UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

DFT-based and microkinetic analysis of zeolite-catalyzed conversion of bio-alcohols

Marie-Françoise Reyniers and Guy B. Marin

honoring Rutger van Santen

Laboratory for Chemical Technology, Ghent University

http://www.lct.UGent.be

1989 :Schuit Katalyse Institute

1991: NIOK hetero, homo and biocatalysis

Het eerste bestuur van NIOK:

prof. dr. G. van Koten, RUU, voorzitter

prof. dr. P.W.N.M. van Leeuwen, UvA, voorzitter onderzoekcommissie

prof. dr. R.M. Kellogg, RUG

prof. dr. V. Ponec, RUL

prof. dr. J.A. Moulijn, TUD, voorzitter onderwijscommissie

prof. dr. ir. G.B. Marin, TUE

vacature, UT (wordt ad interim vervuld door dr. J. van Ommen)

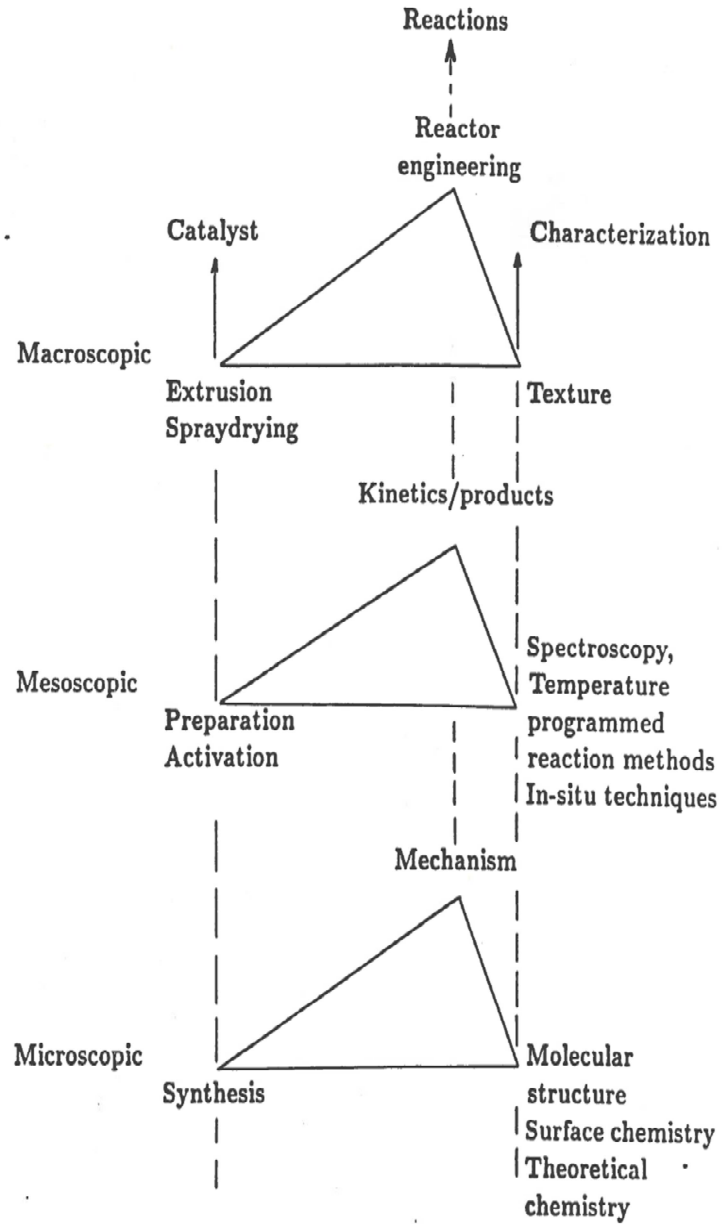
Wetenschappelijk directeur:

prof. dr. R.A. van Santen, TUE (voorlopig)

Secretaris:

drs. A. van der Schuyt, Civi Consultancy

1992: NIOK the van Santen prism



1996 Research "Visitation": P1 Catalysis

Programme 1. Inorganic Chemistry and Catalysis

Overview of subprogrammes and projects

Subprogramme 1: Catalytic reactivity
- Transition metal sulfide catalysis
- Transition metal catalysis
- Positron emission profiling
- Ammoxidation
- Plasma catalysis

Subprogramme 2: Catalytic synthesis
- Preparation and characterisation of new zeolitic materials and their catalytic applications
- Polyhedral oligometallasilsesquioxanes as catalytic materials
- Zeolite-supported organometallics as catalyst precursors

Subprogramme 3: Physical chemistry of zeolites
- Applications of NMR to catalysis
- Formation and ageing of porous silica and synthesis of zeolites
- Application of infrared spectroscopy to catalysis
- Calorimetry

Subprogramme 4: Theoretical catalytic chemistry
- Transition metal reactivity
- Zeolites
- Molecular dynamics and Monte Carlo studies

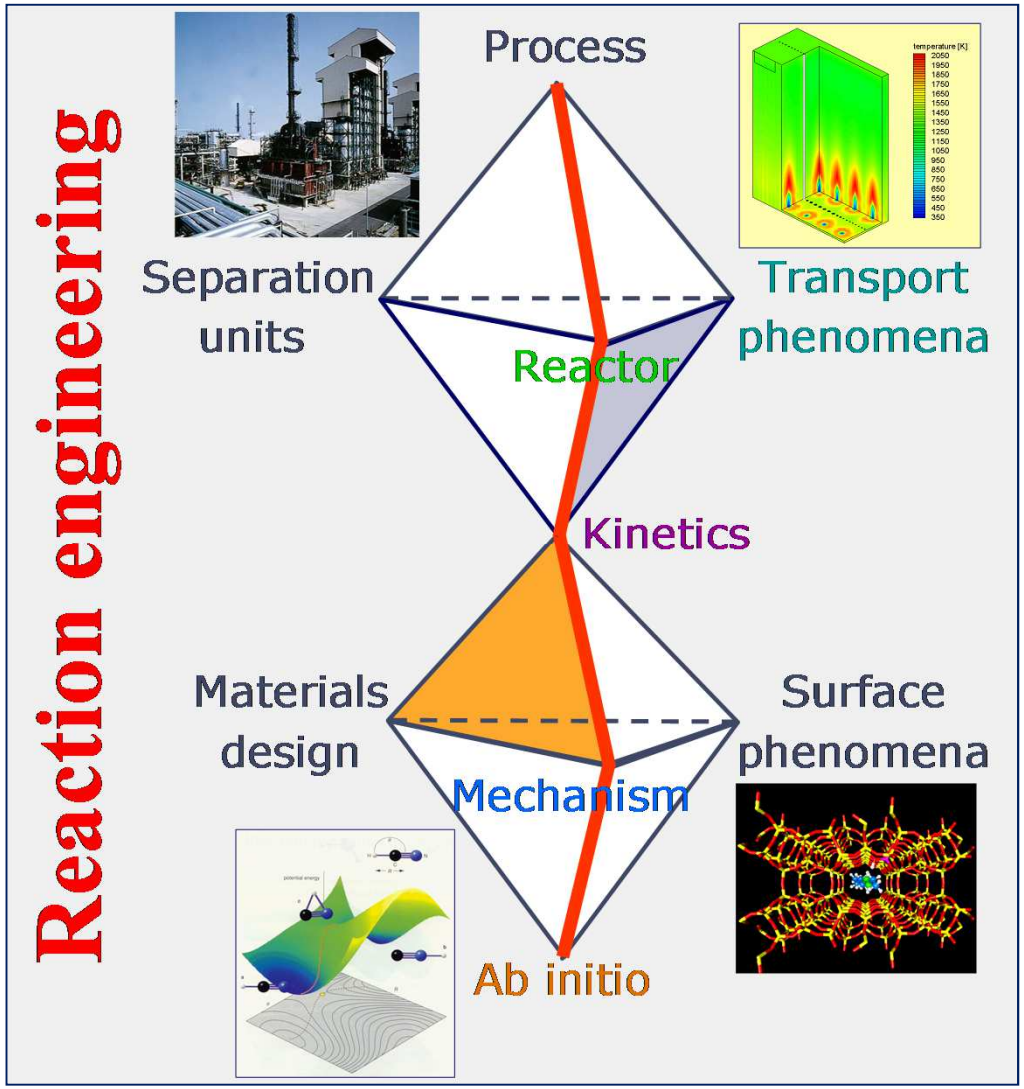
Subprogramme 5. Molecular surface chemistry of catalytic reactions
- Reactivity of catalytic surfaces
- Surface chemistry of catalyst preparation
- Catalyst characterisation and miscellaneous projects

Subprogramme 6: Electrocatalysis
- Electrocatalysis with transition-metal chelates
- Noble metal (electro)catalysts

1996: P2 Reaction Engineering

2016: Laboratory for Chemical Technology

from atom (nm) to full process (m)



Process level

Molecular level

UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Vakgroep Chemische Proceskunde en Technische Chemie

