EtOH,0}$ = 6.5 kg s / mol

$P_{EtOH,0}$ = 24 kPa

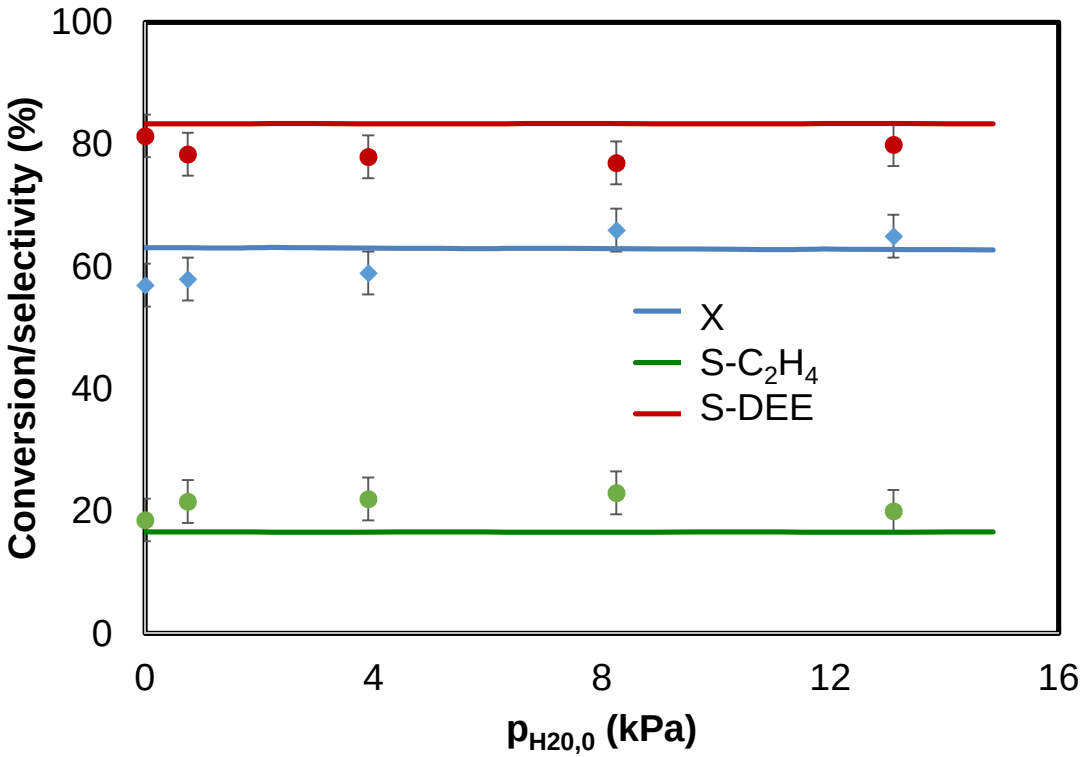


Effect of water

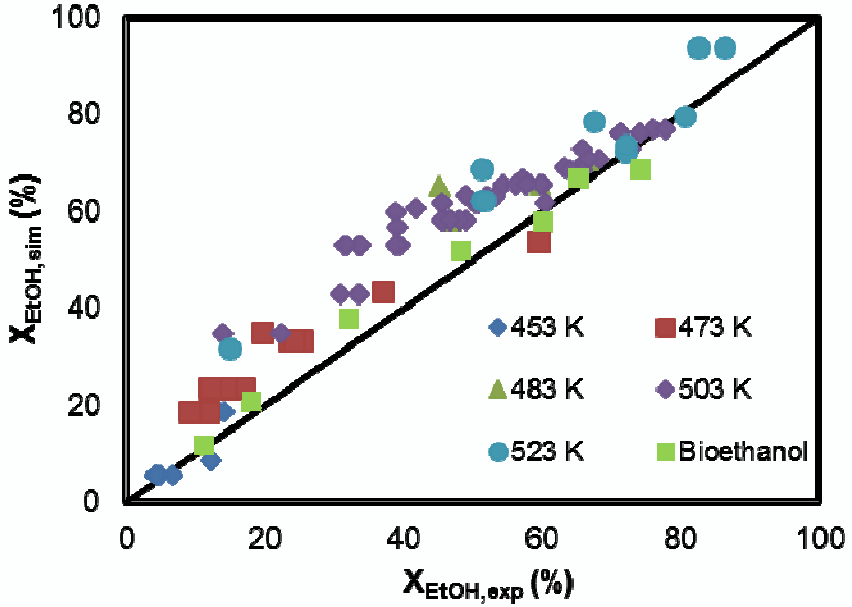
$W_{cat}/F_{EtOH,0}$ = 8.3 kg s / mol

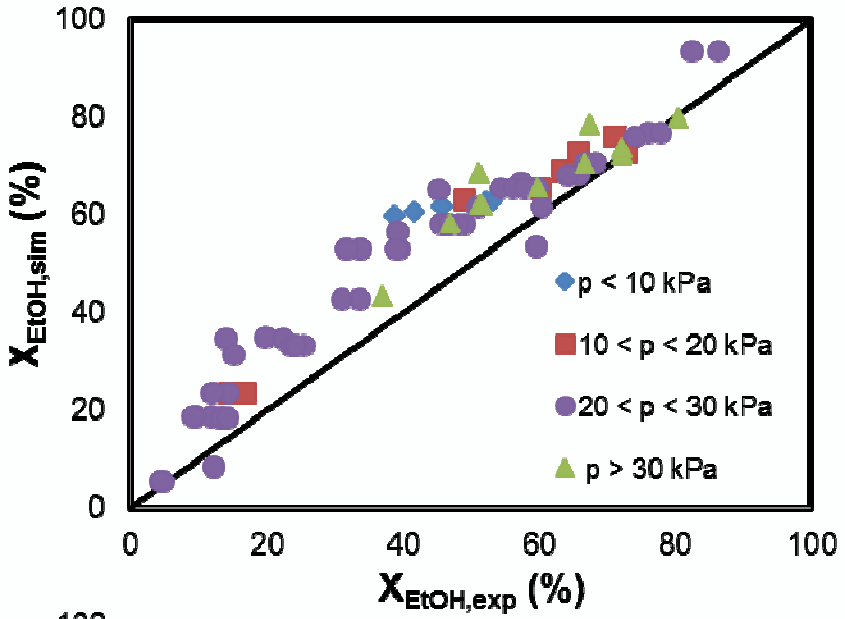
$P_{EtOH,0}$ = 29 kPa

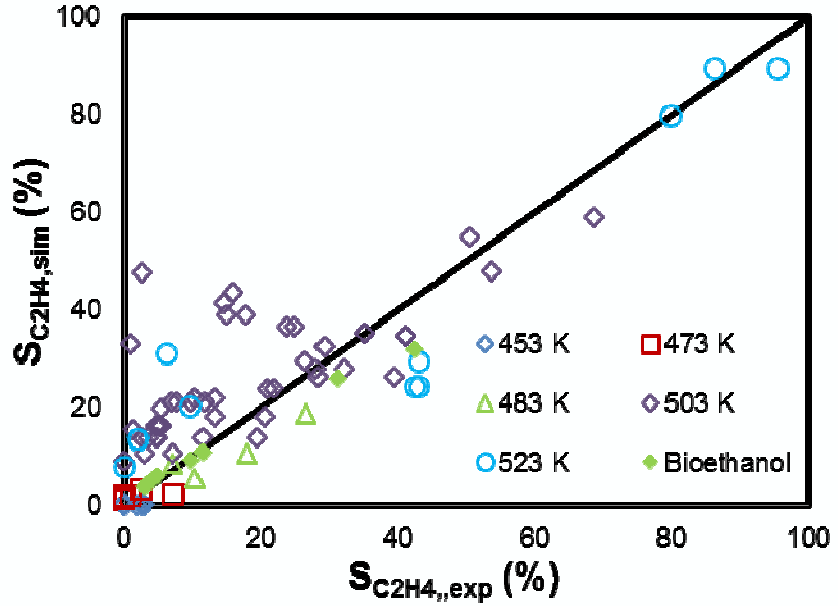
T = 503 K

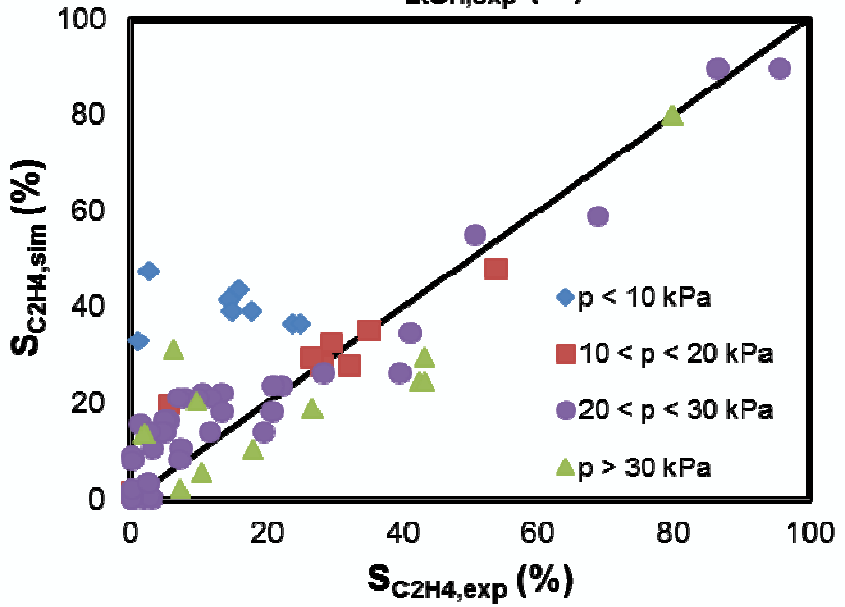


Parity diagrams









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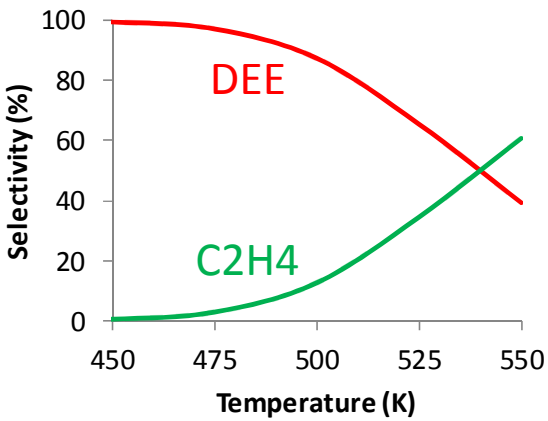
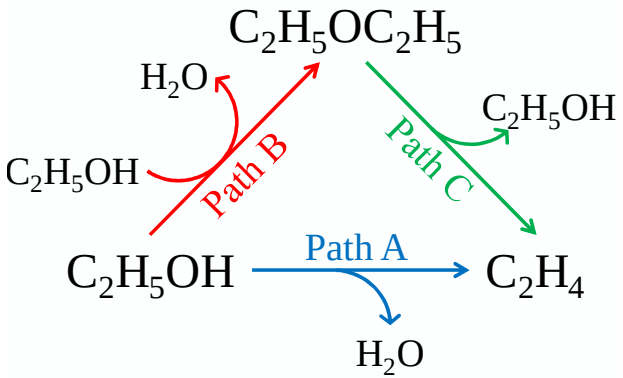
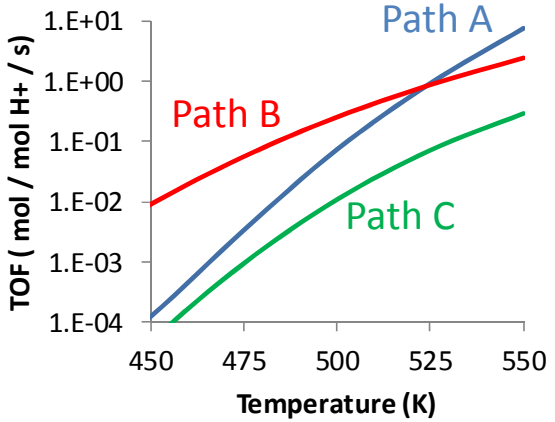
Reaction path analysis: effect of T