Laboratorium voor Chemische Technologie

Guy B. Marin

Geraldine Heynderickx

Marie-Françoise Reyniers

Mark Saeys

Joris Thybaut

Kevin Van Geem

Dagmar D'hooge

Maarten Sabbe

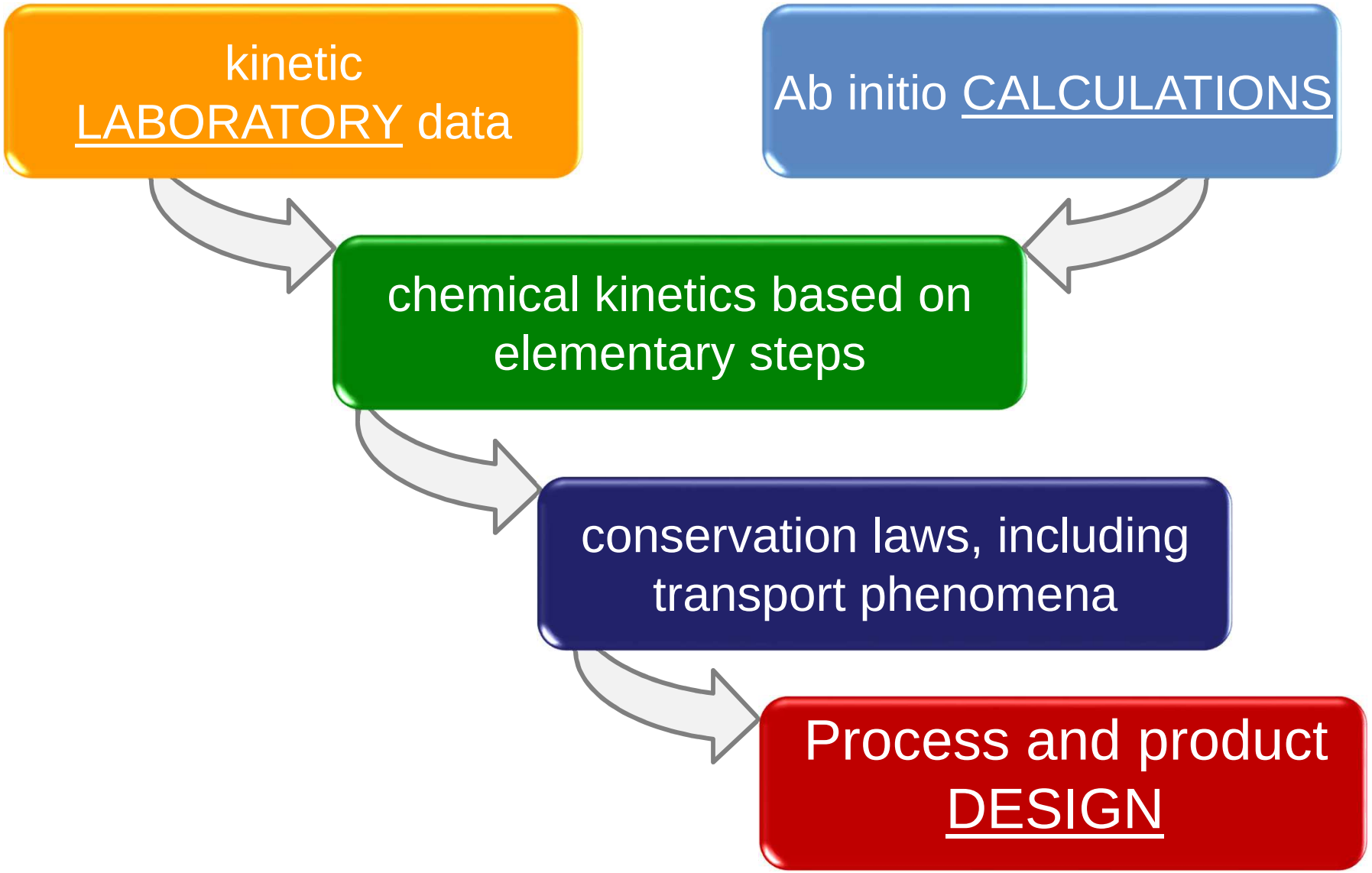
http://www.lct.ugent.be

European Research Institute of Catalysis

2016 LCT People

- assistant professors: 3
- Visiting/senior scientists: 4
- Post-docs: 10
- PhD students: 65
- Technical staff: 11
- Administrative staff: 3

Multi-scale modeling: la voie royale



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

Overview

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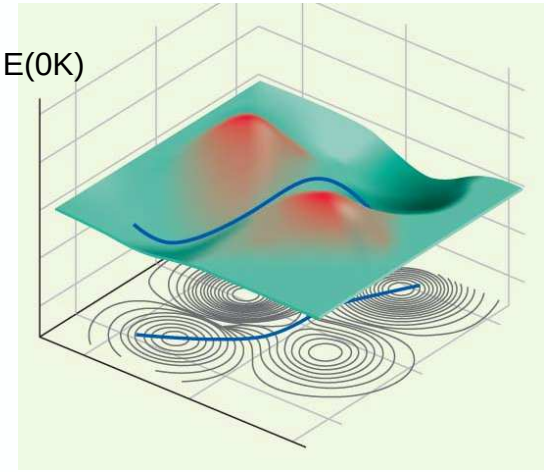
  - First principles kinetic model development
  - Experimental validation
  - Reaction-path analysis
  - Effect of zeolite
  - Industrial reactor scale
- Conclusions

First-principles based multiscale modeling

Electronic structure calculation (0 K)

Vibrational analysis

Statistical thermodynamics



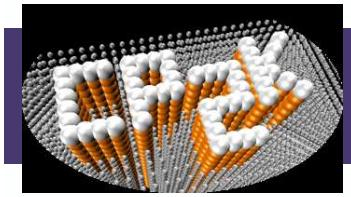
H(T), S(T), G(T)

Thermo & Kinetics
K(T), k_+(T), k_-(T)

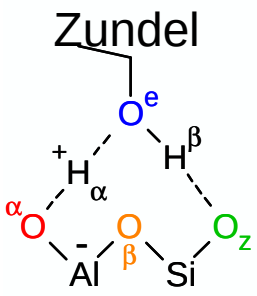
Reactor hydrodynamics
mass/heat transport

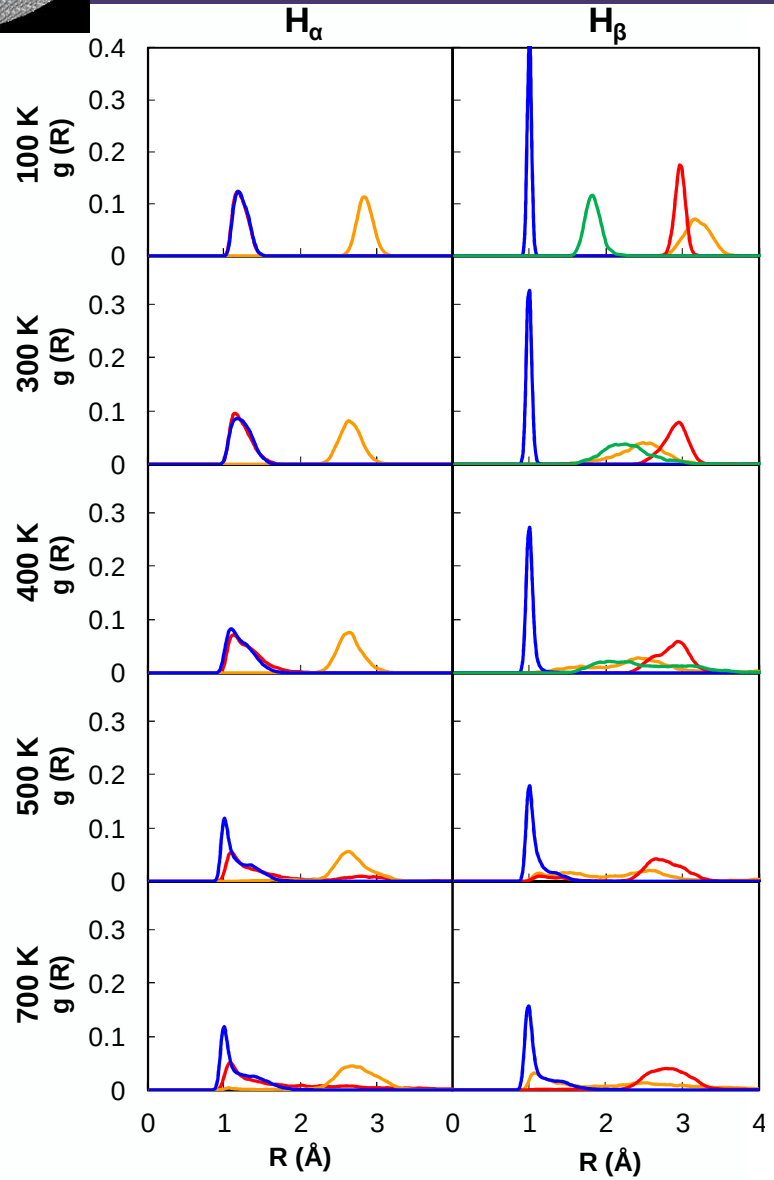
- conversion and product yields
- rate analysis

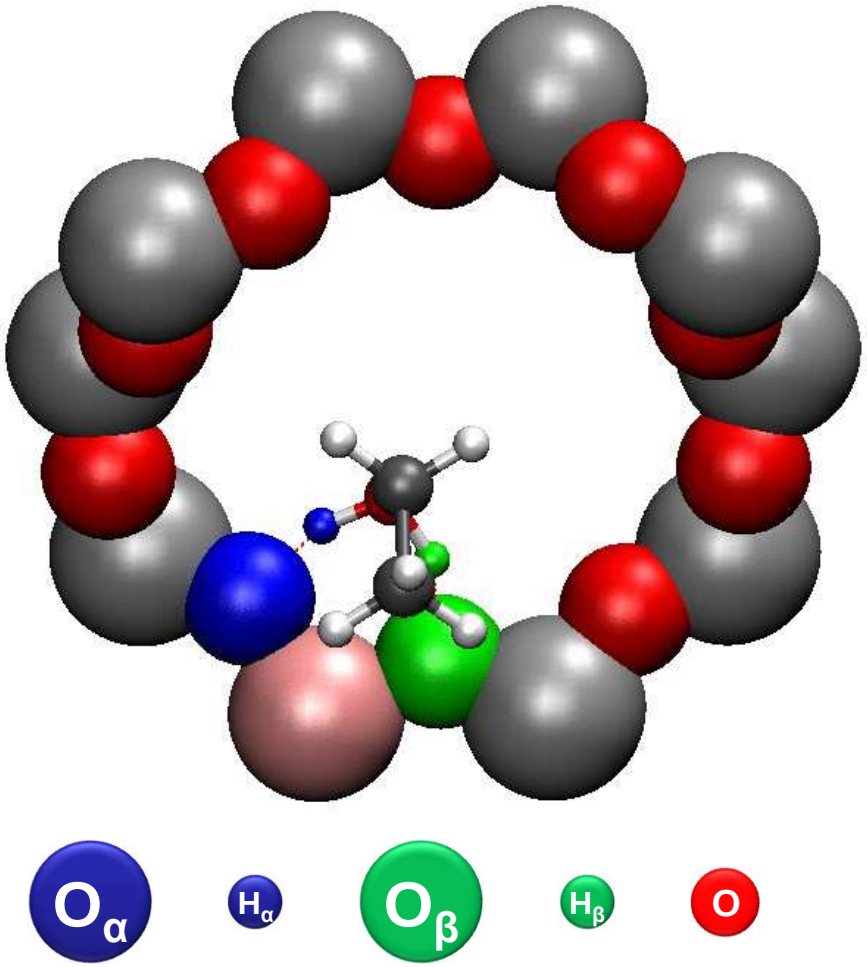
- guidelines process conditions
- guidelines catalyst properties