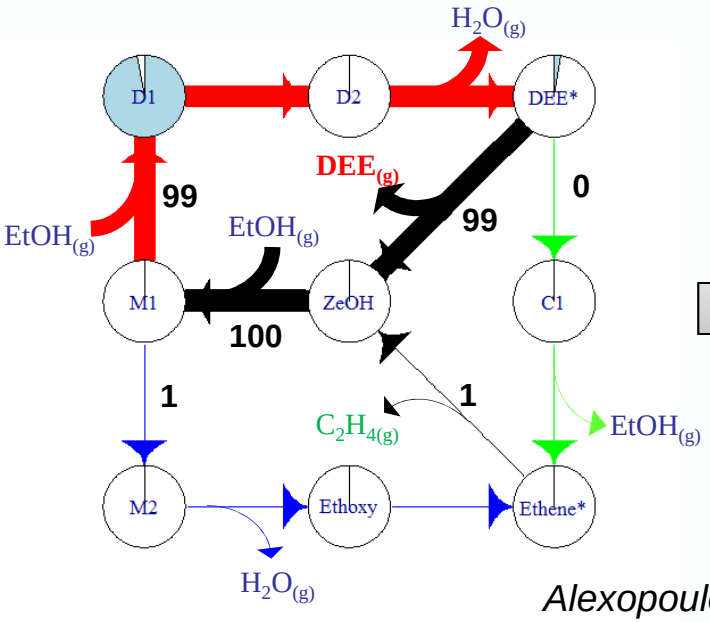




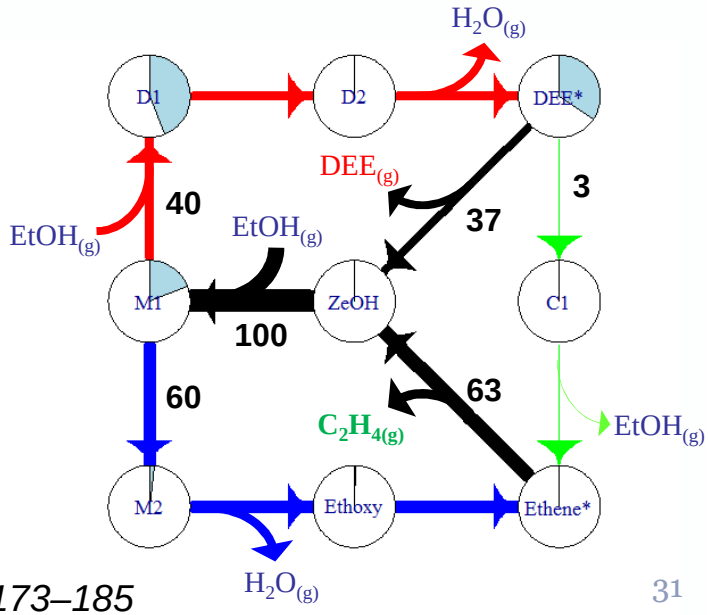
450 K

H-ZSM-5, $p_{EtOH,0}$ = 10kPa, *X_{EtOH}* = 10 %

550 K

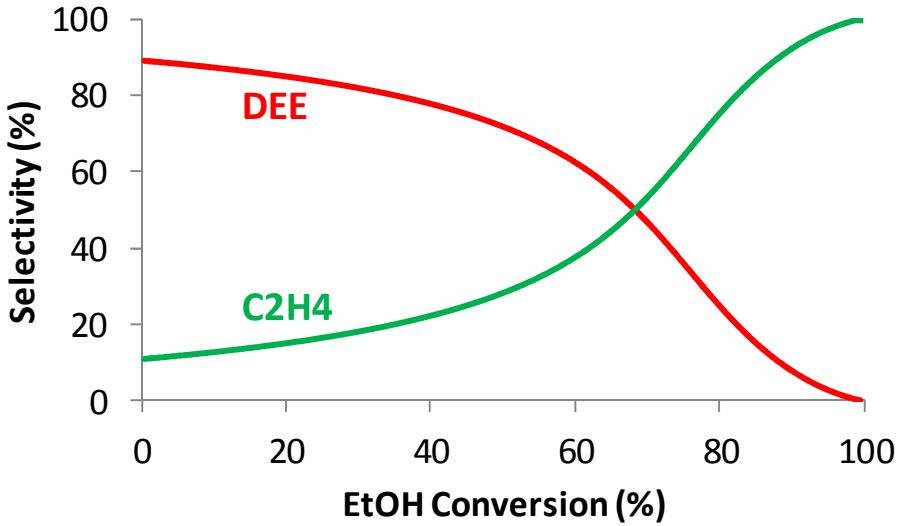


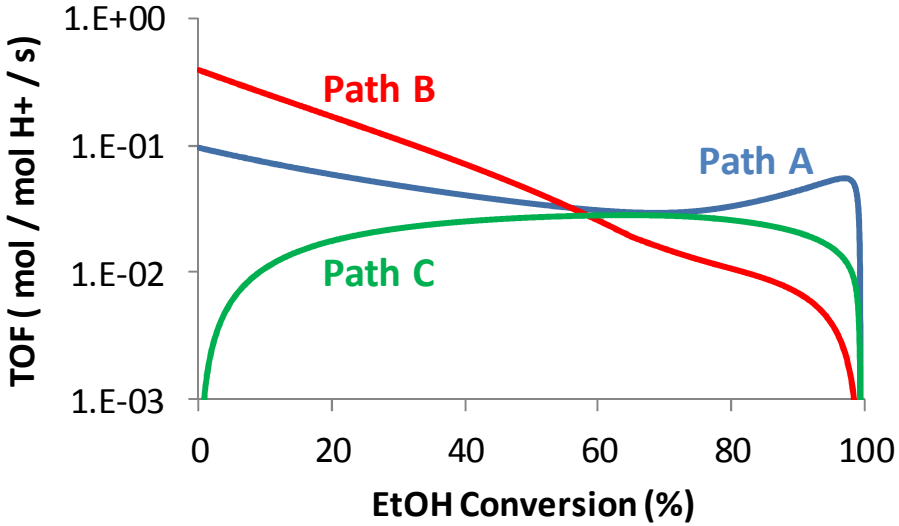
T ↗

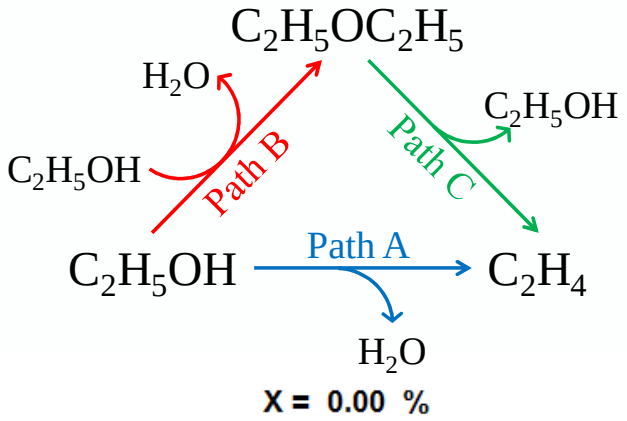


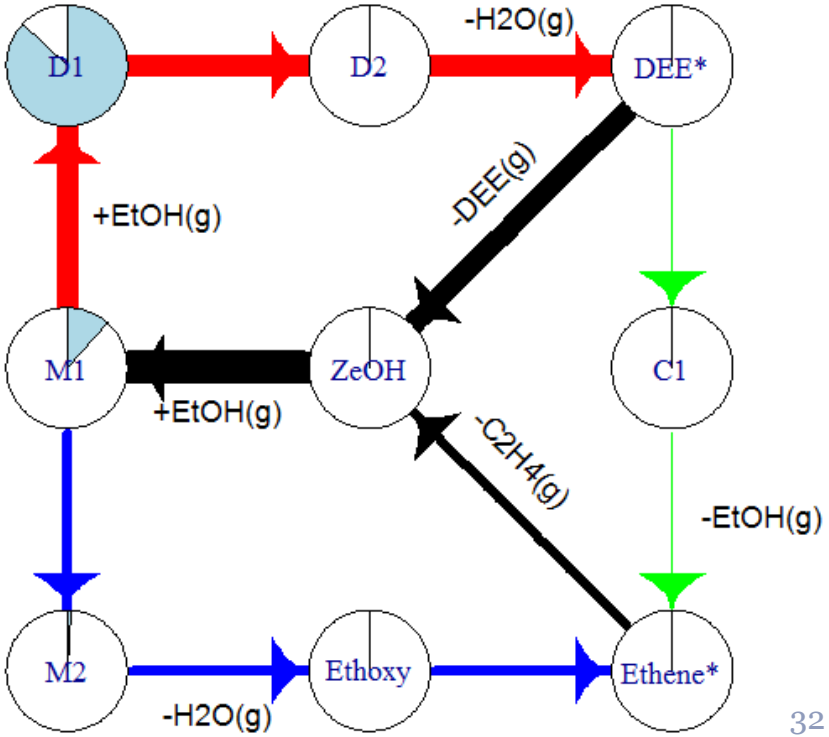
Alexopoulos et al., J Catal. (2016),339, 173–185

Reaction path analysis: effect of conversion





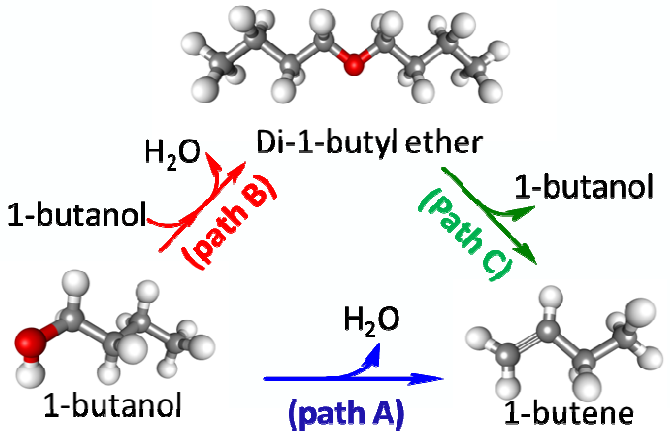


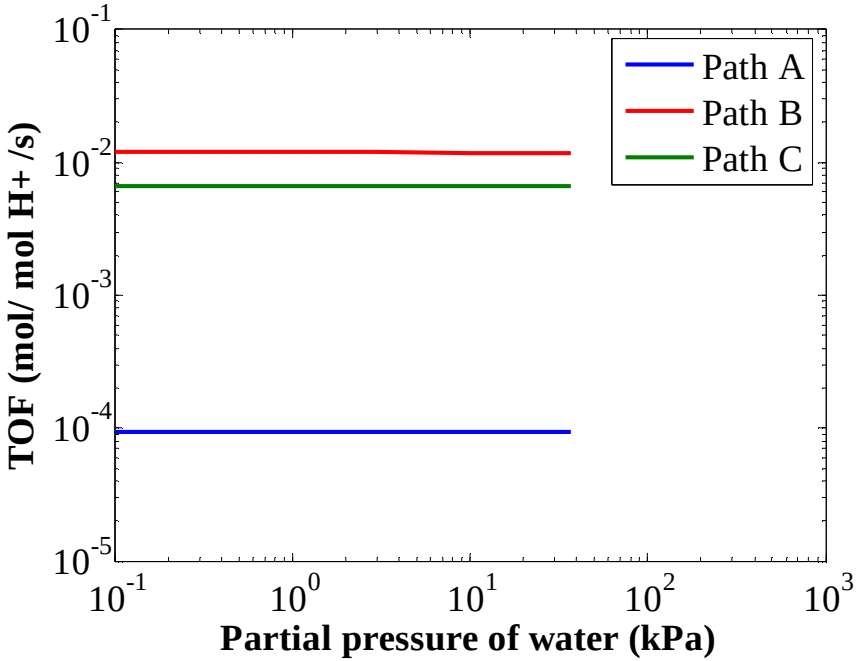


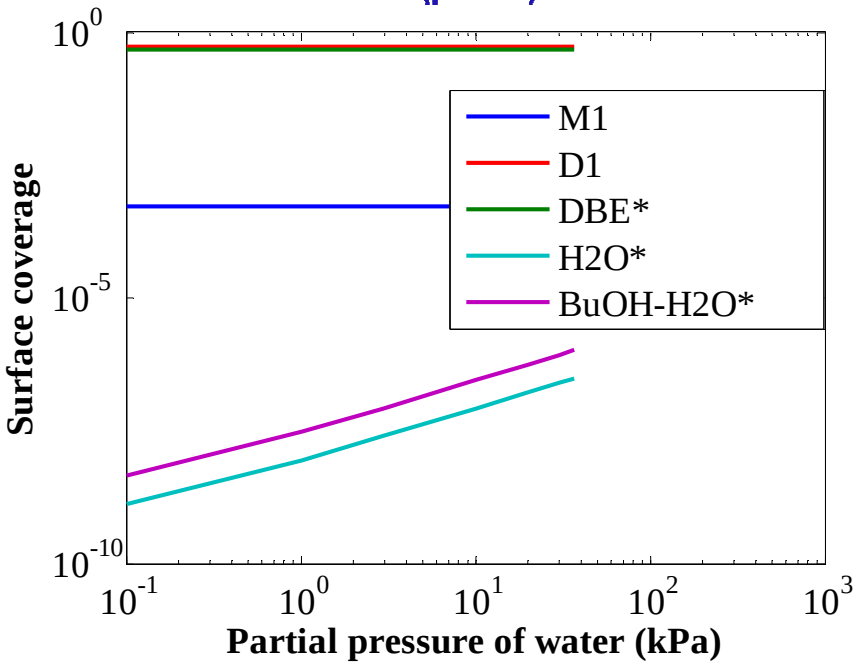
H-ZSM-5, $p_{EtOH,0}$ = 10kPa, T = 500 K

Reaction path analysis: Effect of water

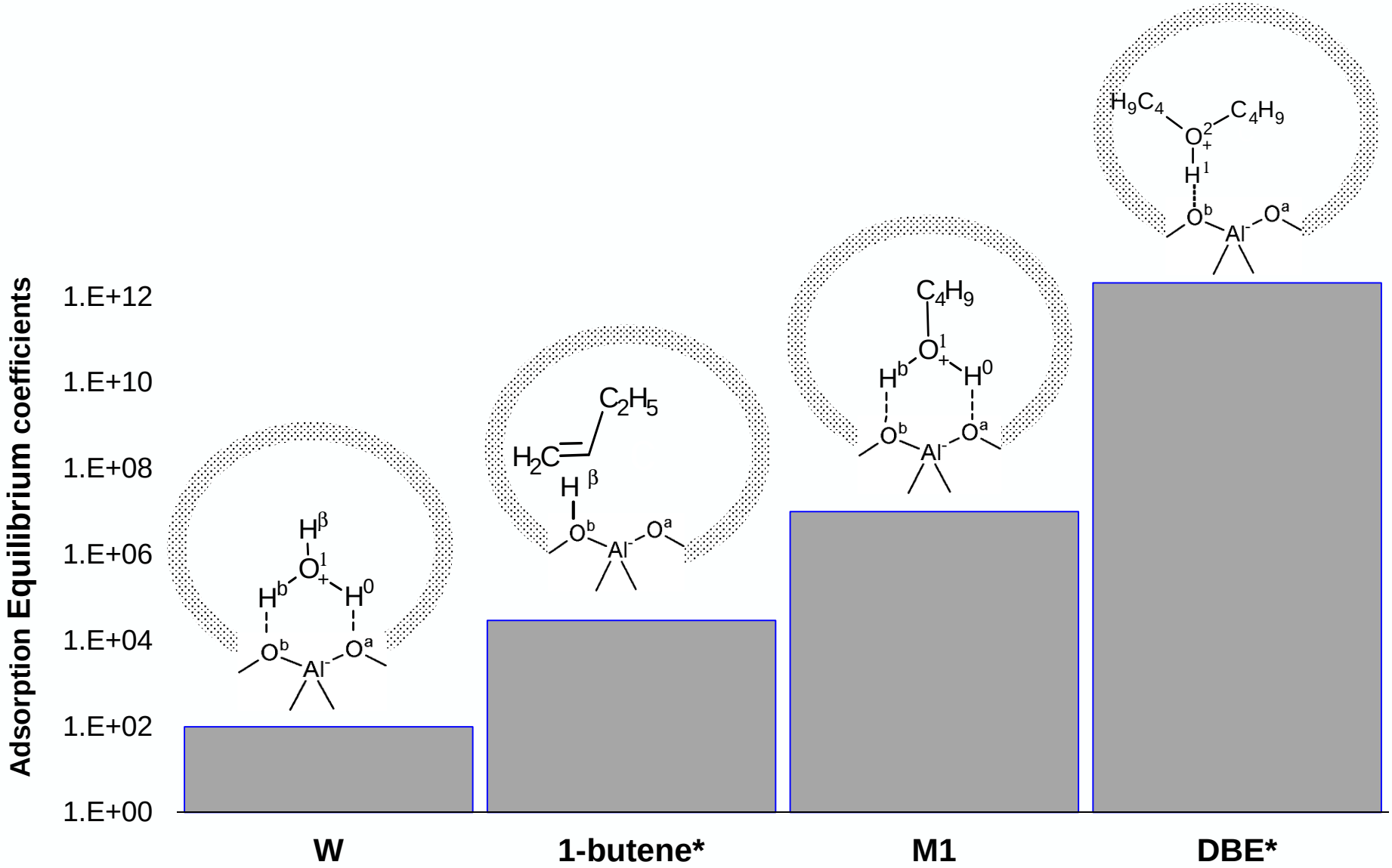
Zeolite: H-ZSM-5
T: 450 K
$P_{BuOH,0}$: 1 kPa,
$P_{H2O,0}$: 1 - 40 kPa,
X_{BuOH} : 10%







Equilibrium coefficients for adsorption @ 450K



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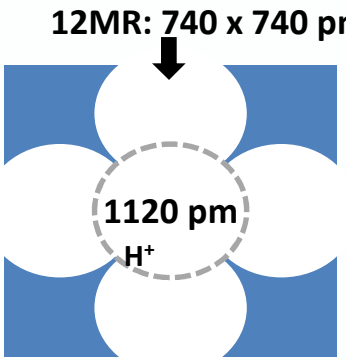
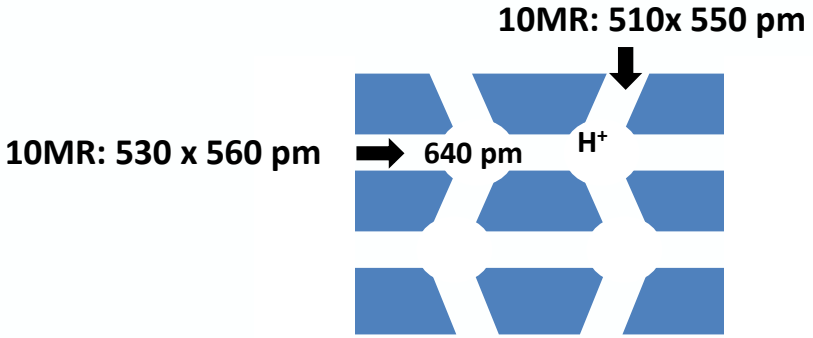
Zeolite Frameworks

3D zeolites

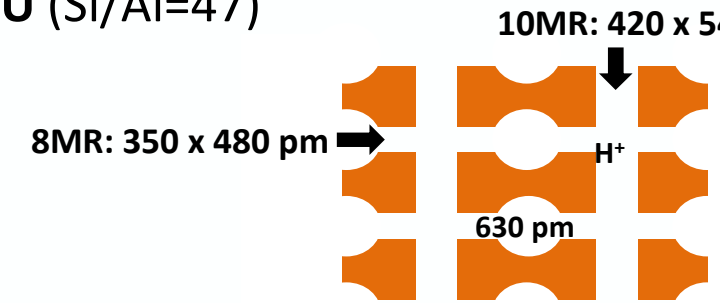


H-FAU (Si/Al=47)



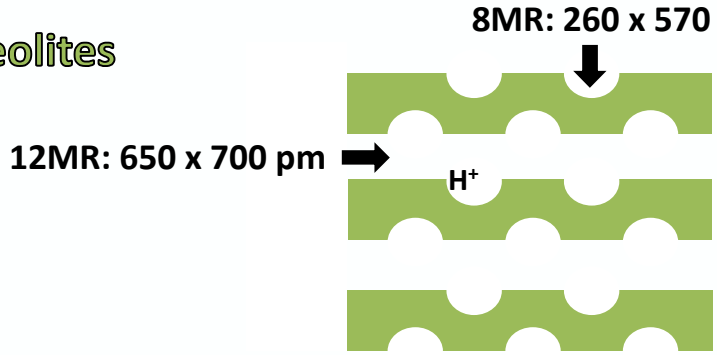
H-ZSM-5 (Si/Al=95)