Ab Initio Molecular Dynamics



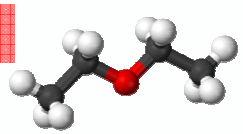


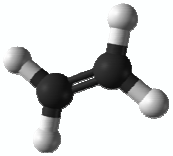


Alexopoulos et al. J. Phys. Chem. C (2016) 7172-7182

Acid catalyzed ethanol conversion

DEE

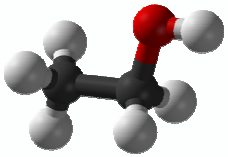


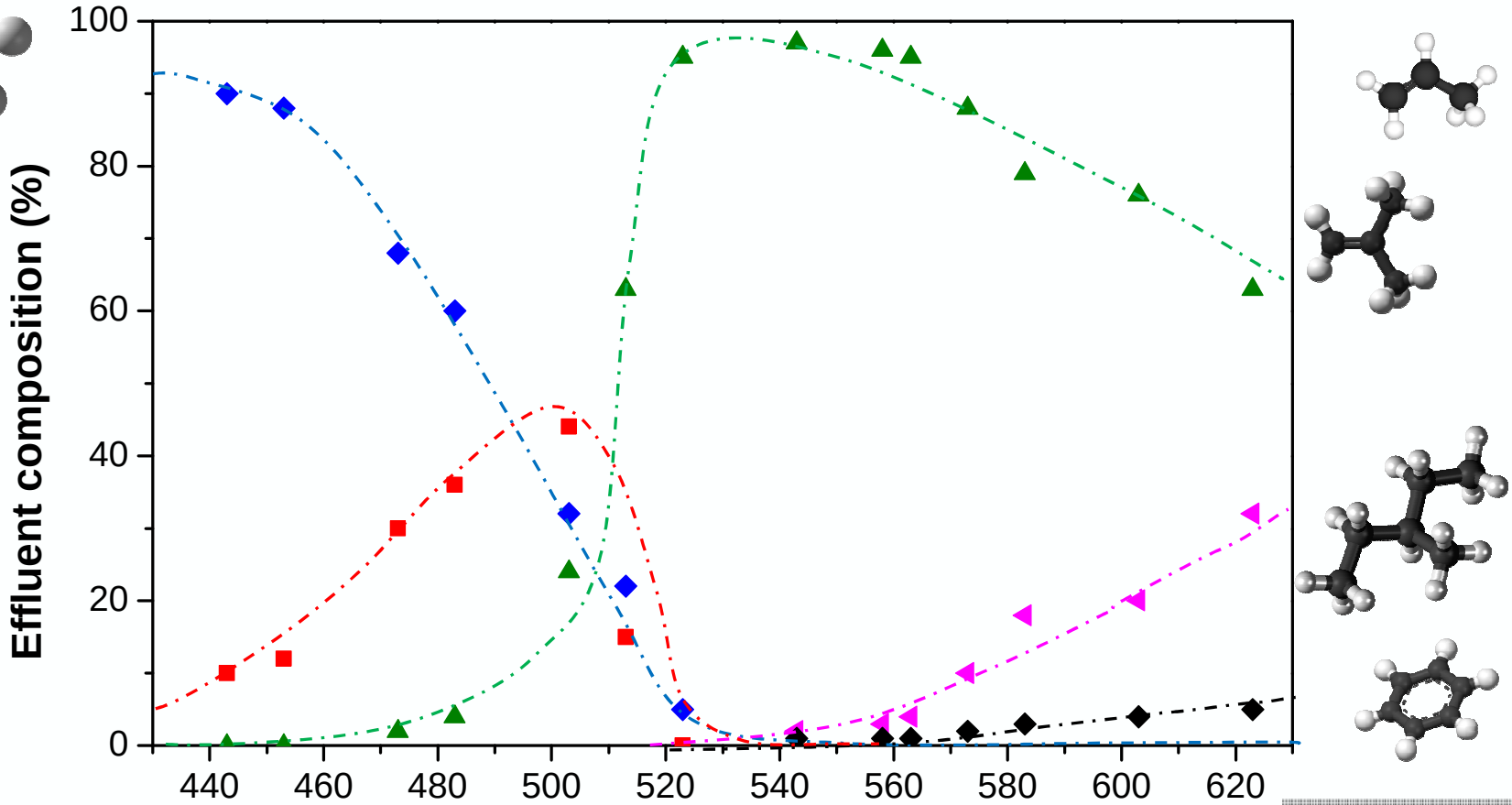


Ethanol

Ethylene

Light olefins





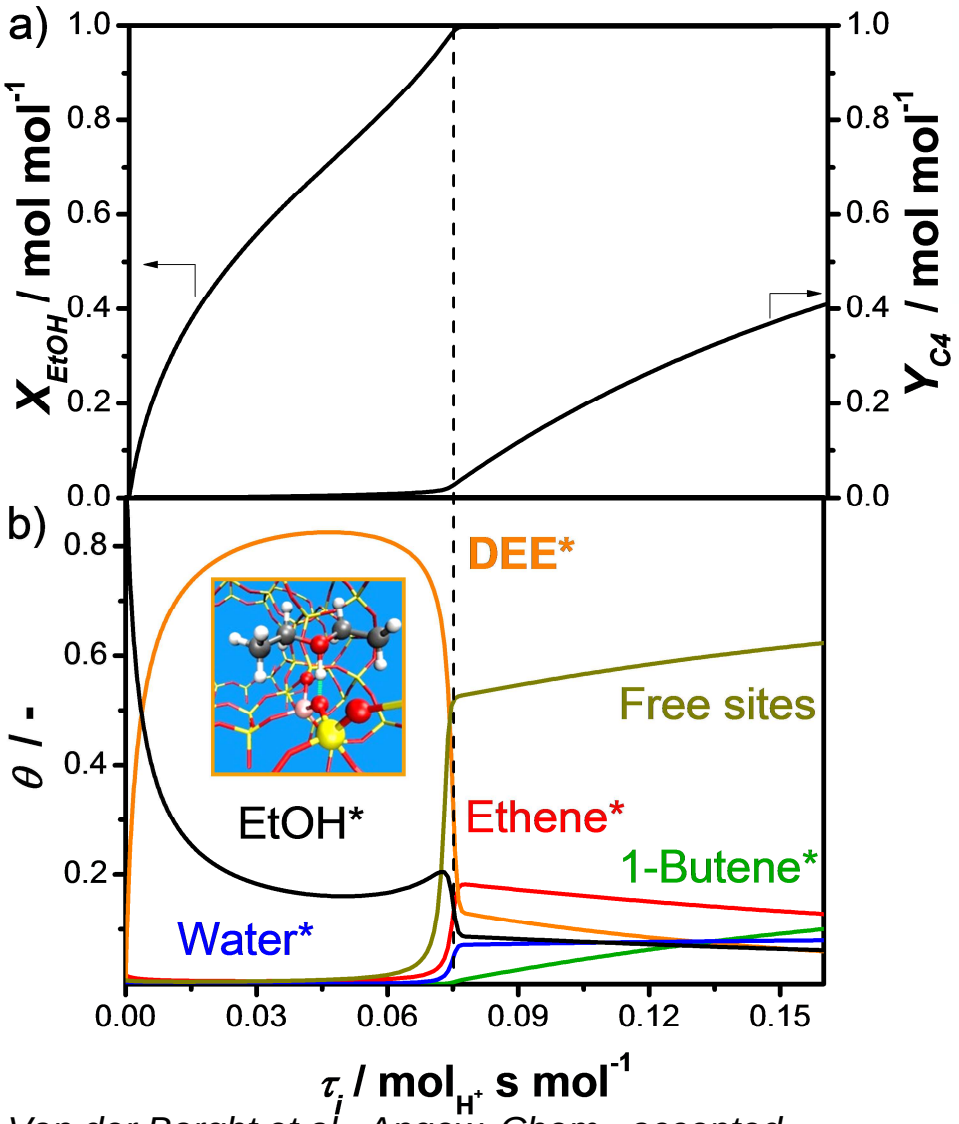
C_{5+} hydrocarbons

H-ZSM-5

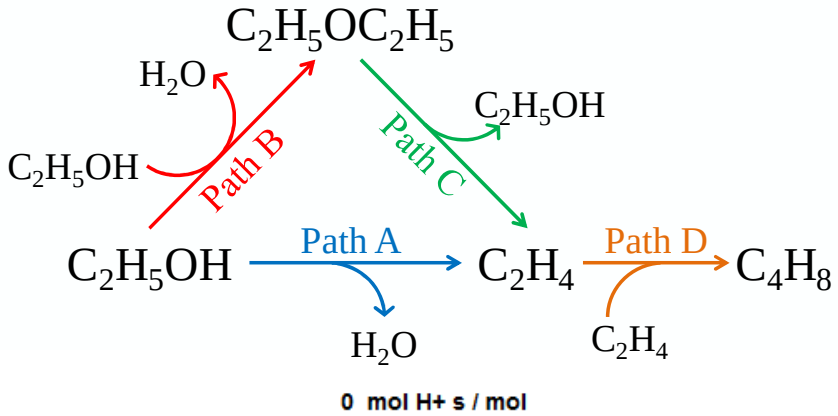
$p_{EtOH,0}$= 20 kPa : $W/F_{EtOH,0}$ = 8 kg s mol^{-1}

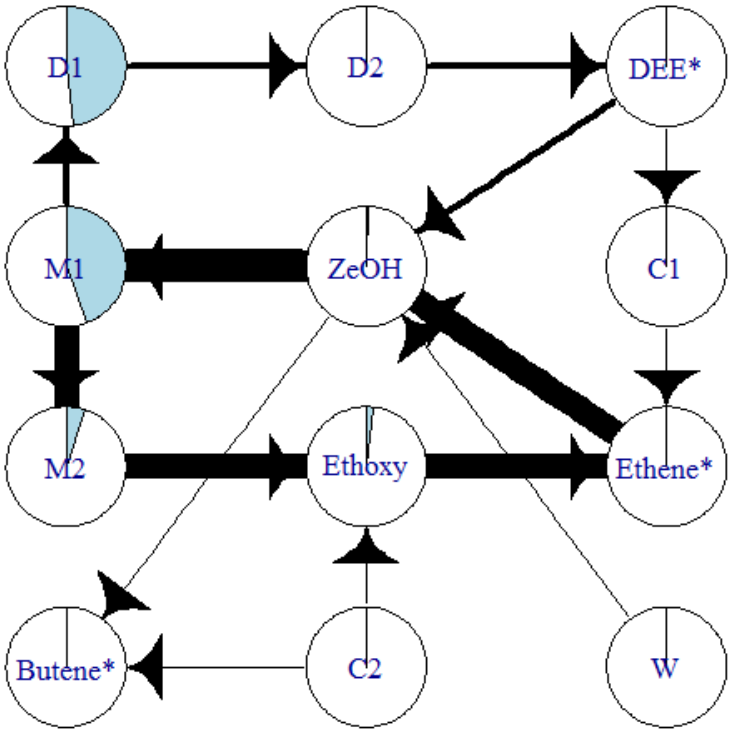
Ethanol conversion to higher HC

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



Van der Borght et al., Angew. Chem., accepted





Overview

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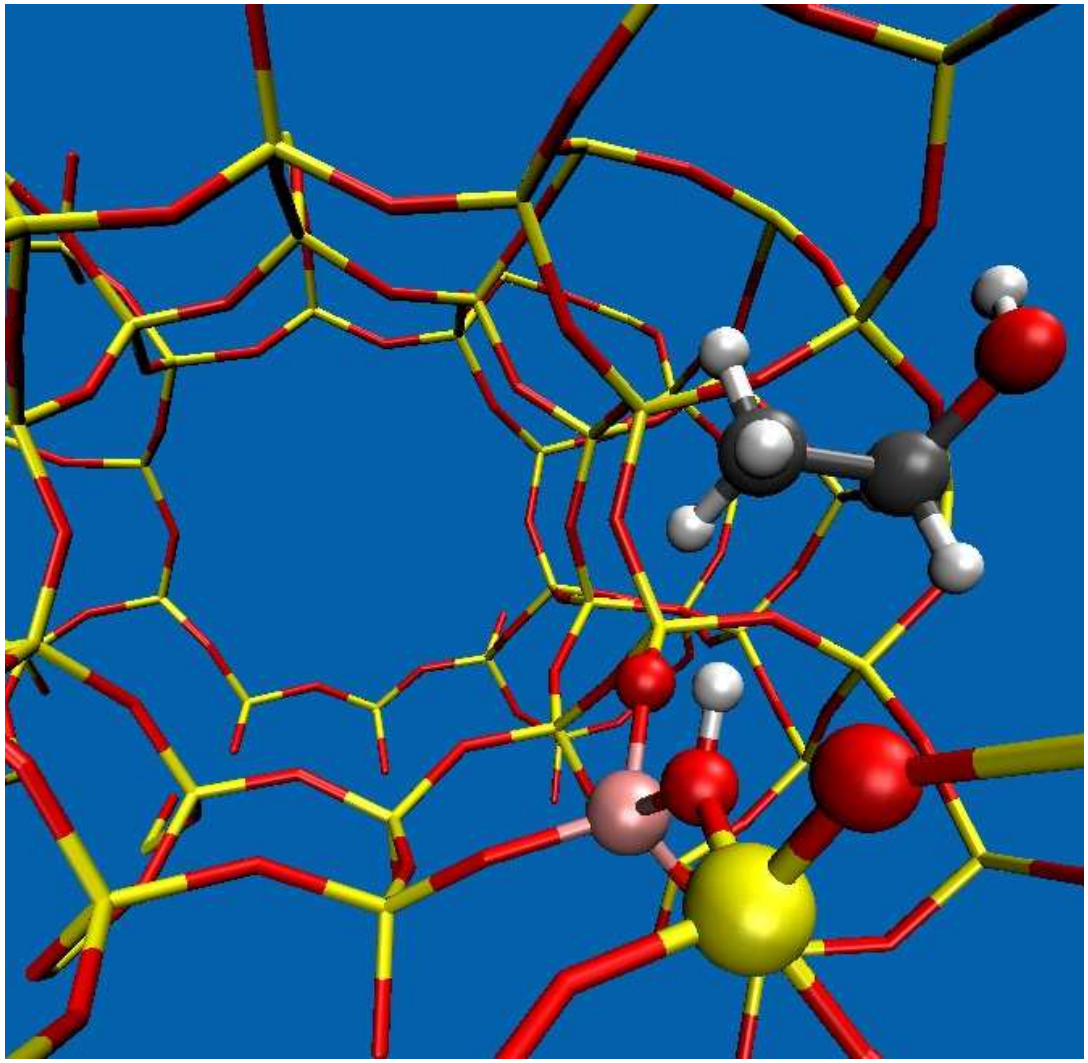
  - Industrial reactor scale
- Conclusions

Alcohol adsorption in zeolites

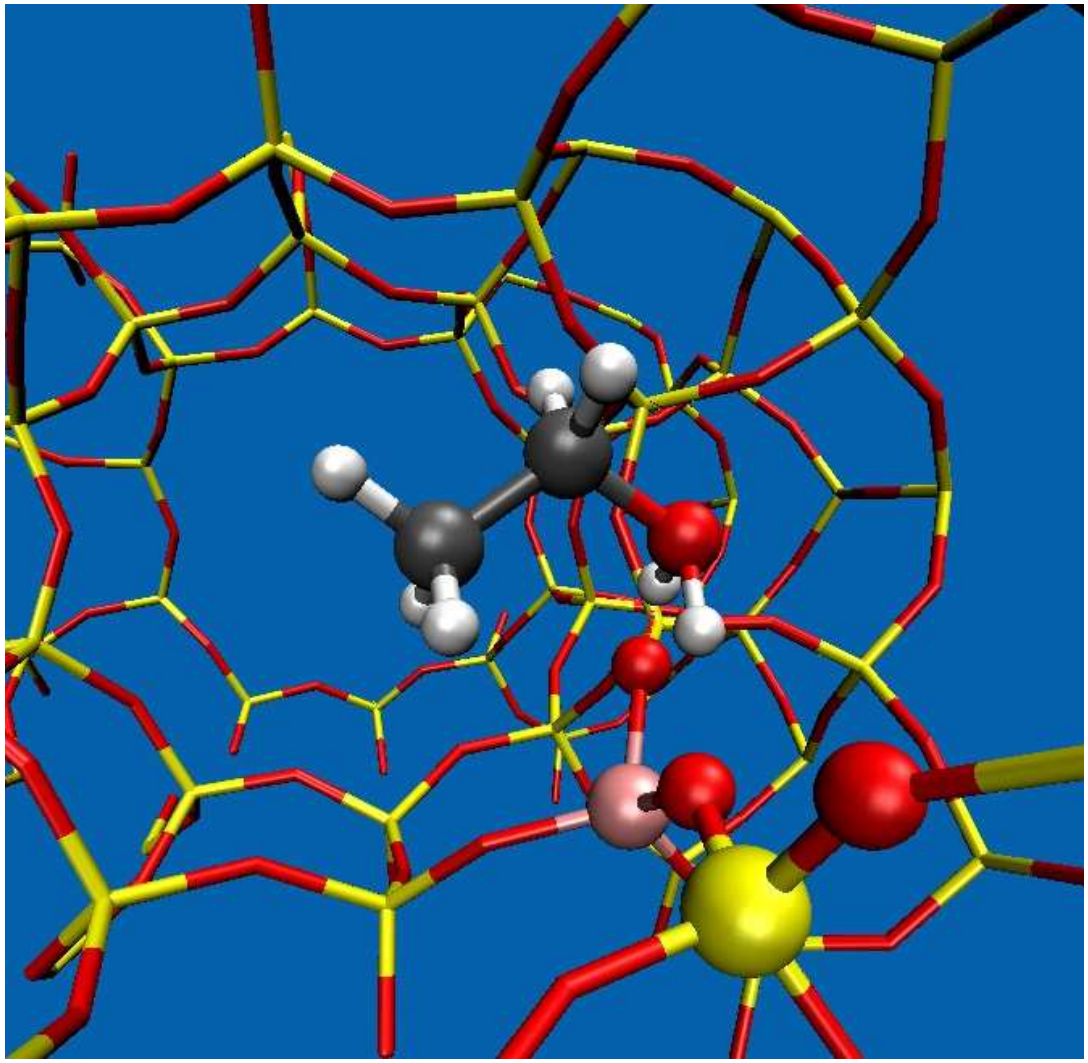
Ethanol physisorption in H-ZSM-5



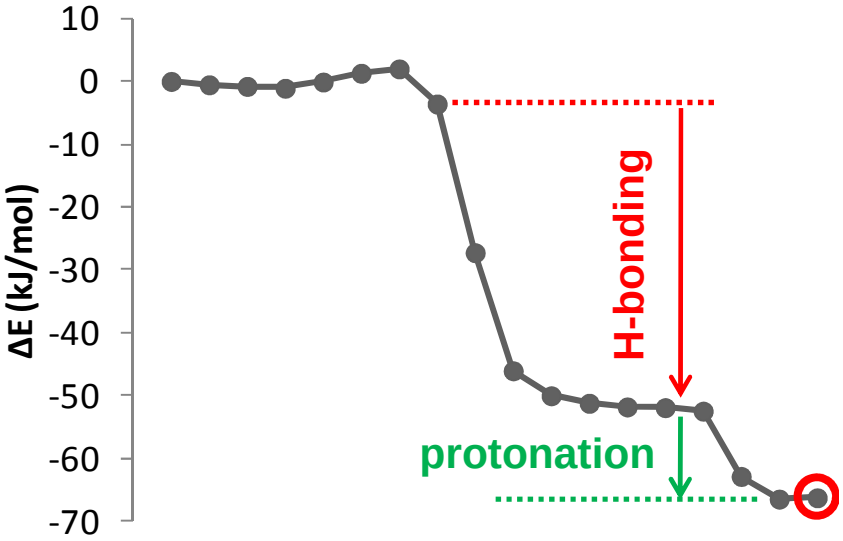
- van der Waals:
  - dipole-dipole
  - dipole-induced dipole
  - dispersive
- H-bonding
- electrostatic interactions

H-bonding and protonation: chemisorption

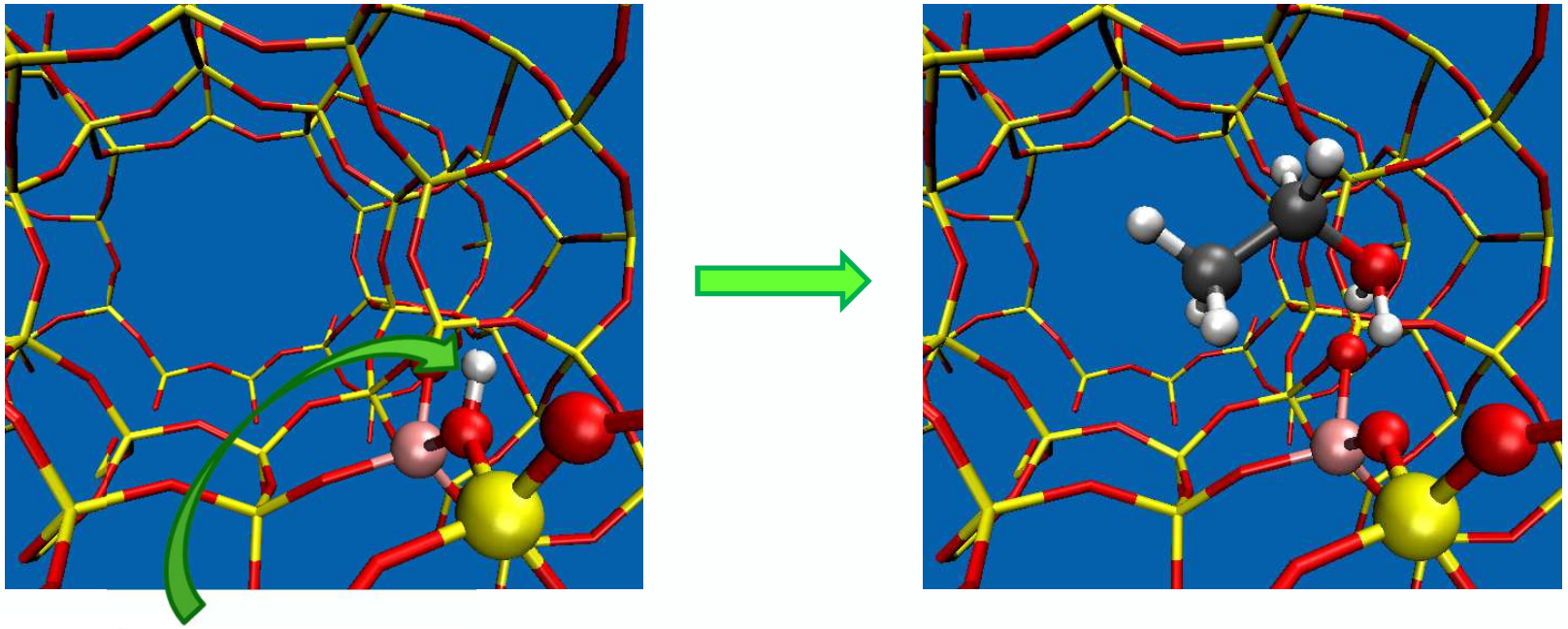
Ethanol adsorption and protonation in H-ZSM-5