2D zeolite

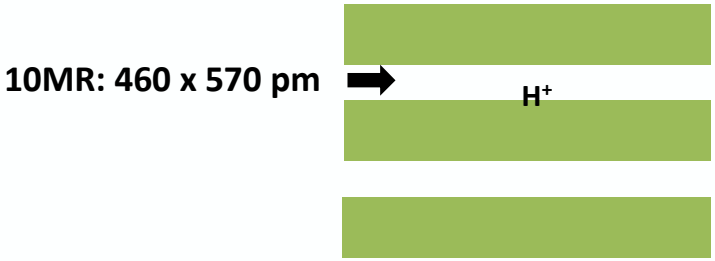


H-FER (Si/Al=71)

1D zeolites

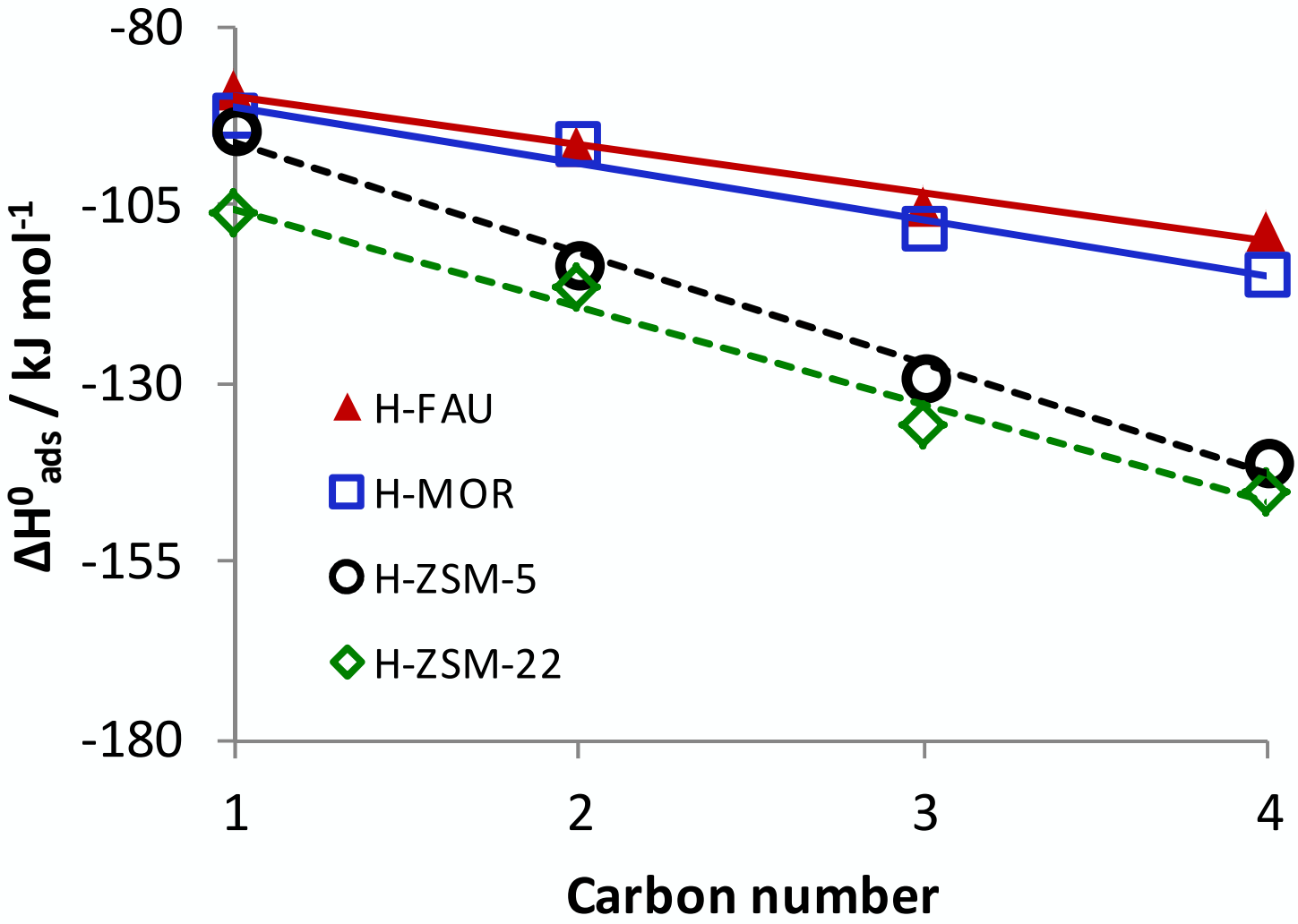


H-MOR (Si/Al=95)



H-ZSM-22(Si/Al=35)

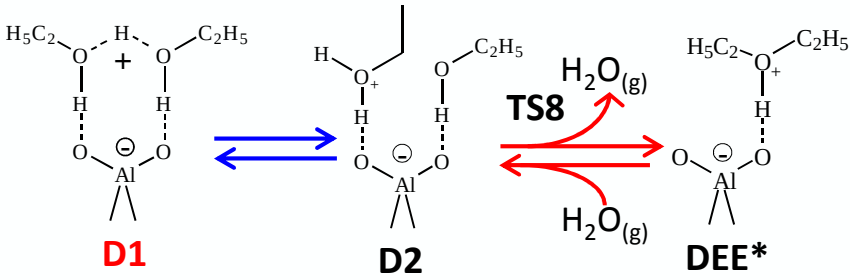
Chemisorption



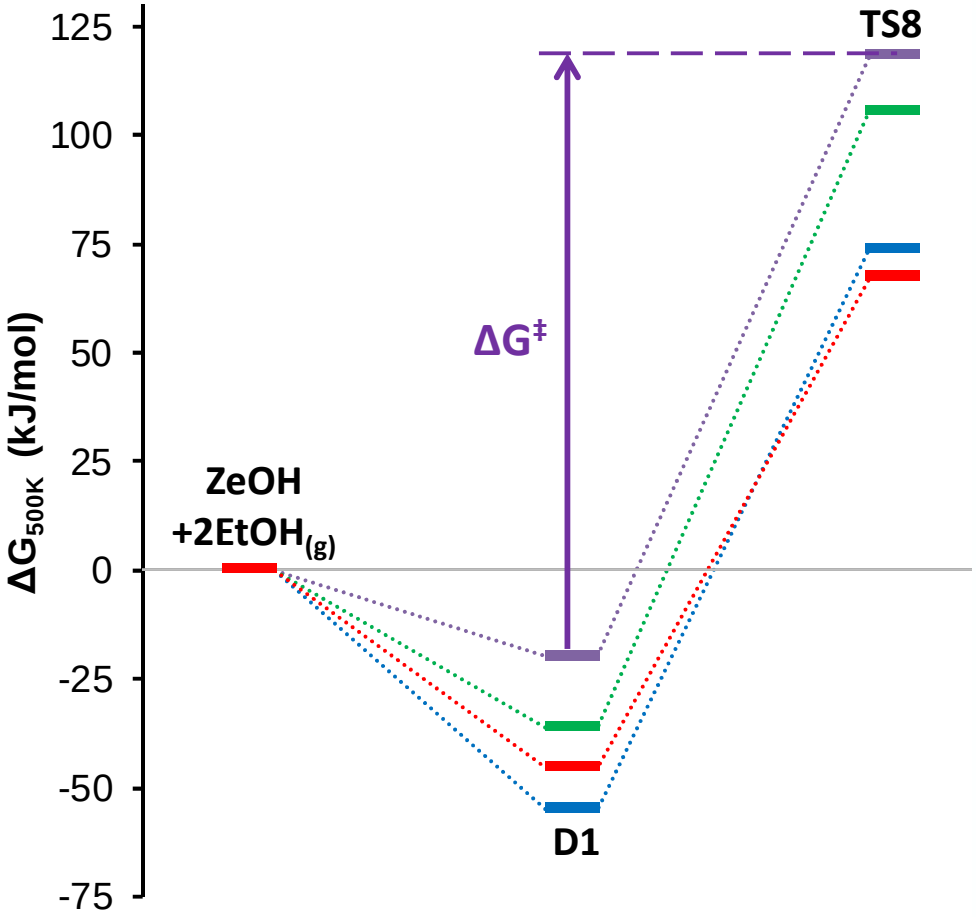
Nguyen et al., J. Catal. (2015) 322,91-103

Effect of zeolite: B Ethanol to Diethyl ether

ZeOH	$\Delta G^{\ddagger} = G_{TS8} - G_{D1}$ (kJ/mol)
H-FAU	138
H-MOR	142
H-ZSM-5	129
H-ZSM-22	113

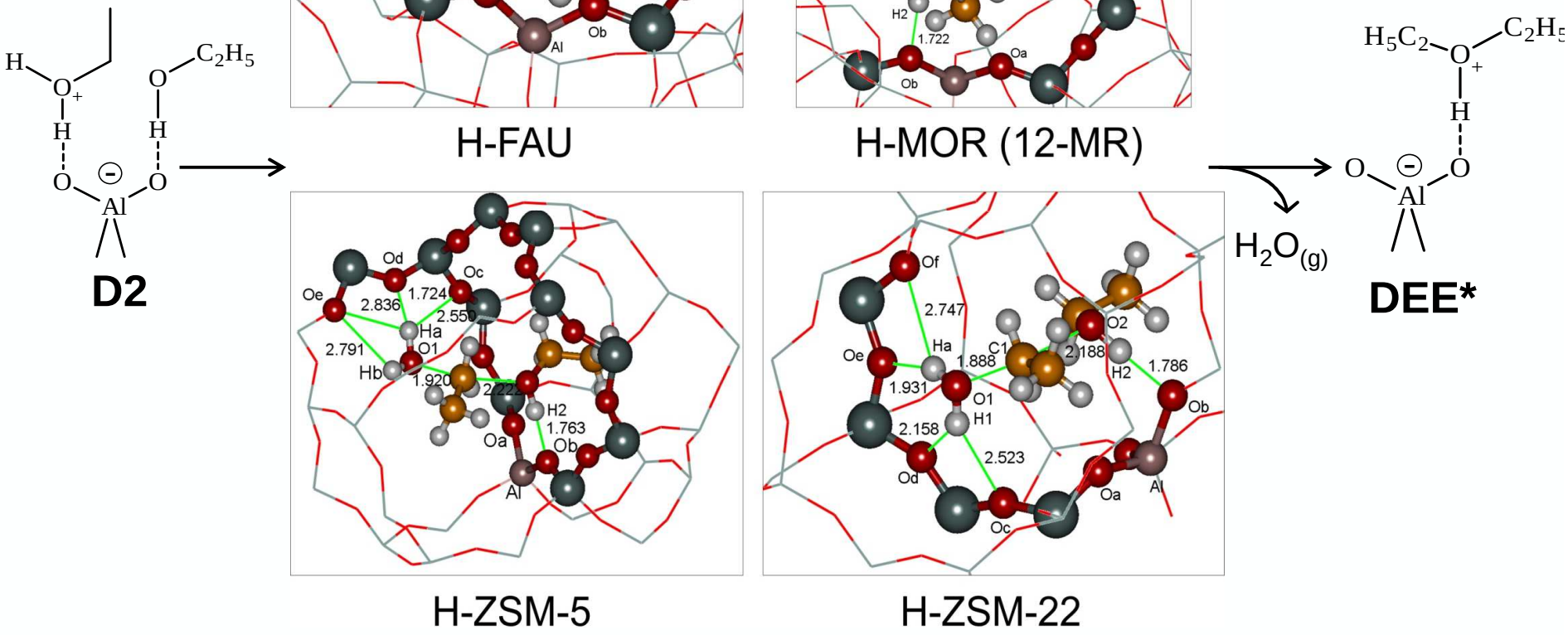


10-MR zeolites more active than 12-MR zeolites



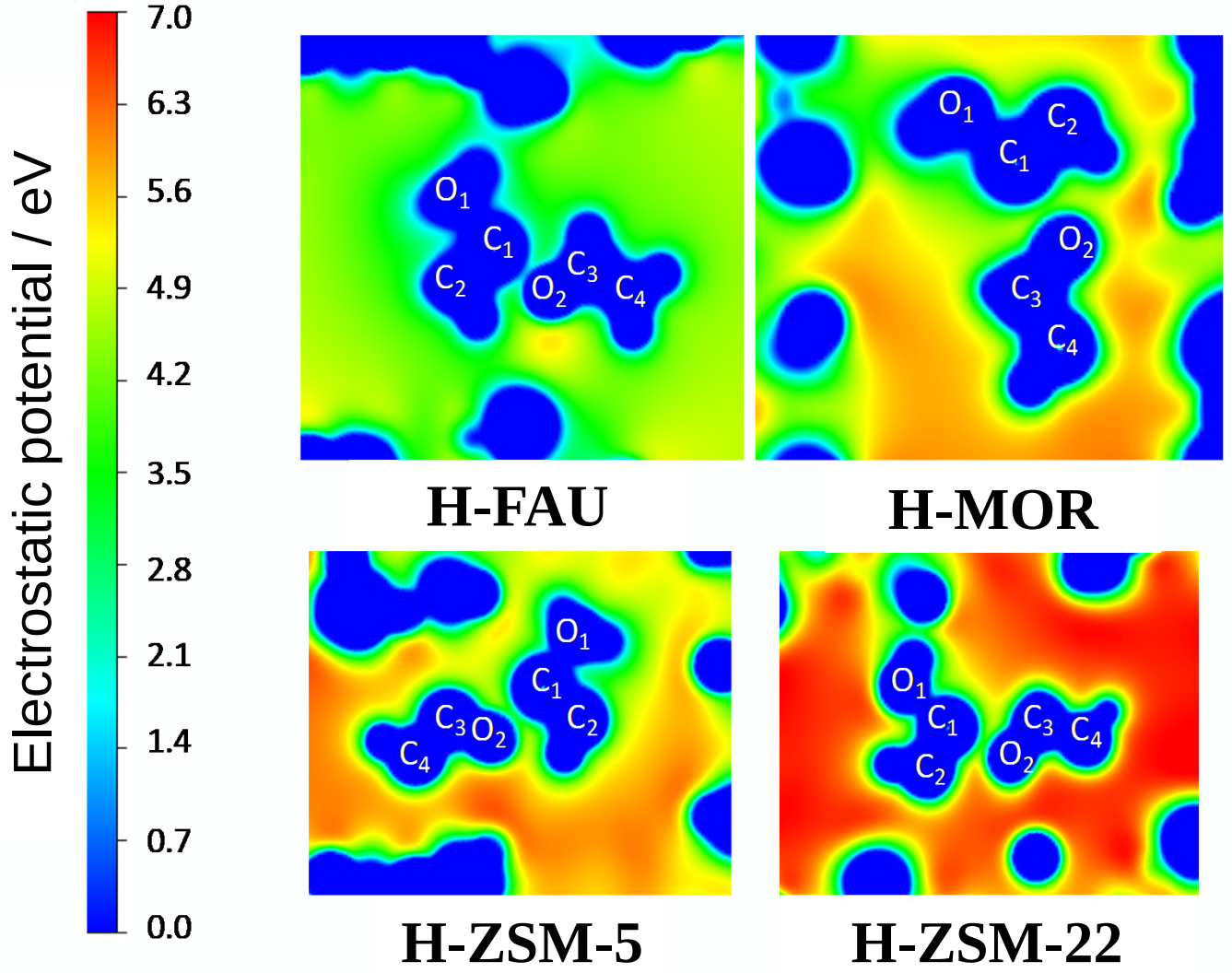
TS stabilization: vdW & hydrogen bonds

TS-8



12-MR (FAU; MOR) < 10-MR (ZSM-5; ZSM-22)

TS 8 stabilization: electrostatic interactions



FAU < MOR < ZSM-5 < ZSM-22

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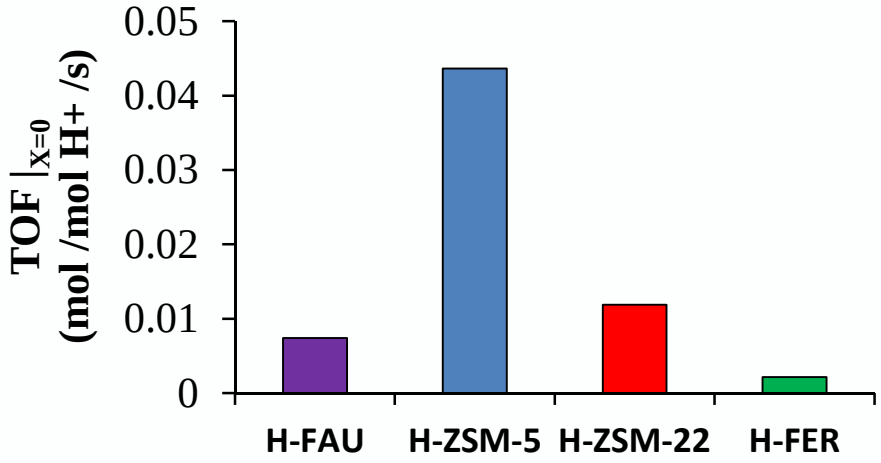
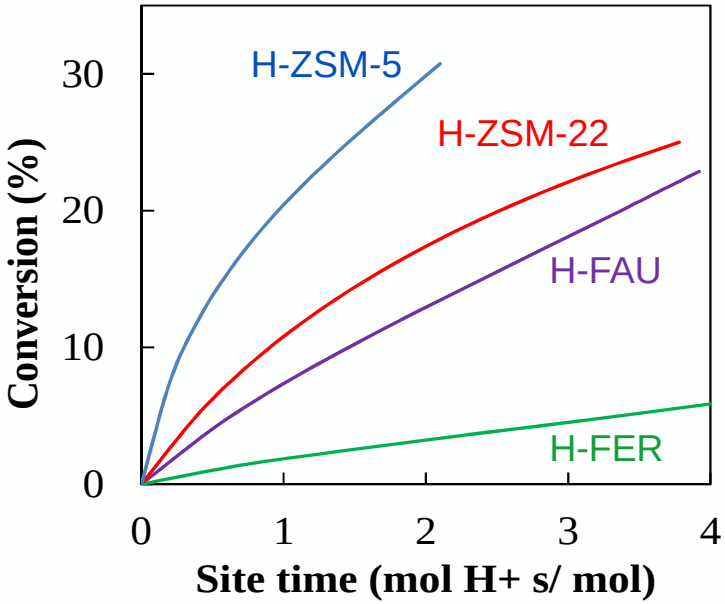
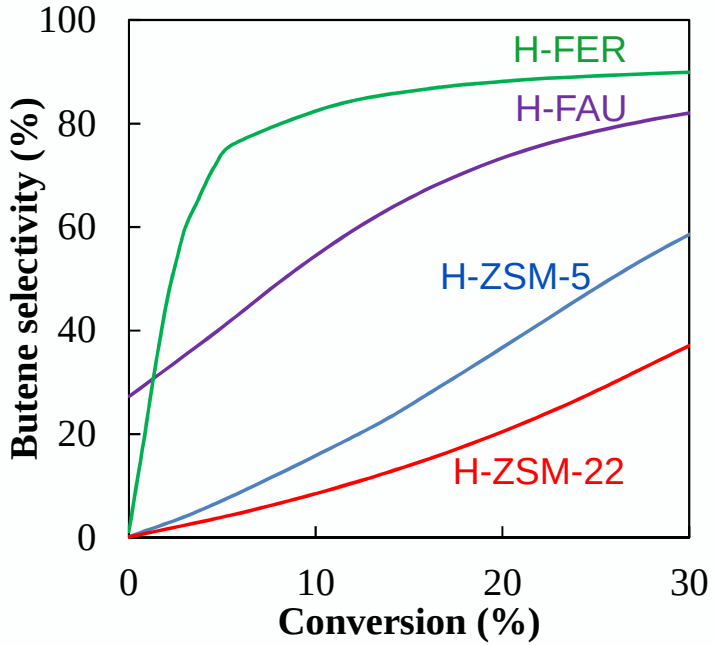
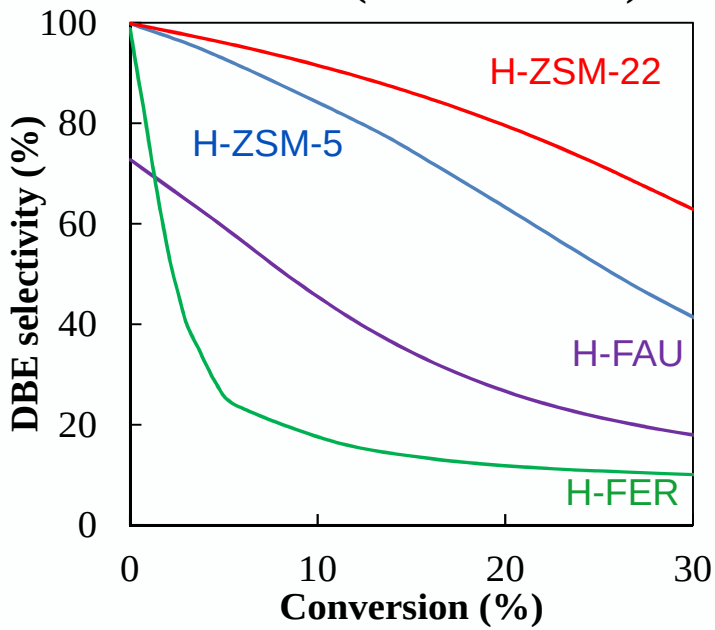
Butanol dehydration

$P_{BuOH,0}$ = 10 kPa Temperature = 450 K





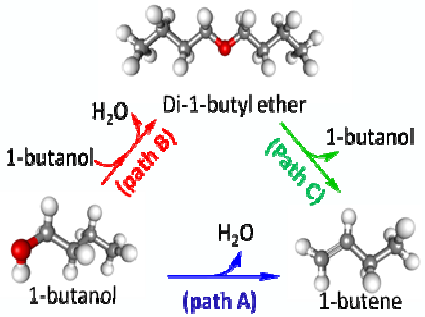




Effect of Zeolite: reaction path analysis

$P_{BuOH,0}$ = 10 kPa

Temperature= 450 K

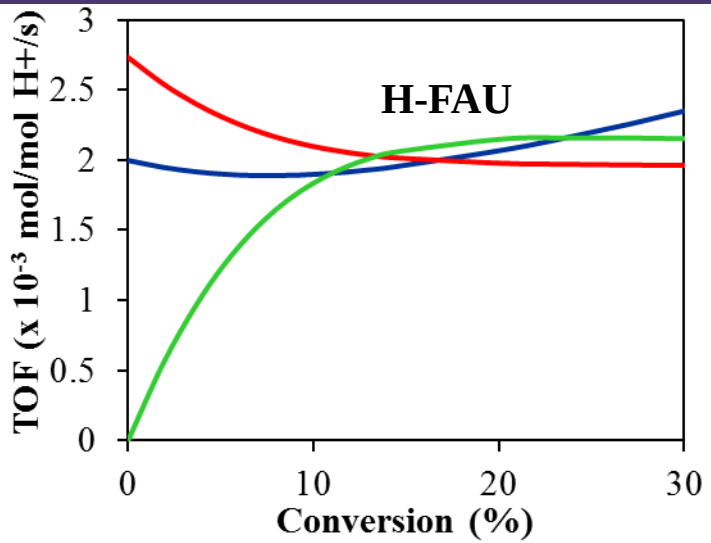


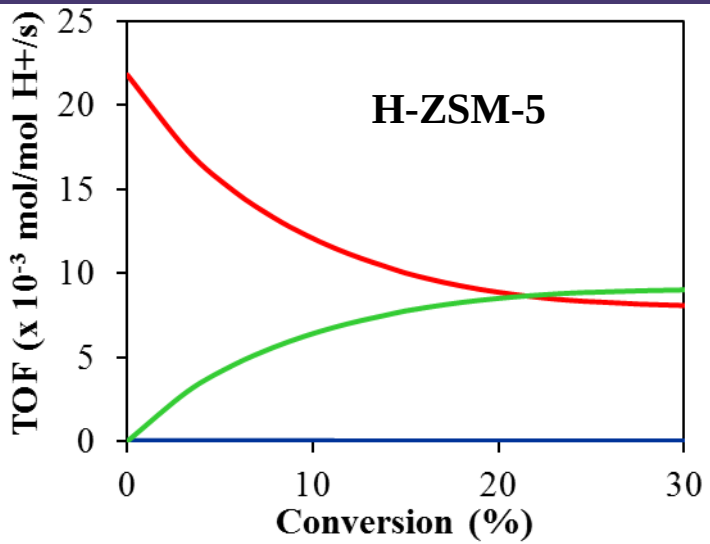
path A

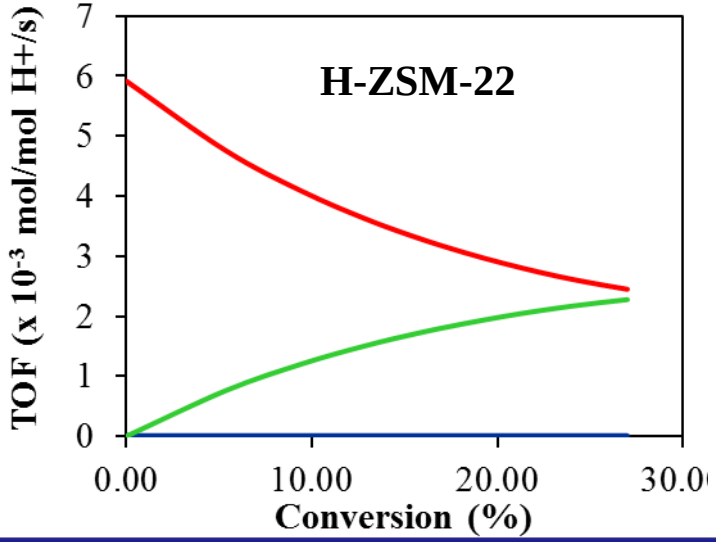
path B

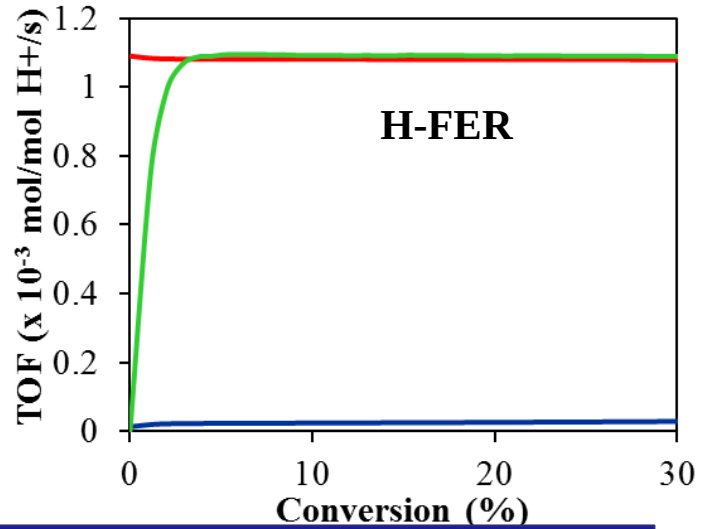
path C

H-FER and H-FAU: selective for butene







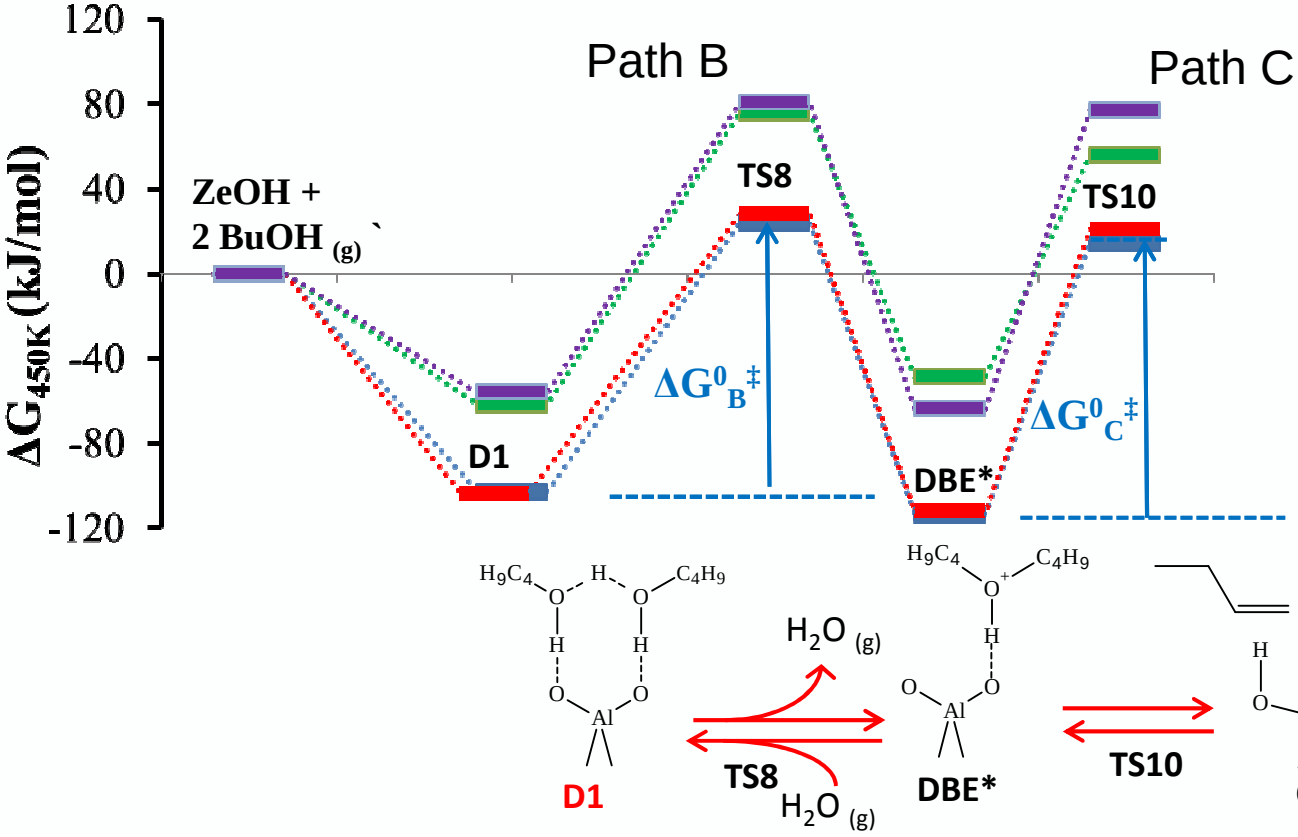


H-FER: ether-mediated route (path B followed by path C) favored to produce 1-butene

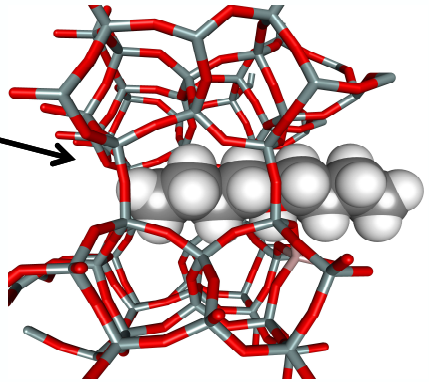
H-FAU: significant contribution from path A favors formation of 1-butene

Effect of zeolite: path B and C

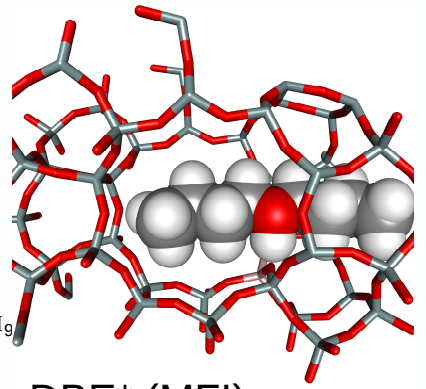
Zeolite	$\Delta G^{\ddagger}_{B} = G_{TS8} - G_{D1}$ (kJ/mol)	$\Delta G^{\ddagger}_{C} = G_{TS10} - G_{DBE*}$ (kJ/mol)
H-FAU	134	132
H-ZSM-5	127	128
H-ZSM-22	131	132
H-FER	137	105



Steric constraints

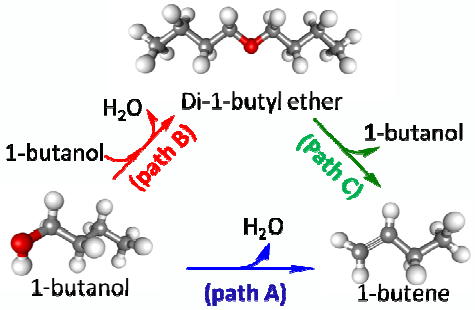


DBE* (FER)



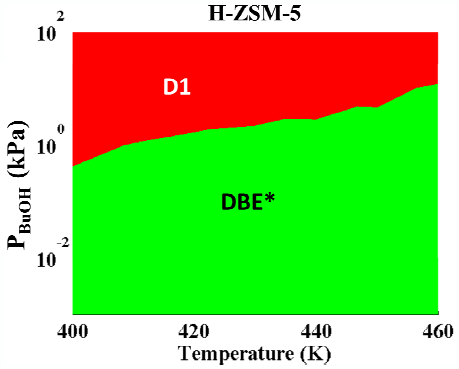
DBE* (MFI)