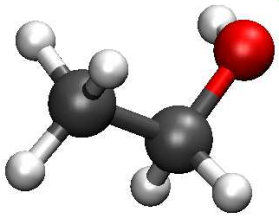


Nudged Elastic Band calculation with PBE-D2 functional



Alcohol adsorption & reaction in zeolites



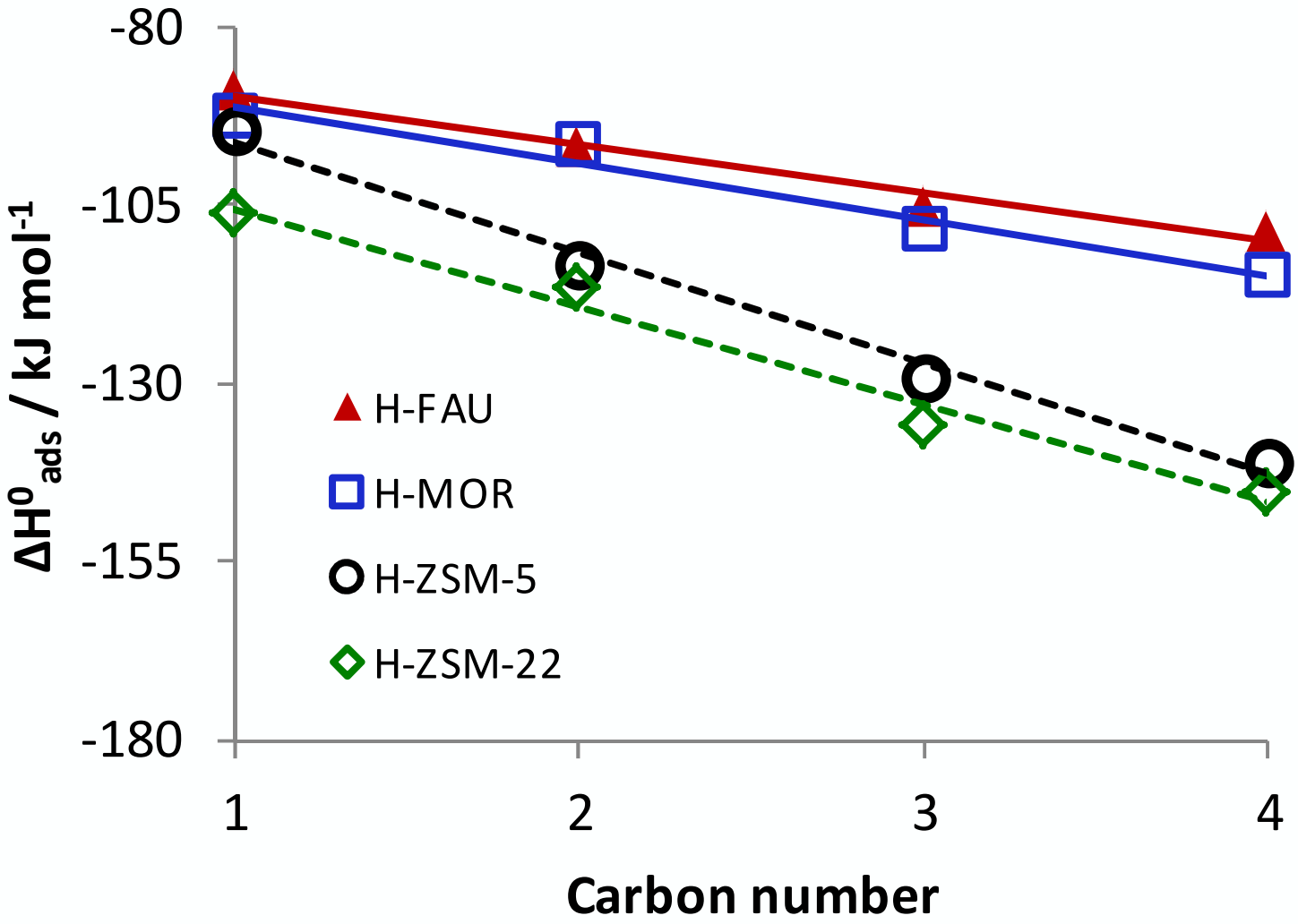


$$r = k\,\theta_{ads,alcohol} = k\,K_{ads}\,p_{alcohol}$$

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

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

Chemisorption: effect of chain length



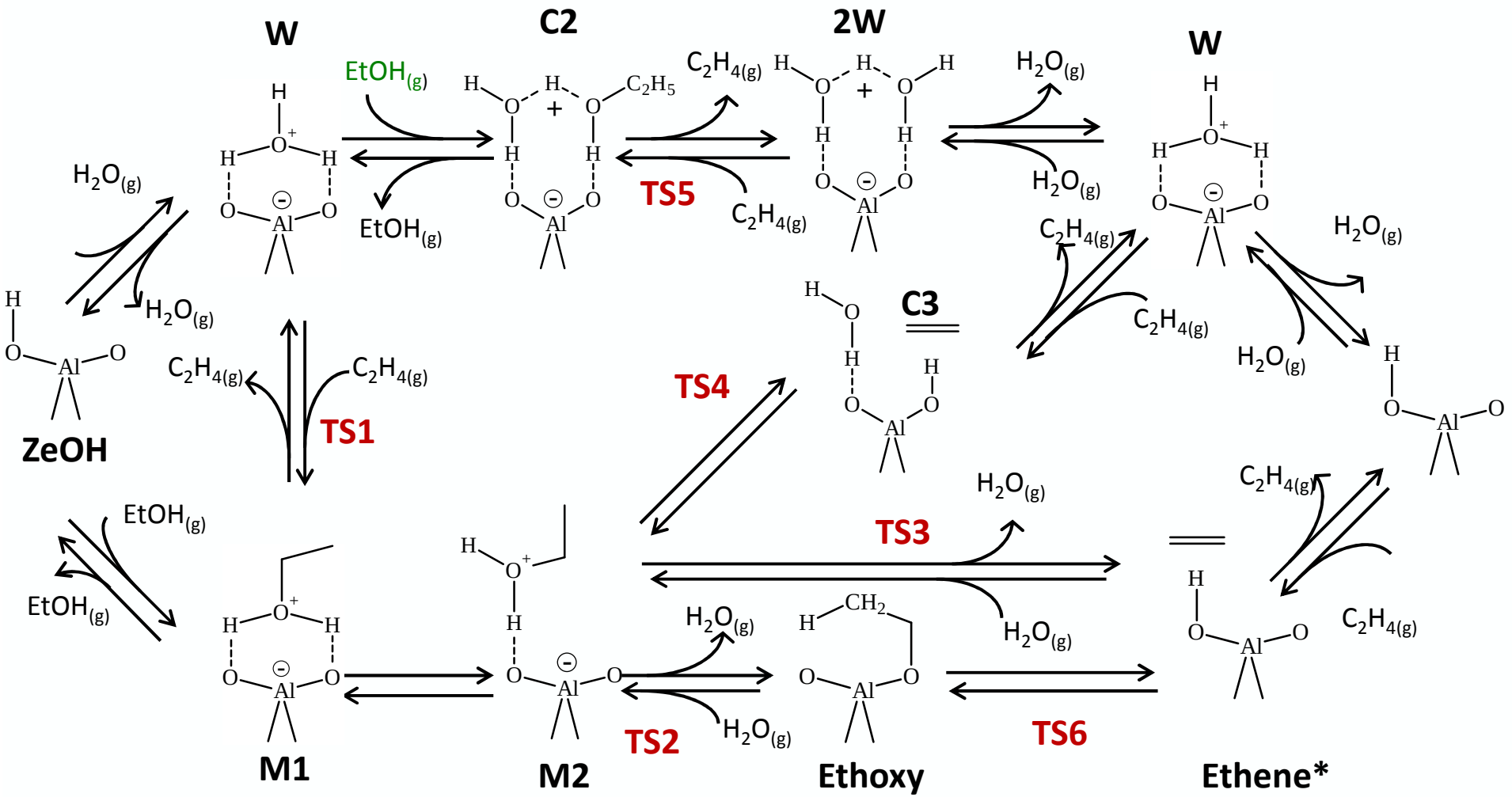
Nguyen et al., J. Catal. (2015) 322,91-103