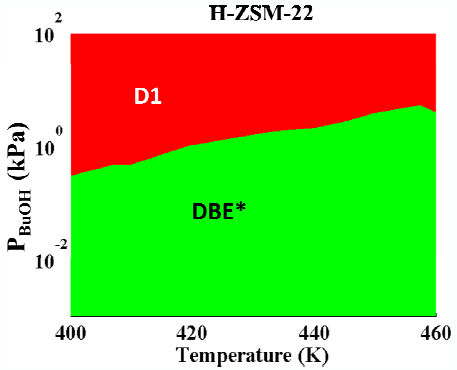
Caveat: effect of reaction conditions

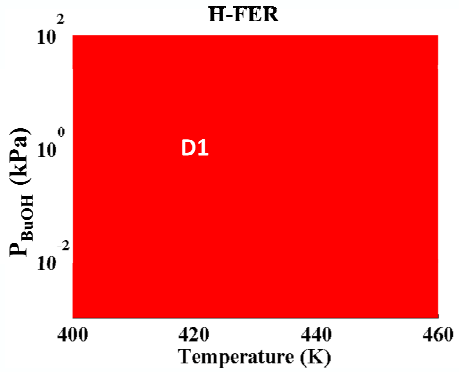


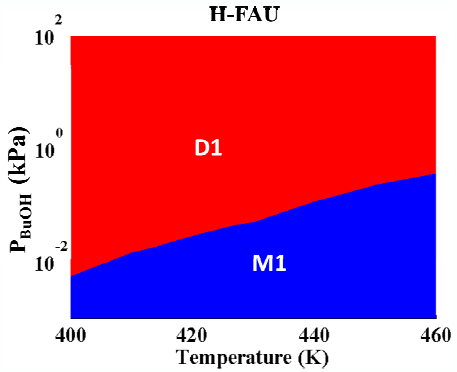
	Low	High
Temperature	B	A
P_{ROH}	A	B
Conversion (X)	A / B	A / C

MARI (at X= 10 %)

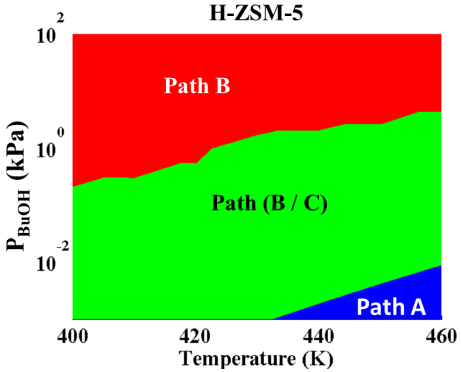


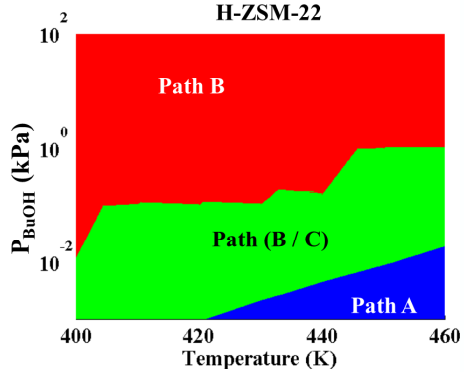


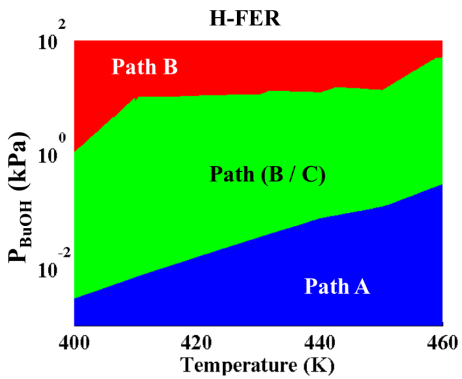


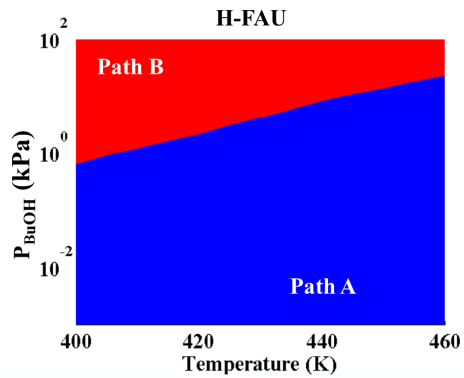


dominant path (at X= 10 %)

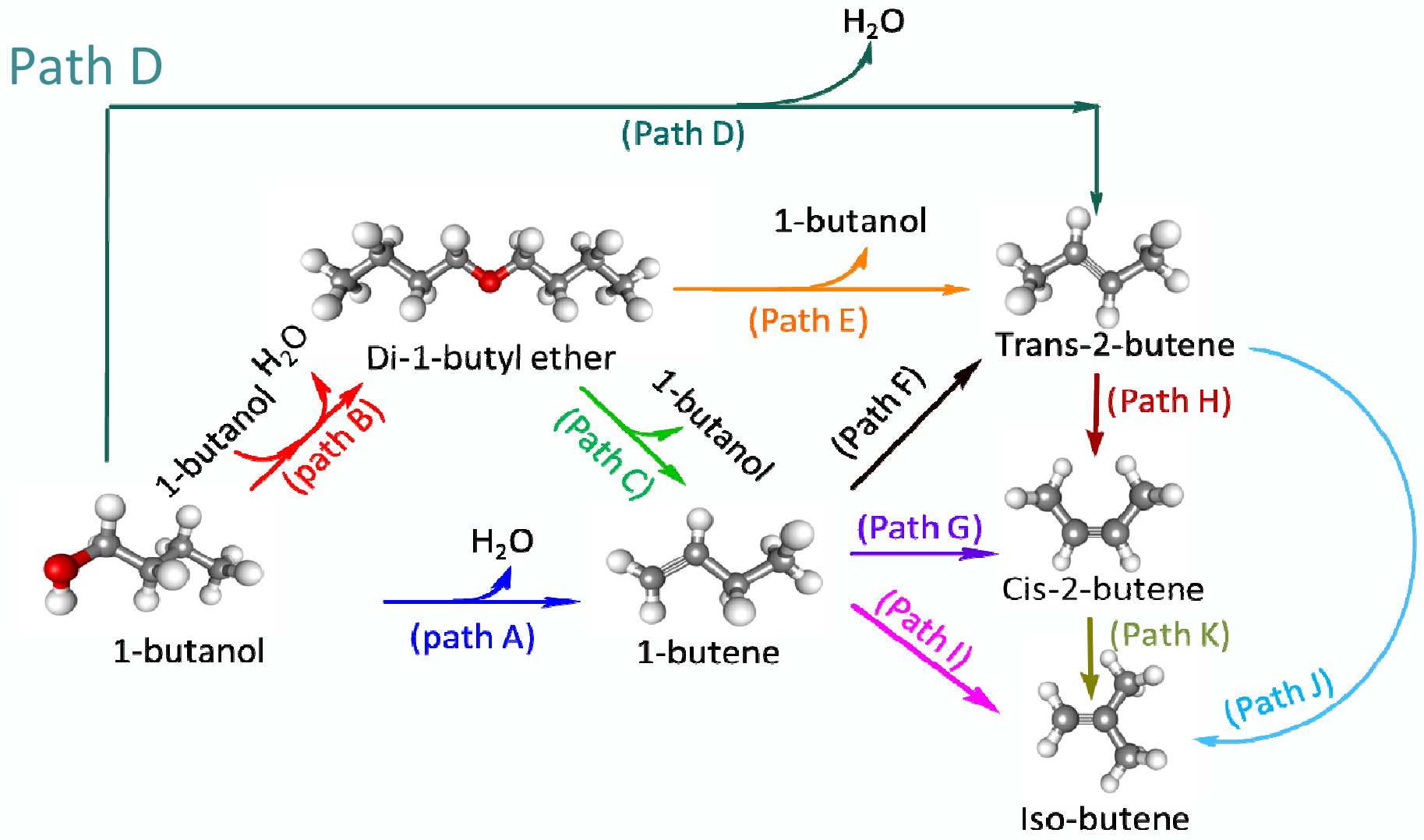






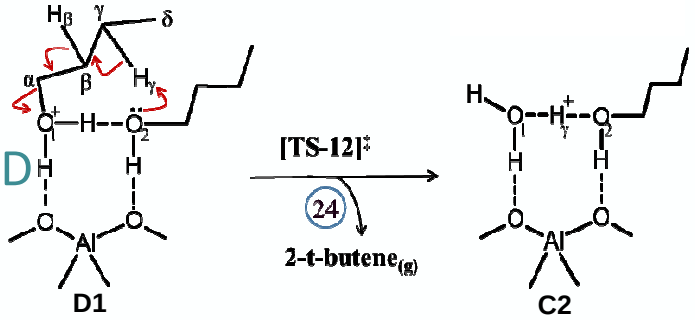


Dehydration of 1-butanol to butene isomers

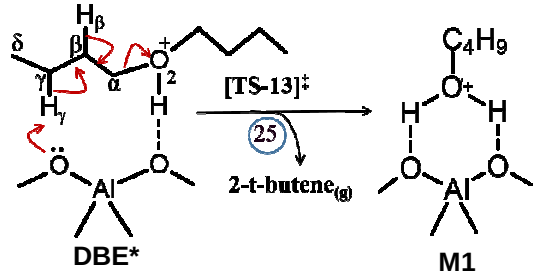


Dehydration of 1-butanol to 2-t-butene

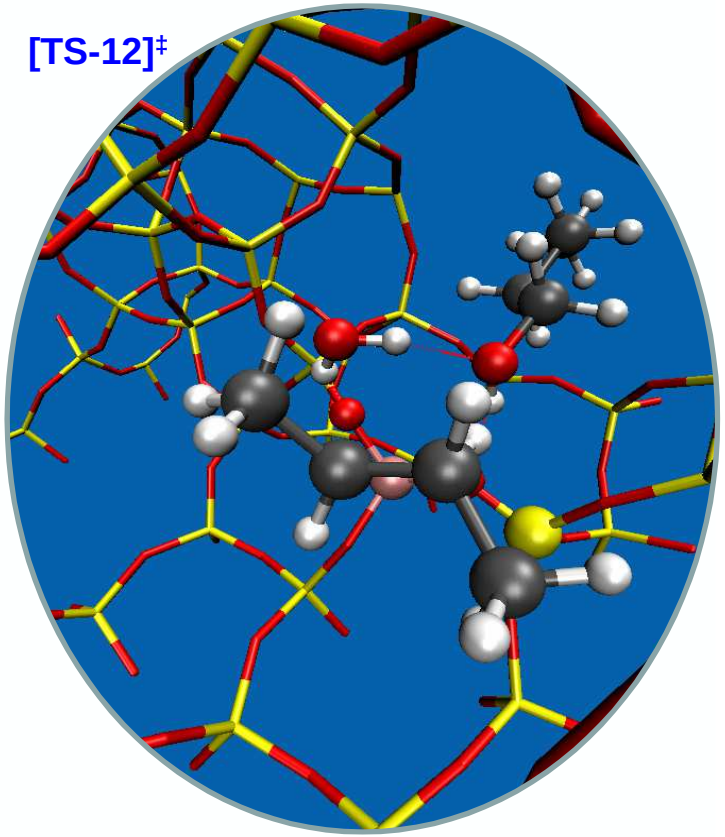
Path D



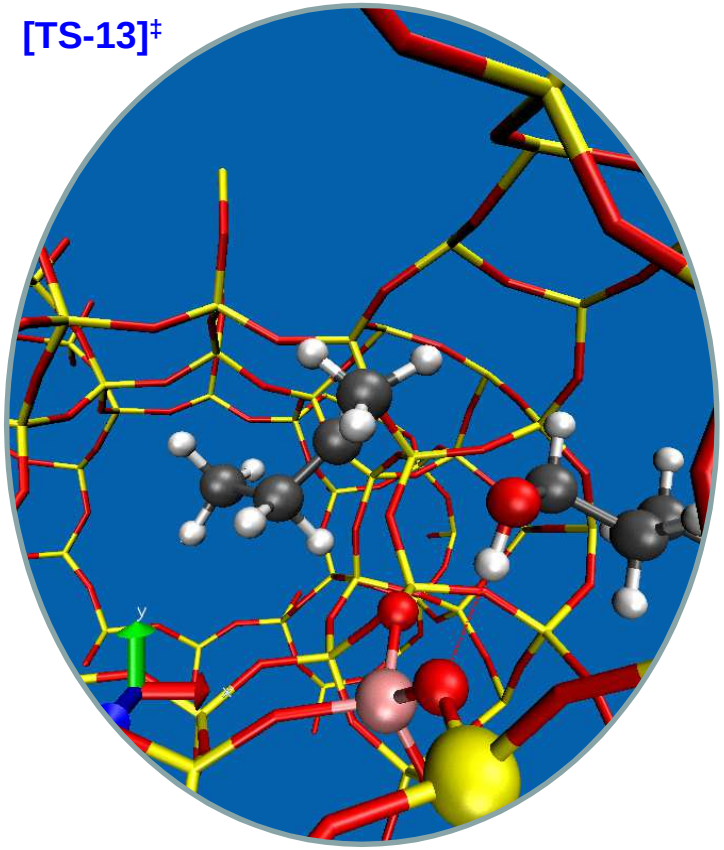
Path E



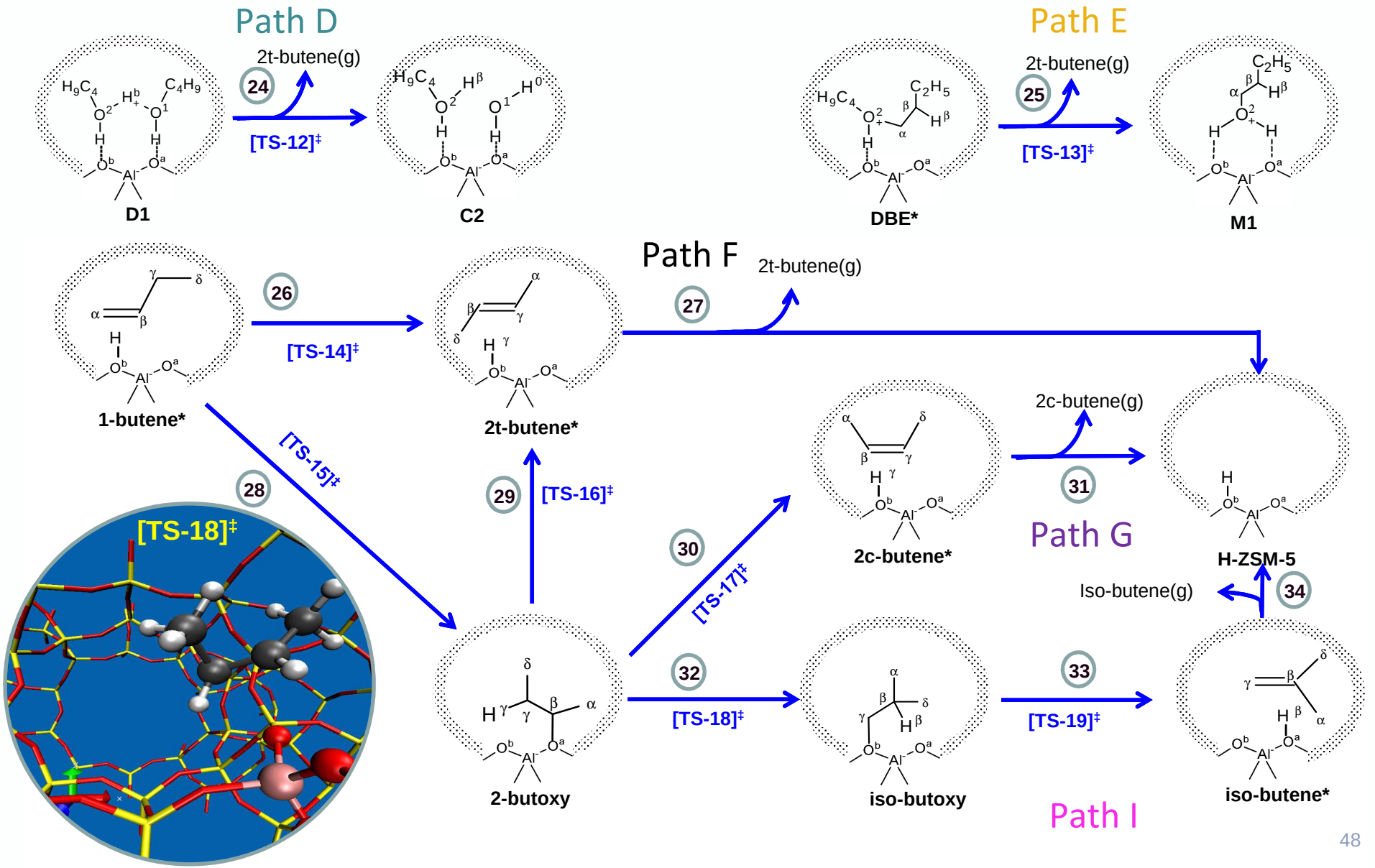
[TS-12]‡



[TS-13]‡



Dehydration of 1-butanol to butene isomers



Butanol dehydration: Temkin table

		Path A					Path B			Path C	
	Mechanism #	*m1*	*m2*	*m3*	*m4*	*m5*	*m6*	*m7*	*m8*	*m9*	*m10*
R1	$1\text{-BuOH}_{(g)} + * \leftrightarrow M1$	1	1	1	1	1	1	1	1	0	0
R2	$M1 \leftrightarrow W + 1\text{-Butene}_{(g)}$	1	0	0	0	0	0	0	0	0	0
R3	$W \leftrightarrow H_2O_{(g)} + *$	1	1	0	0	0	0	0	0	0	0
R4	$M1 \leftrightarrow C1$	0	1	0	0	0	0	0	0	0	0
R5	$C1 \leftrightarrow W + 1\text{-Butene}_{(g)}$	0	1	0	0	0	0	0	0	0	0
R6	$M1 \leftrightarrow M2$	0	0	1	1	0	0	1	1	0	0
R7	$M2 \leftrightarrow 1\text{-Butene}^* + H_2O_{(g)}$	0	0	1	0	0	0	0	0	0	0
R8	$1\text{-Butene}^* \leftrightarrow 1\text{-Butene}_{(g)} + *$	0	0	1	1	0	0	1	1	1	1
R9	$M2 \leftrightarrow Butoxy + H_2O_{(g)}$	0	0	0	1	0	0	1	1	0	0
R10	$Butoxy \leftrightarrow 1\text{-Butene}^*$	0	0	0	1	0	0	0	0	0	0
R11	$M1 + BuOH_{(g)} \leftrightarrow D1$	0	0	0	0	1	1	0	0	0	0
R12	$D1 \leftrightarrow D2$	0	0	0	0	1	1	0	0	0	0
R13	$D2 \leftrightarrow C2 + 1\text{-Butene}_{(g)}$	0	0	0	0	1	0	0	0	0	0
R14	$C2 \leftrightarrow M1 + H_2O_{(g)}$	0	0	0	0	1	0	0	0	0	0
R15	$D2 \leftrightarrow DBE^* + H_2O_{(g)}$	0	0	0	0	0	1	0	0	0	0
R16	$DBE^* \leftrightarrow DBE_{(g)} + *$	0	0	0	0	0	1	1	1	-1	-1
R17	$Butoxy + BuOH_{(g)} \leftrightarrow C3$	0	0	0	0	0	0	1	1	0	0
R18	$C3 \leftrightarrow DBE^*$ (Sn2)	0	0	0	0	0	0	1	0	0	0
R19	$C3 \leftrightarrow DBE^*$ (Sn1)	0	0	0	0	0	0	0	1	0	0
R20	$DBE^* \leftrightarrow C4$	0	0	0	0	0	0	0	0	1	0
R21	$C4 \leftrightarrow 1\text{-Butene}^* + BuOH_{(g)}$	0	0	0	0	0	0	0	0	1	0
R22	$DBE^* \leftrightarrow DBE2$	0	0	0	0	0	0	0	0	0	1
R23	$DBE2 \leftrightarrow 1\text{-Butene}^* + BuOH_{(g)}$	0	0	0	0	0	0	0	0	0	1

All reaction paths involving all the suggested mechanism are included in the microkinetic model

$$TOF_{path} = \sum_i^n TOF_{mech}$$

$TOF_{A} = TOF_{m1} + TOF_{m2} + TOF_{m3} + TOF_{m4} + TOF_{m5}$

$TOF_{m1} = TOF_{R2}$

$TOF_{m2} = TOF_{R4}$

$TOF_{m3} = TOF_{R7}$

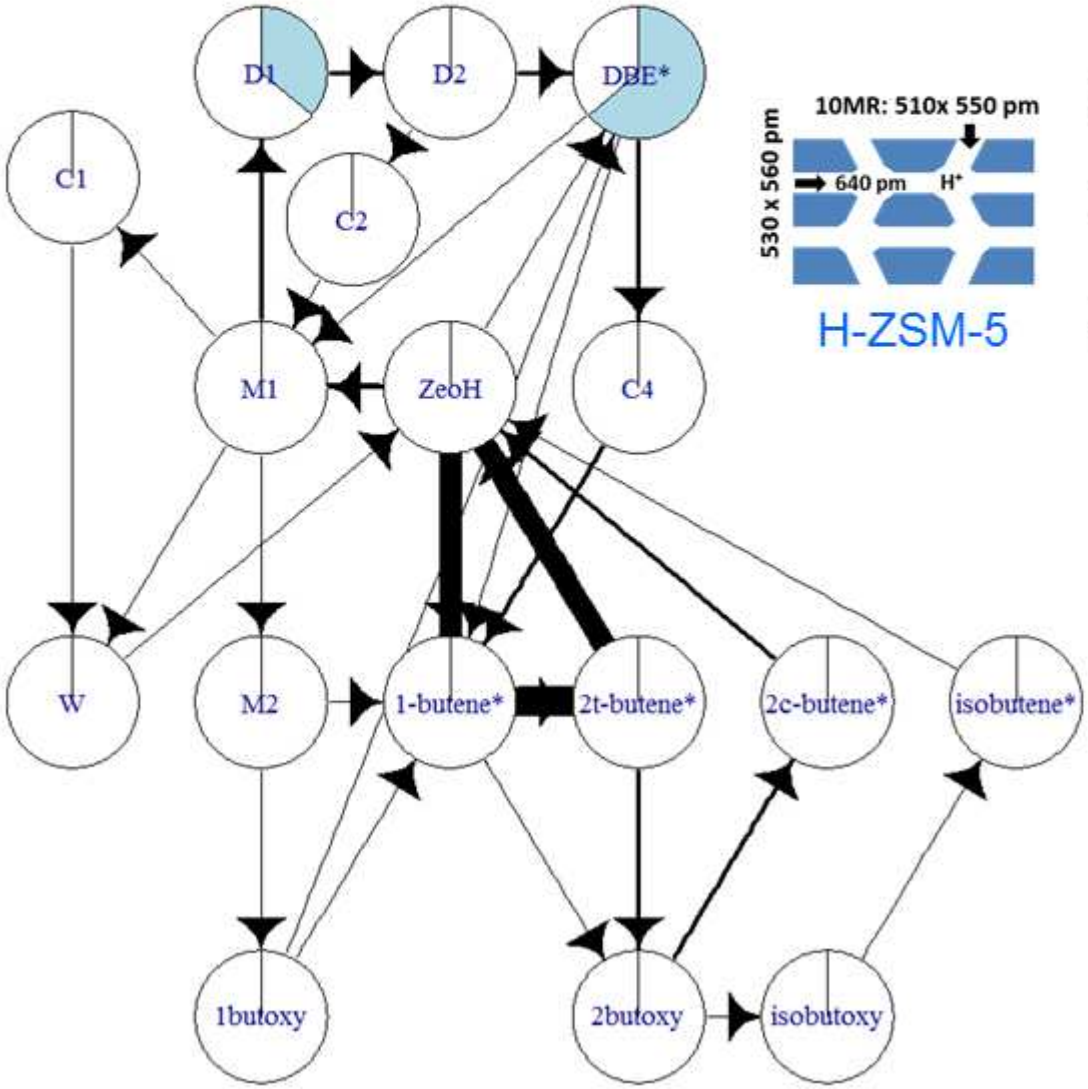
$TOF_{m4} = TOF_{R9}$

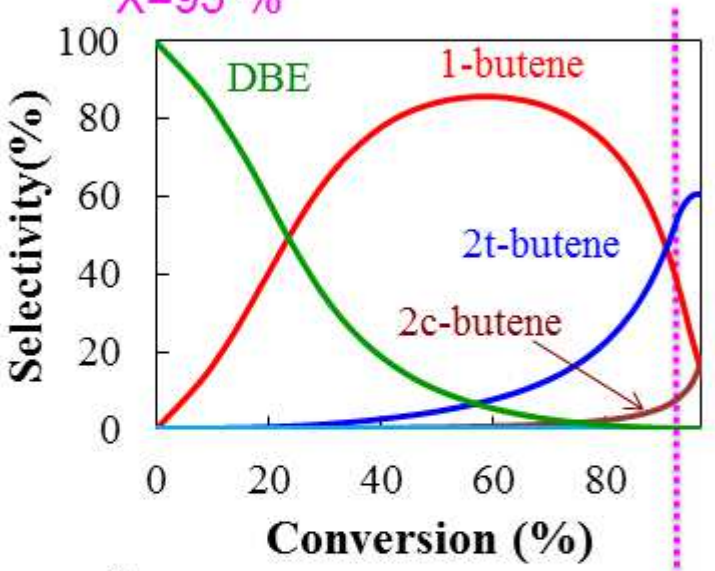
$TOF_{m5} = TOF_{R13}$

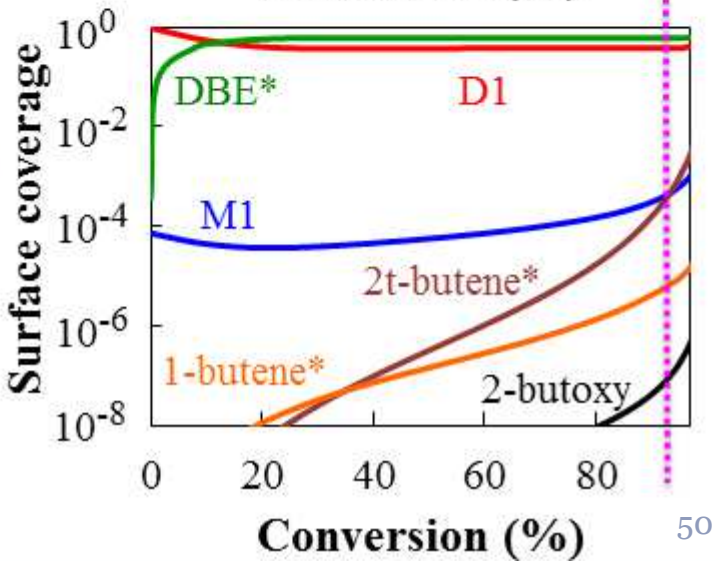
Reaction path analysis

Path F : 1-Butene(g) ↔ 2-t-Butene(g) *{concerted mechanism}*

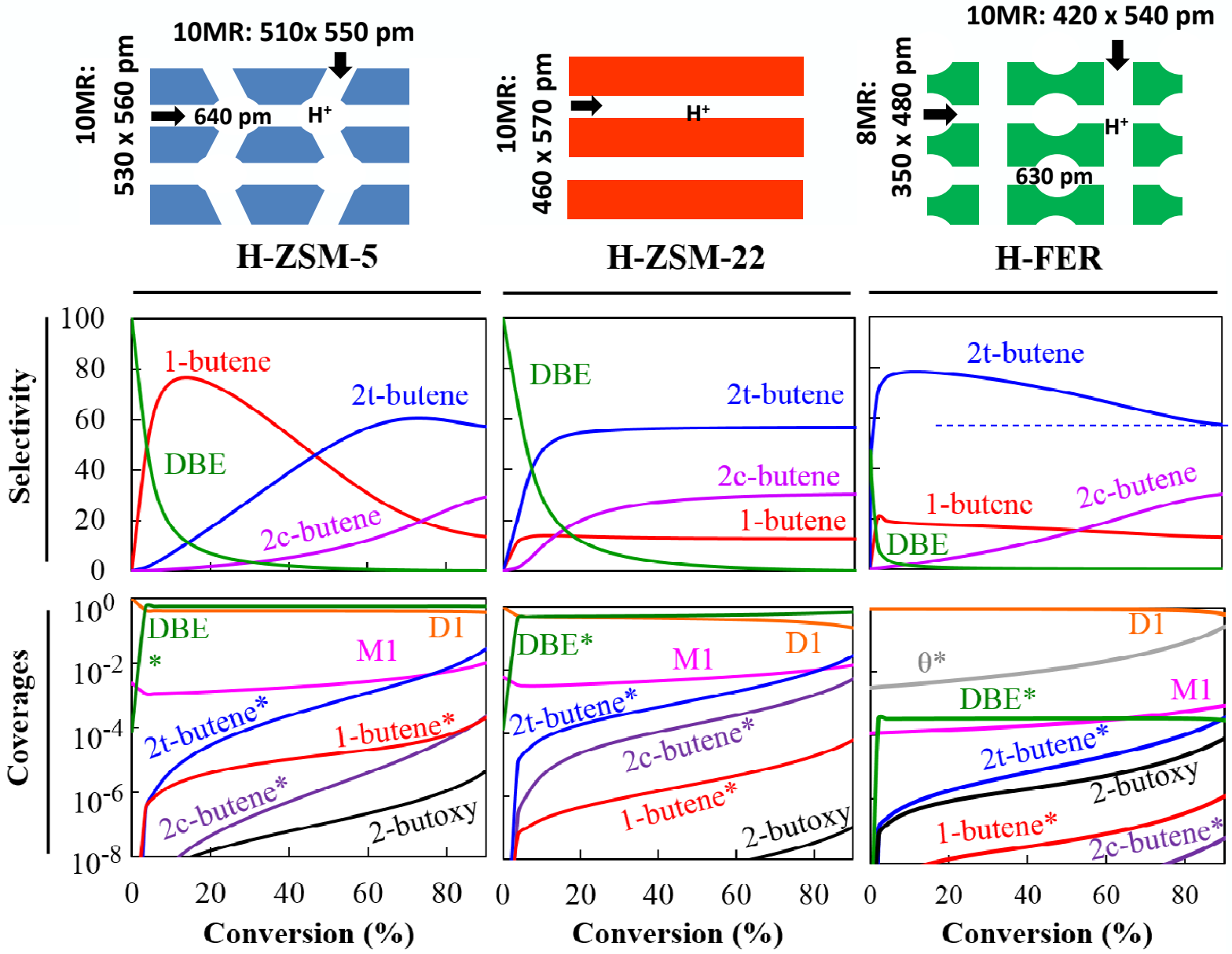
T : 450 K $P_{BuOH,0}$: 10 kPa







Butene isomer selectivity: Effect of zeolite type



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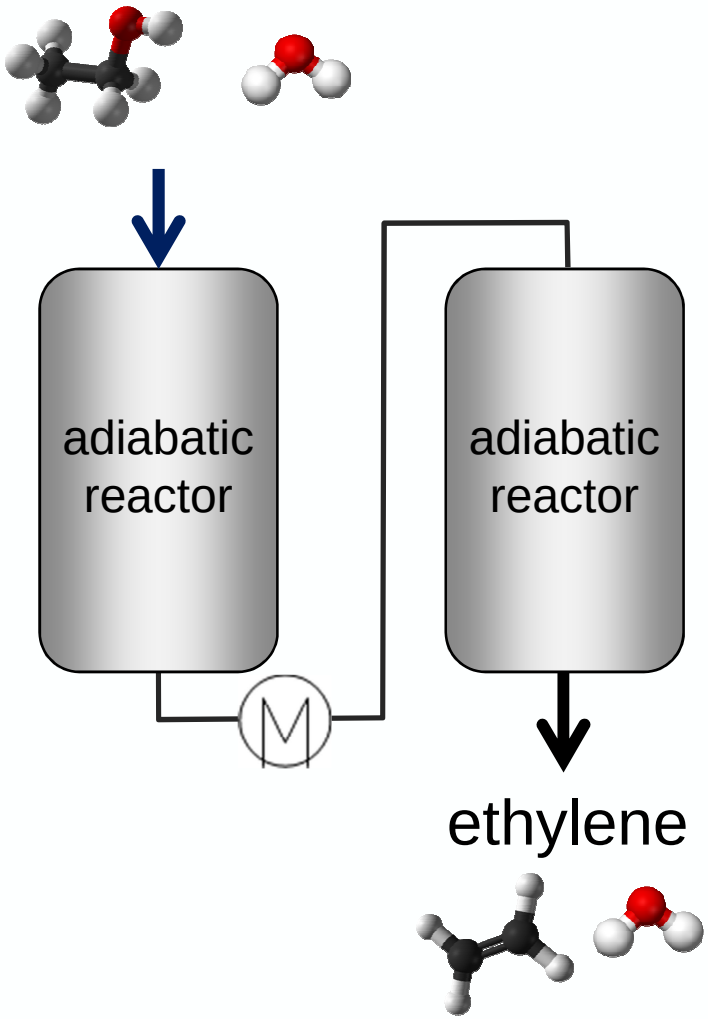
Industrial dehydration reactor

bio-ethanol (aqueous ethanol solution)