Overview

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

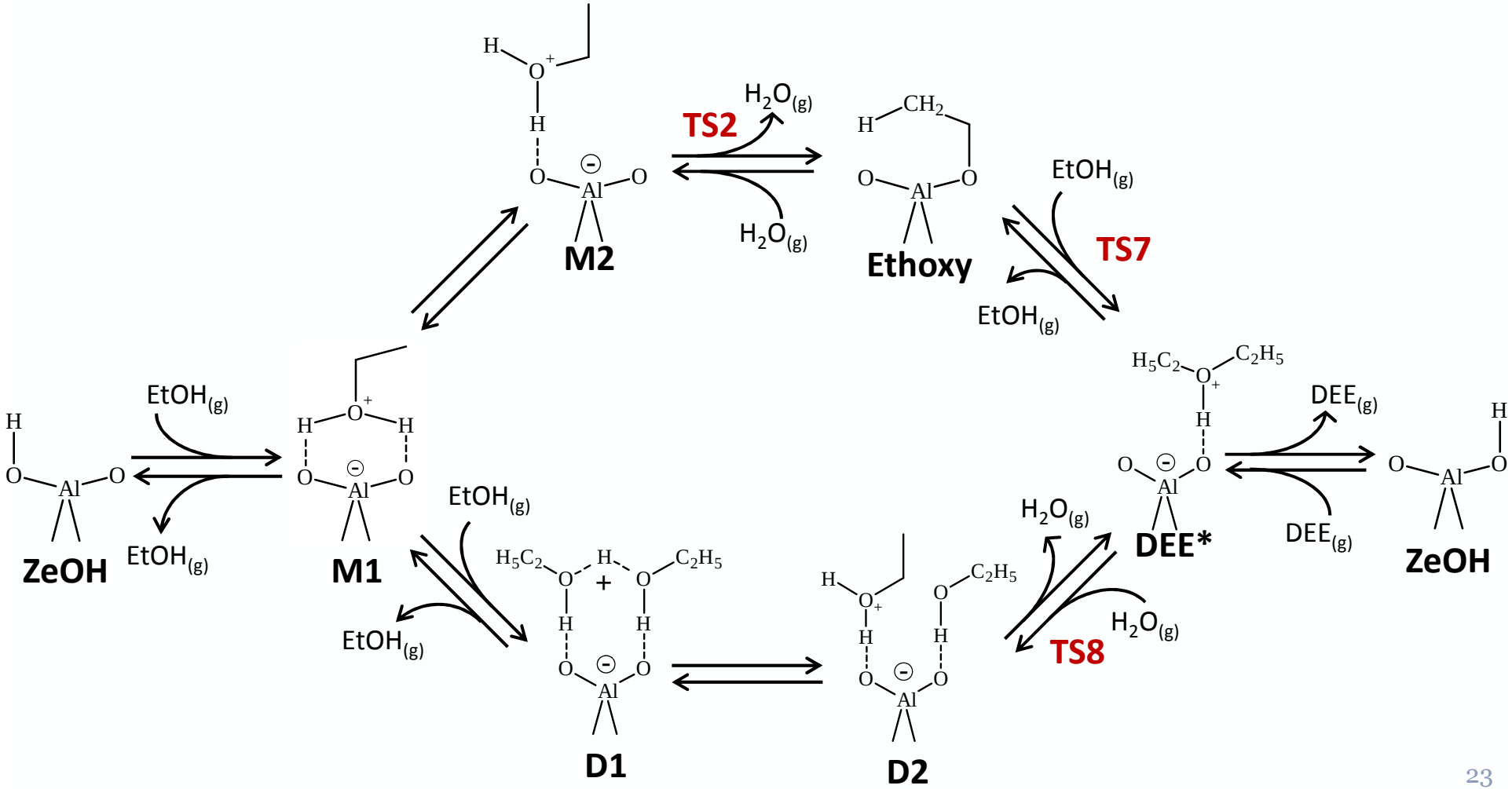
Ethanol to Ethene: H-ZSM-5

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

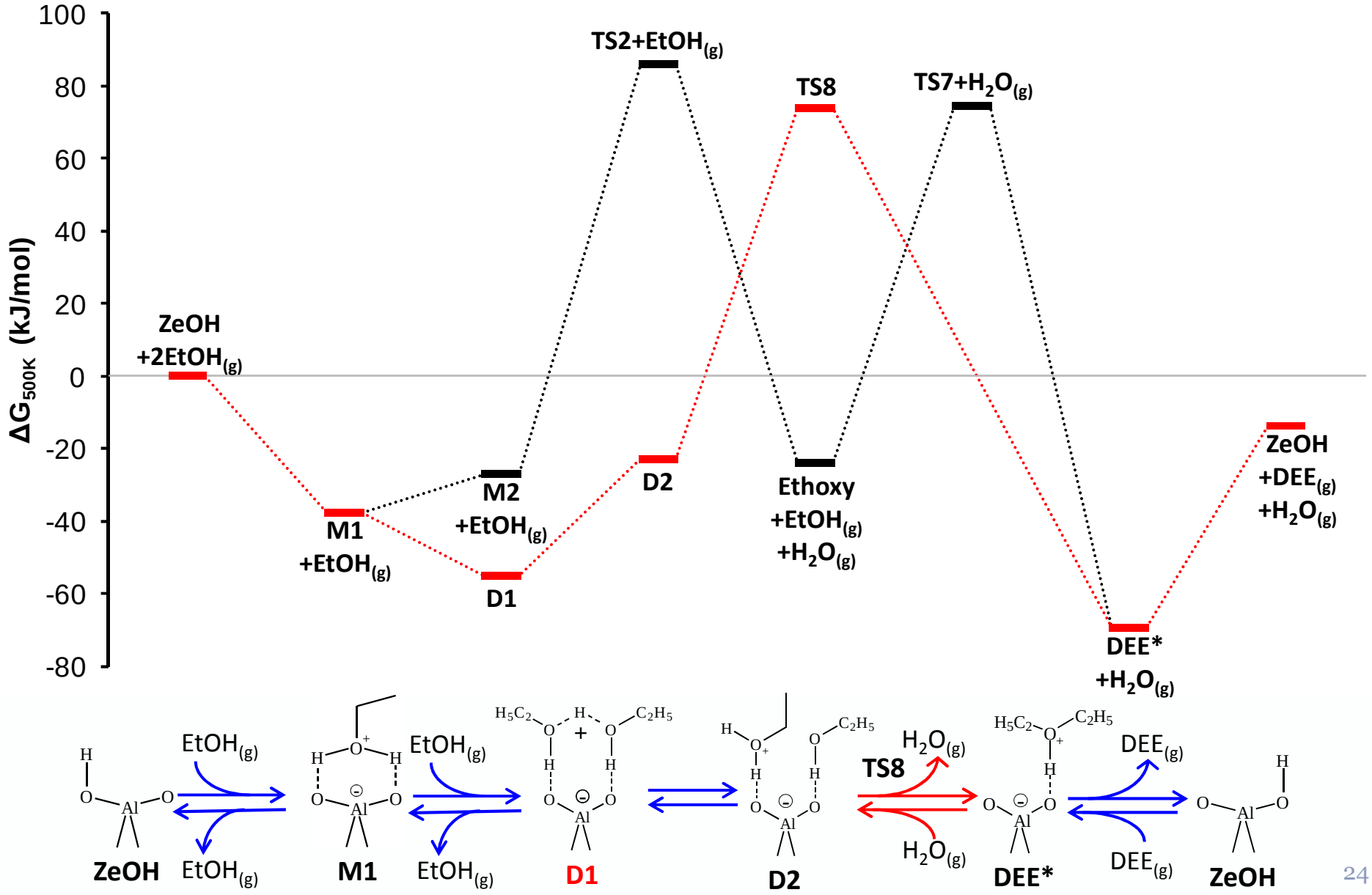


Ethanol to Diethyl ether: H-ZSM-5

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

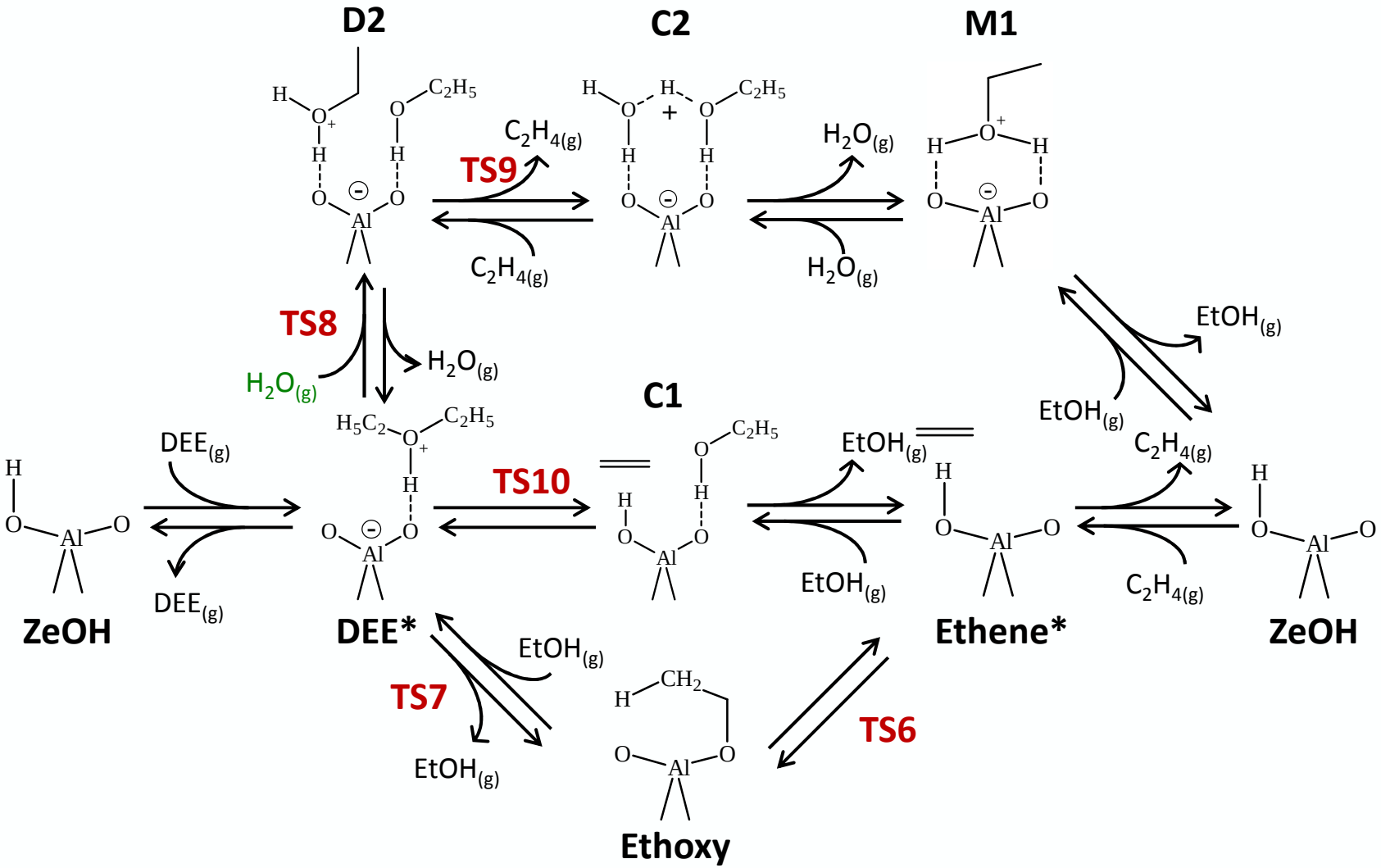


Ethanol to Diethyl ether: H-ZSM-5



Diethyl ether to Ethene:H-ZSM-5

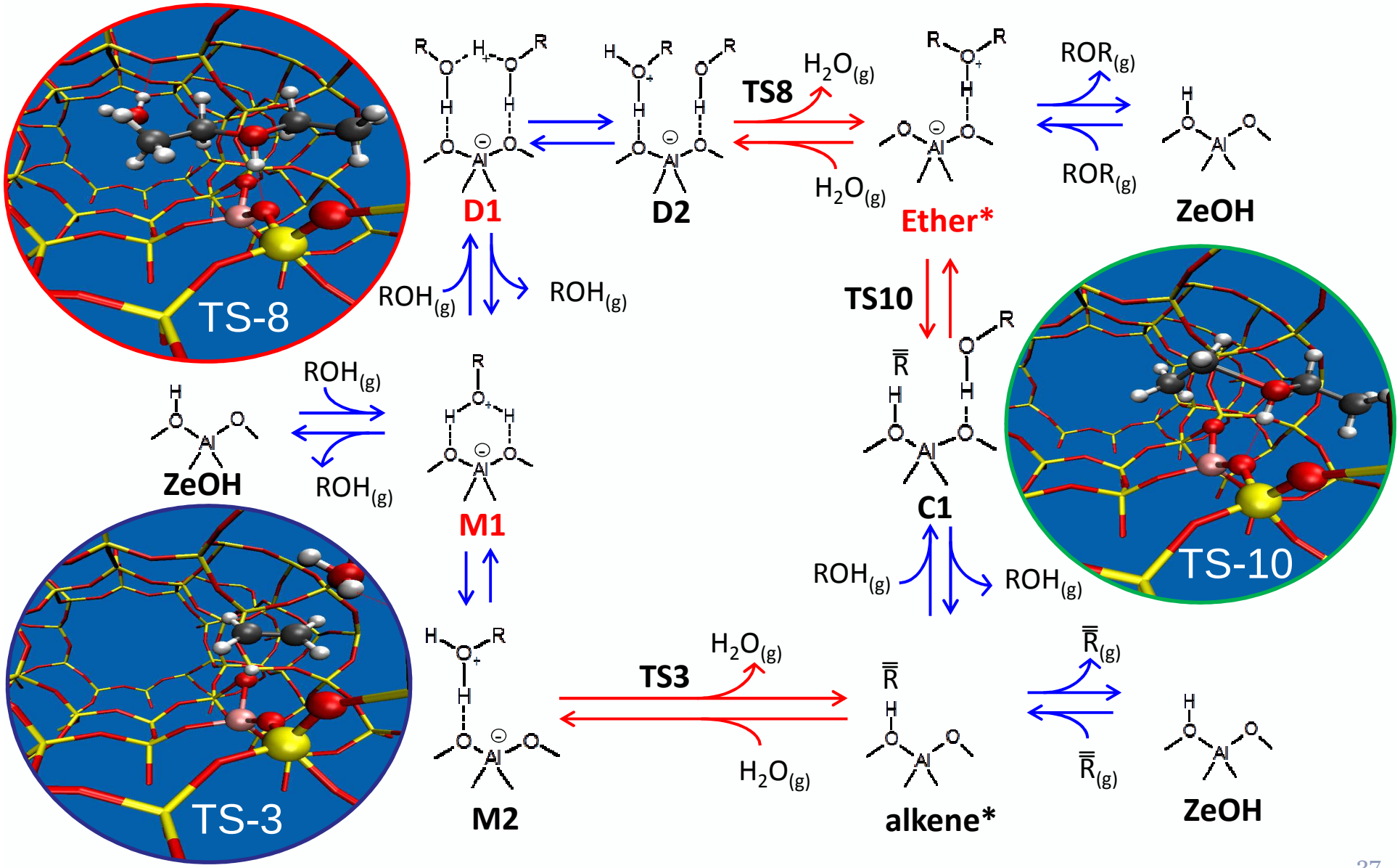
C: $DEE_{(g)} \rightarrow EtOH_{(g)} + C_2H_{4(g)}$



Overview