Design specifications[1]	
T^0 (K)	673
P^0 (kPa)	590
Ethylene production (kT y^{-1})	220
Ethanol content (wt.%)	26
Catalyst mass (ton)	6

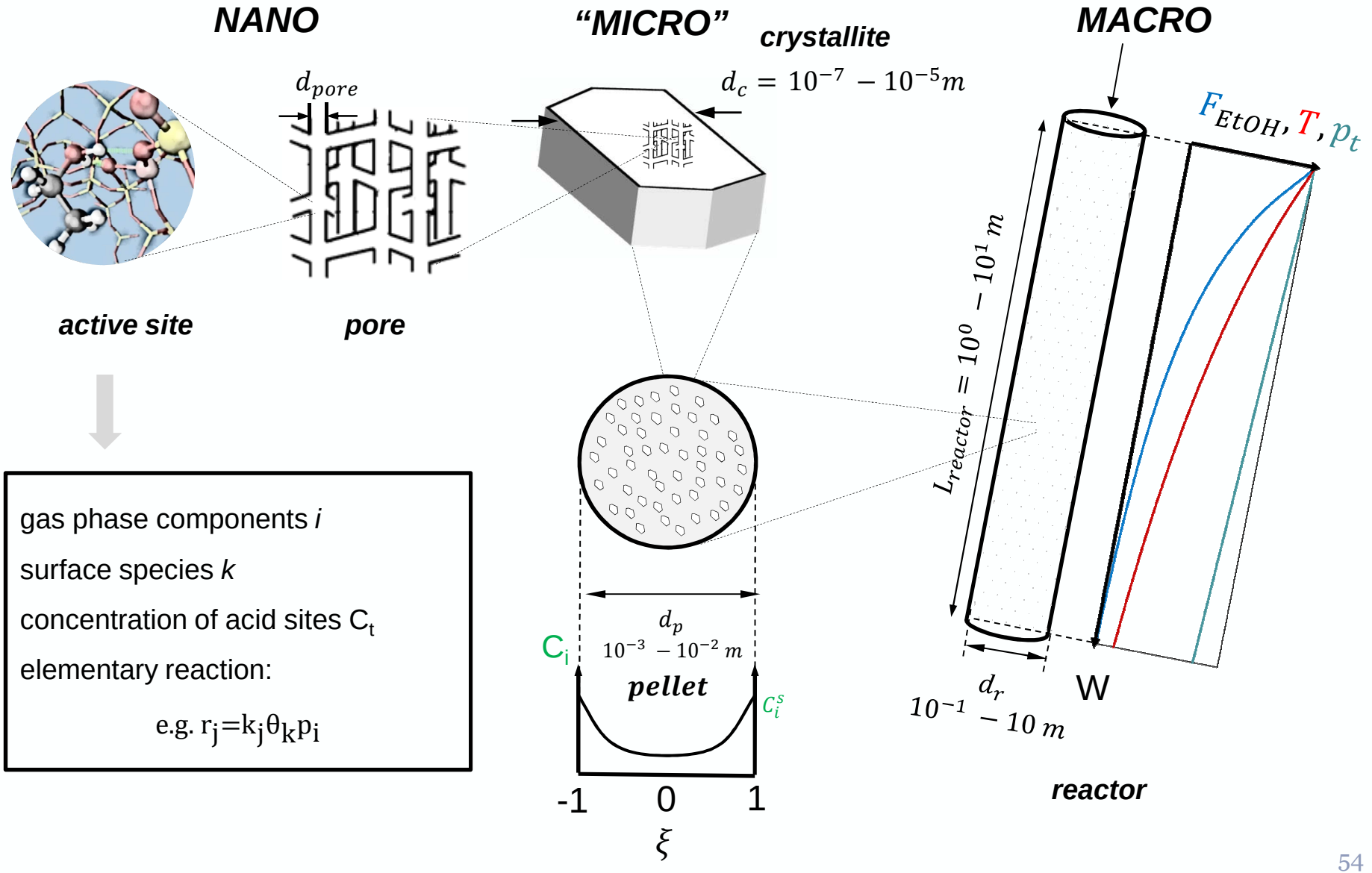
$C_2H_5OH \rightarrow C_2H_4 + H_2O$ $\quad \Delta H = 46$ kJ/mol$_{EtOH}$

$2\ C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$ $\quad \Delta H = -12$ kJ/mol$_{EtOH}$

$(C_2H_5)_2O \rightarrow C_2H_4 + C_2H_5OH$ $\quad \Delta H = 70$ kJ/mol$_{EtOH}$

[1] US Patent 2013/0090510 A1 assigned to IFP Energies Nouvelles and Total Research & Technology

Multiscale modeling of an industrial reactor



gas phase components *i*

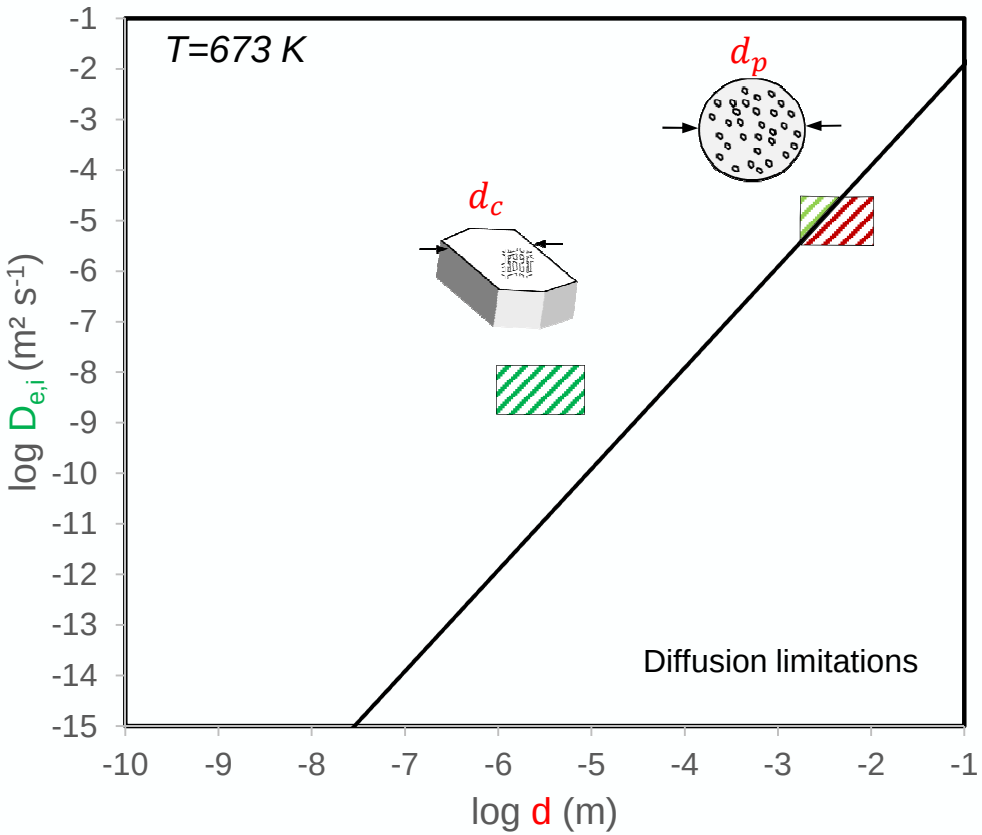
surface species *k*

concentration of acid sites C_t

elementary reaction:

e.g. $r_j = k_j \theta_k p_i$

Microscale: possible diffusion limitations



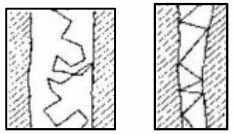
Weisz-Prater criterion:

$$\frac{(n+1)}{2}\frac{d^2\rho R_i^{obs}}{6D_{e,i}C_i^s} < 0.08$$

$$D_{e,i} = \frac{\varepsilon_p D_i}{\tau_p}$$

Bosanquet equation:

$$\frac{1}{D_i} = \frac{1}{D_{i,m}} + \frac{1}{D_{i,K}}$$



Knudsen diffusion coefficient:

$$D_{i,K} = \frac{2}{3}\frac{d_{pore}}{2}\sqrt{\frac{8RT}{\pi M_i}}$$

Molecular diffusion coefficient:

$$D_{i,j} = 1 \times 10^{-7}\frac{T^{1.75}}{P_{tot}((\Sigma v)_i^{1/3} + (\Sigma v)_j^{1/3})^2}\left(\frac{1}{M_i} + \frac{1}{M_j}\right)^{1/2}$$

Reactor model equations

NANO

$$R_k = \sum_j v_{jk} r_j = 0$$

with $e.g. r_j = k_j \theta_k p_i$

$$\theta_{H^+} + \sum_k \theta_k = 1$$

"MICRO"

$$0 = C_t R_i \rho_s - \frac{4}{d_p^2}\left(\frac{2}{\xi} D_{e,i} \frac{dC_i}{d\xi} + \frac{dD_{e,i}}{d\xi}\frac{dC_i}{d\xi} + D_{e,i}\frac{d^2 C_i}{d\xi^2}\right)$$

$$C_i = C_i^s \quad \xi = 1$$

$$\frac{dC_i}{d\xi} = 0 \quad \xi = 0$$

MACRO

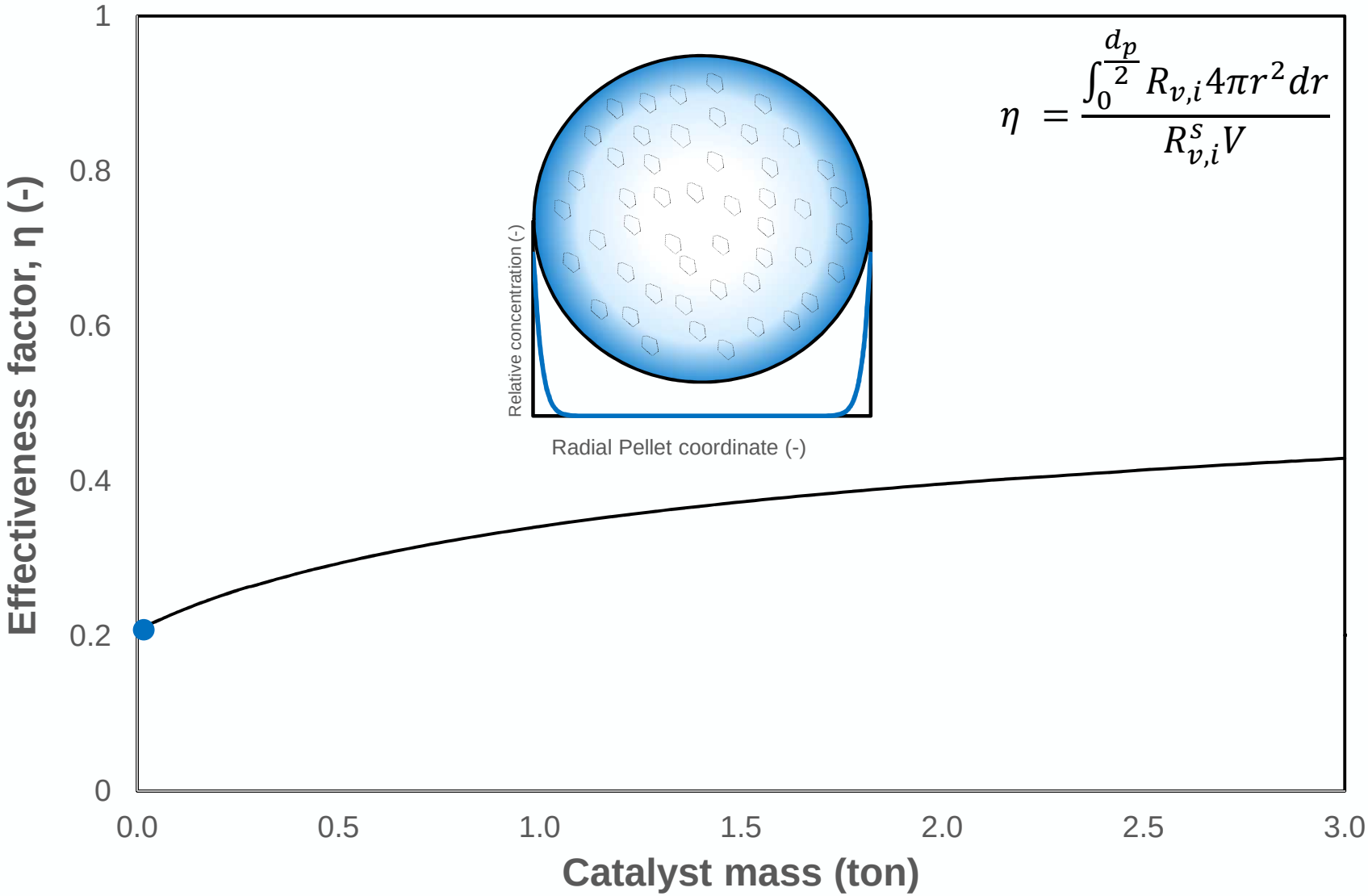
$$\frac{dF_i}{dW} = C_t \overline{R_i} \qquad F_i = F_{i,0} \text{ at } W=0$$

$$\frac{dT}{dW} = \frac{1}{G c_p} \sum_{i=1} \Delta H_{f,i} \overline{R_i} C_t \qquad T = T^0 \text{ at } W=0$$

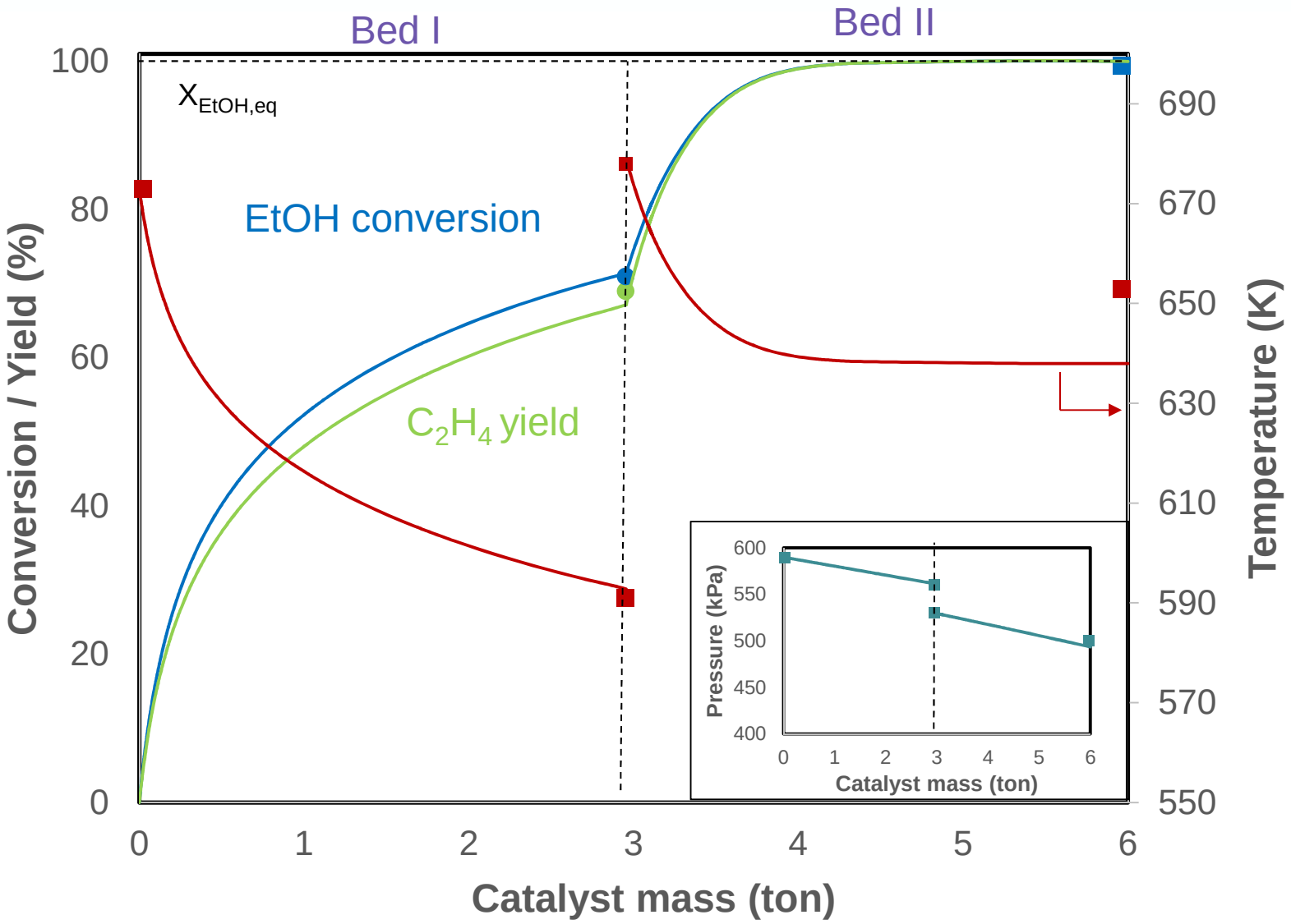
$$\frac{dp_t}{dW} = -f \frac{G^2}{\rho_b \rho_f A_r^3 d_p} \qquad p = p^0 \text{ at } W=0$$

- F_i molar flow rate of component *i* (mol s^{-1})
- W catalyst mass (kg)
- C_t acid site concentration (mol H^+ kg^{-1})
- R_i net production frequency of component i (molecules $site^{-1}$ s^{-1} = mol $mol_{H^+}^{-1}$ s^{-1})
- r_j turnover frequency of elementary step j (molecules $site^{-1}$ s^{-1} = mol $mol_{H^+}^{-1}$ s^{-1})
- k_j rate coefficient of elementary step j
- θ_k coverage of surface species k
- p_i partial pressure of gas phase component *i*
- v_{jk} stoichiometric coefficient of component k in the elementary step *j*
- T temperature (K)
- c_p specific heat capacity (J kg^{-1} K^{-1})
- G mass flow rate (kg s^{-1})
- $\Delta H_{f,i}$ enthalpy of formation of component *i* (J mol^{-1})
- $D_{e,i}$ effective diffusion coefficient (m^2 s^{-1})
- C_i concentration inside the catalyst pellet (mol m^{-3})
- ξ position coordinate within catalyst pellet
- $\overline{R_i}$ net production rate in case of diffusion limitations (mol $mol_{H^+}^{-1}$ s^{-1})
- ρ_f density of the fluid (kg m^{-3})
- ρ_s density of the pellet (kg m^{-3})
- ρ_b density of the bed (kg m^{-3})
- d_p pellet diameter (m)

Effectiveness factor



Industrial multibed adiabatic operation



Overview

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Conclusions I

- Adsorption strength increases with alkyl chain length of alcohols
- Increase of alkyl chain length leads to an increase of $\Delta S^{o\ddagger}$ and explains higher reactivity of large chain alcohols
- Dispersive interactions and H bonding plays a key role in stabilization of adsorbed species and transition states
- "Compensation effect" can be important: dispersive interaction and steric hindrance both increasing with decreasing pore size
- Stronger adsorption of alcohol and ether as compared to alkenes (limit consecutive reactions) and water (no significant inhibition effect)

Conclusions II

- Detailed reaction network can be constructed with limited a priory assumptions
- Kinetic parameters can be calculated ab initio with chemical accuracy i.e. allowing to describe conversion and selectivity at relevant conditions
- Interaction of functional groups with catalyst can be described accurately as well as the effect of catalyst framework
- Dominant reaction path depends strongly both on conditions and catalyst framework
- Selection of optimal catalyst based on reaction path/sensitivity analysis based on microkinetics

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- V. Galvita, C.M. Nguyen, K. Alexopoulos, M. John, K.Van der Borght

People

Glossary

- ***Molecular Dynamics (MD):*** a technique by which one generates the atomic trajectories of a system of N particles by numerical integration of Newton's equation of motion, for a specific interatomic potential, with certain initial and boundary conditions.

- ***Radial Distribution Function (RDF):*** a pair correlation function, which describes how, on average, the atoms in a system are radially packed around each other.

$$g_{\alpha\beta}(r) = \frac{1}{N_\alpha \rho_\beta} \sum_{I\epsilon\alpha, J\epsilon\beta} \delta(r - |\boldsymbol{R}_J - \boldsymbol{R}_I|)$$

- ***Vibrational Density Of States (VDOS):*** the Fourier transform of the velocity-velocity time-correlation function

$$D(\omega) = \int_0^\infty e^{-i\omega t} \langle \boldsymbol{v}(\tau) \cdot \boldsymbol{v}(\tau + t) \rangle \, dt$$

Glossary

- ***Electrostatic potential:*** evaluated from the interaction between a negative unit charge and the local charge density. This factor is critical in stabilizing positively charged adsorbed complexes and especially transition states in the zeolite.
- ***Elementary step:*** a reaction in which reactants are transformed into products without passing through another reaction intermediate
- ***Transition state theory for reaction rate coefficients:***

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{k_B T} \right) = \frac{k_B T}{h} \frac{q^{\ddagger}}{q} \exp\left(-\frac{\Delta E_0^{\ddagger}}{k_B T} \right)$$

$$where \quad q = q_{vib} \Rightarrow \text{immobile surface species}$$

(apart from Ethene* where a 2D translation and 1D rotation is assumed)

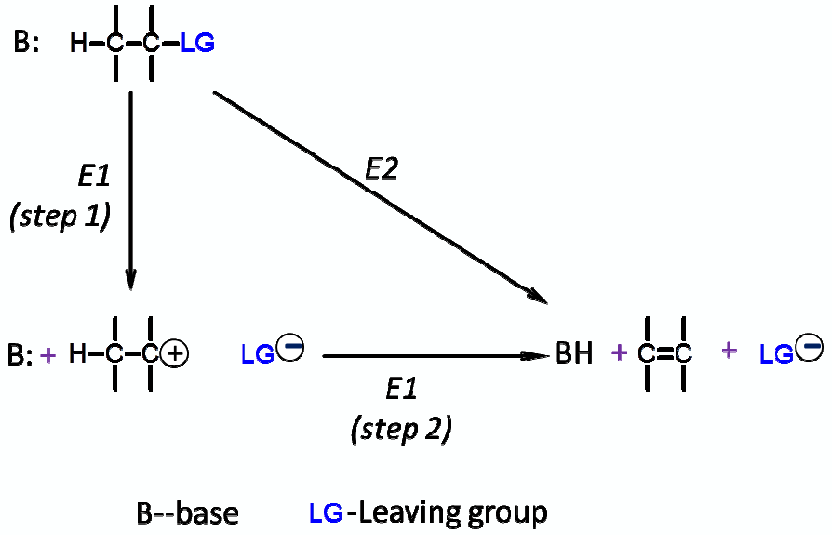
Glossary

- ***van der Waals interactions:*** the attractive or repulsive interactions between molecular entities (or between groups within the same molecular entity) other than those due to bond formation or to the electrostatic interaction of ions or of ionic groups with one another or with neutral molecules. The term includes: dipole–dipole, dipole-induced dipole and dispersive (instantaneous induced dipole-induced dipole) interactions.

- ***Dispersive interactions:*** attractive interactions between any pair of molecules, including non-polar atoms, arising from instantaneous induced dipole-induced dipole forces

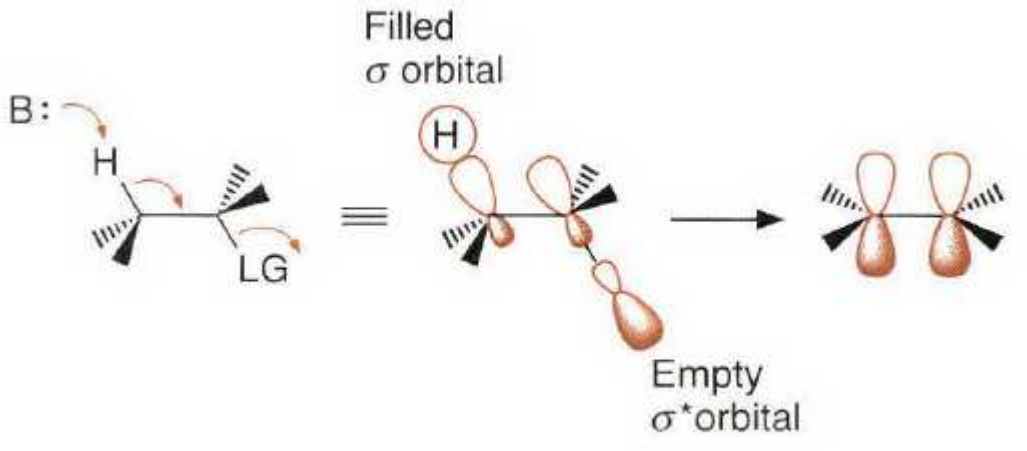
Glossary

- ***E1 reaction (elimination, unimolecular)*** – In this reaction, the rate determining step involves a heterolytic cleavage of the bond between the leaving group and the carbon atom leading to formation of a carbenium ion. The second step involves deprotonation of an adjacent hydrogen by a base.



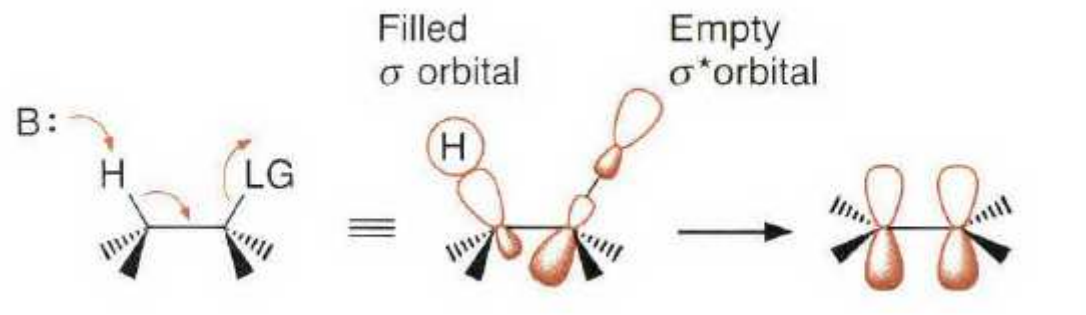
Glossary

- ***E2 reaction(elimination, bimolecular)*** –E2 reaction is a concerted reaction involving a synchronous deprotonation and departure of the leaving group. E2-type elimination requires the atoms or groups involved in the reaction to be in the same plane with a torsional angle θ = 180°, i.e. antiperiplanar orientation of the leaving group (LG) and the β-hydrogen (hence also called as anti-elimination).



Glossary

- ***Syn elimination*** – This is a concerted elimination mechanism, where the leaving group (LG) and the hydrogen atom are in the same plane and have a syn coplanar orientation (torsional angle $\theta \approx 0°$; eclipsed or near eclipsed conformation)

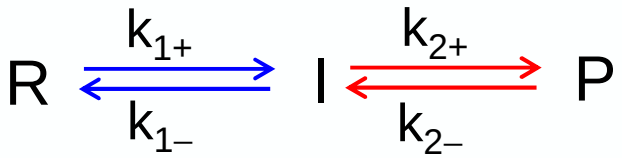


Glossary

- ***SN1 (substitution, unimolecular)*** –In this reaction, the rate determining step involves a heterolytic cleavage of the bond between the leaving group and the carbon atom leading to formation of a carbenium ion which undergoes a substitution reaction with the nucleophile.

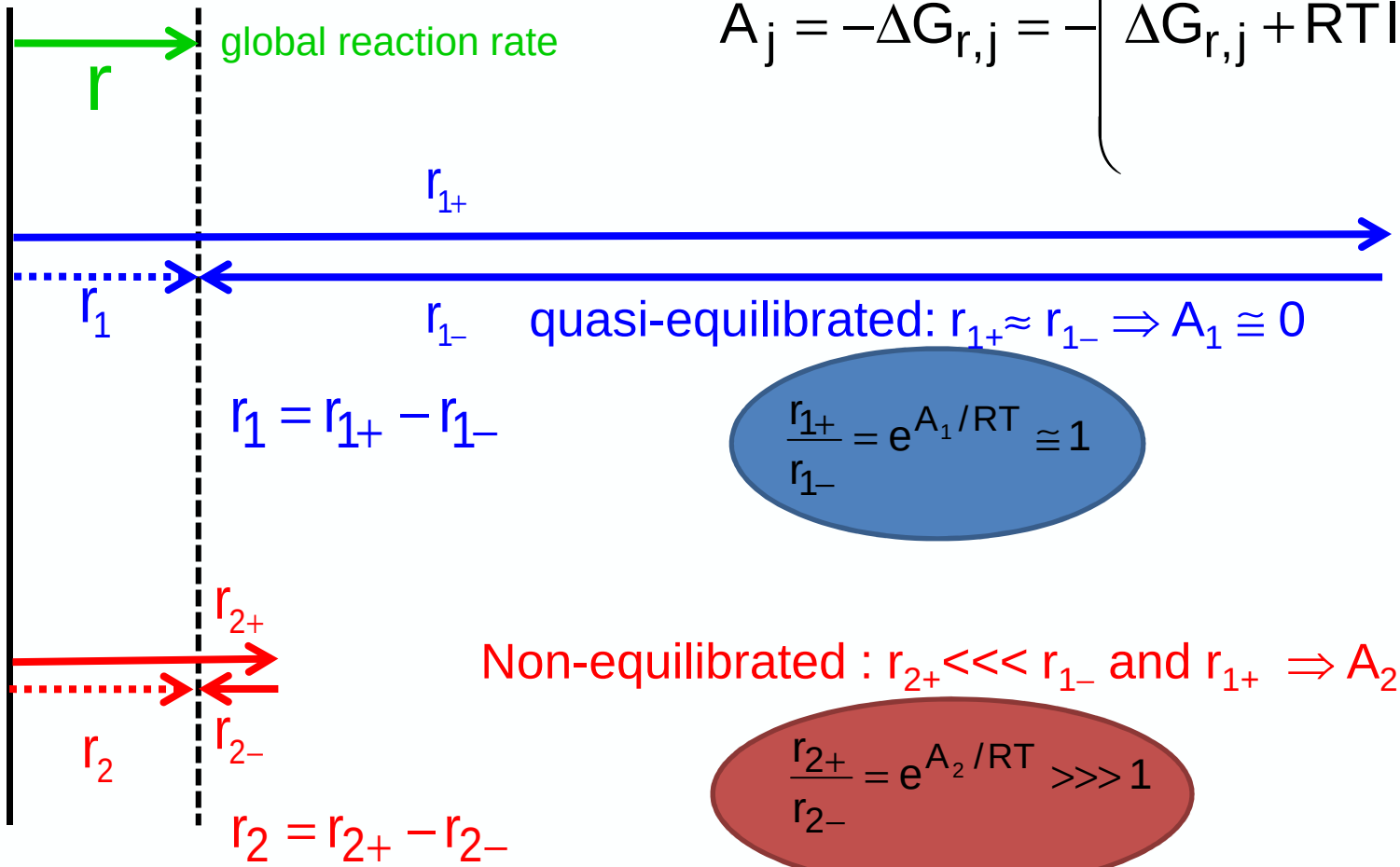
- ***SN2 (substitution, bimolecular)*** is a concerted reaction involving simultaneous bond breaking (between the carbon atom and leaving group) and bond formation(between carbon atom and the attacking nucleophile). The transition state for a SN2 type substitution involves a penta-coordinated carbon atom with a trigonal bipyramidal geometry with the incoming nucleophile and the leaving group occupying the axial positions (bond angle Nu--C--LG ≈ 180°)

Glossary: Rate-determining step



Affinity elementary step j

$$A_j = -\Delta G_{r,j} = -\left(\Delta G^{\circ}_{r,j} + RT \ln \frac{\prod_{prod} c_i^{n_i}}{\prod_{react} c_i^{n_i}} \right)$$



Glossary

- **Sensitivity analysis:** normalized sensitivity coefficient ($NSC_{i,j}$) of response R_j to pre-exponential factor A_i of reaction i:

$$NSC_{i,j} = \frac{d(lnR_j)}{d(lnA_i)} = \frac{A_i dR_j}{R_j dA_i}$$

  where R_j can correspond to conversion of reactants, turnover frequency, or selectivity to a product j

- **Reaction-path analysis:** analyzes the reaction rates that contribute to the rate of production or disappearance of a selected species, which allows to determine actual reaction path to form intermediates and products