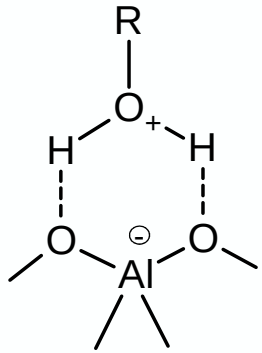
- Introduction
- Dehydration of bioalcohols on zeolites
  - First principles kinetic model development
    - ➢ Butanol dehydration: idem

Dehydration : dominant mechanisms

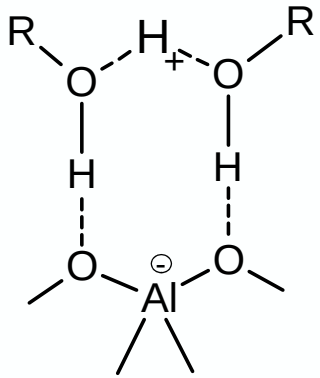


M. John et al., J. Catal. 330 (2015) 28

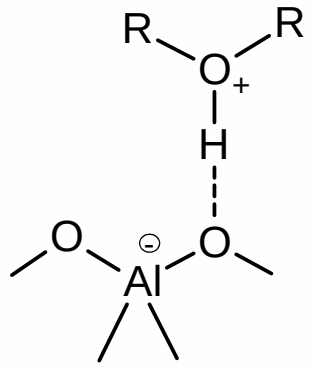
Dehydration: MARI's



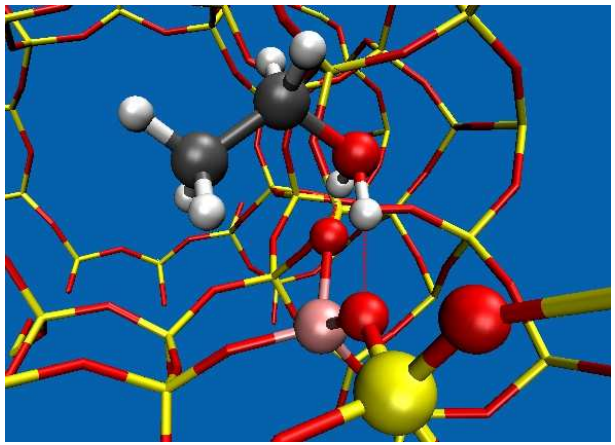
Monomer M1

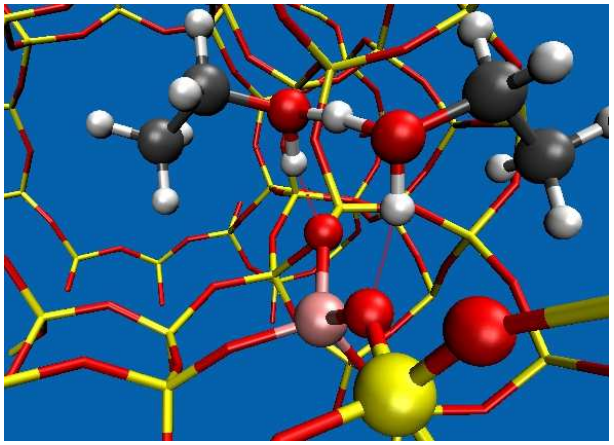


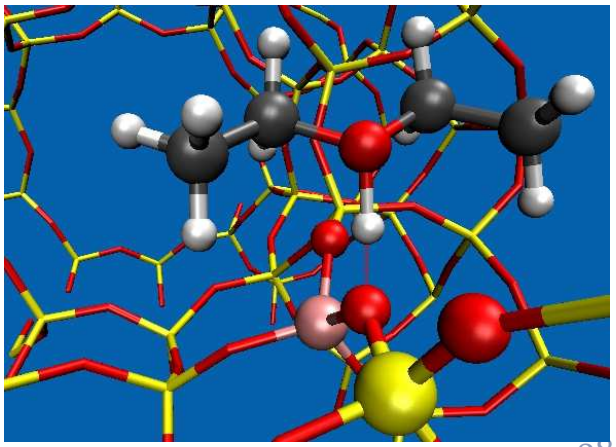
Dimer D1



Adsorbed ether DRE*



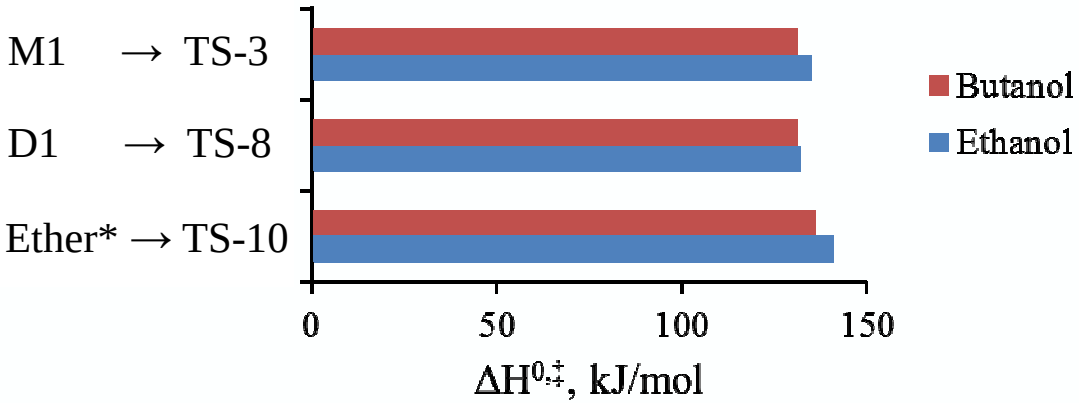




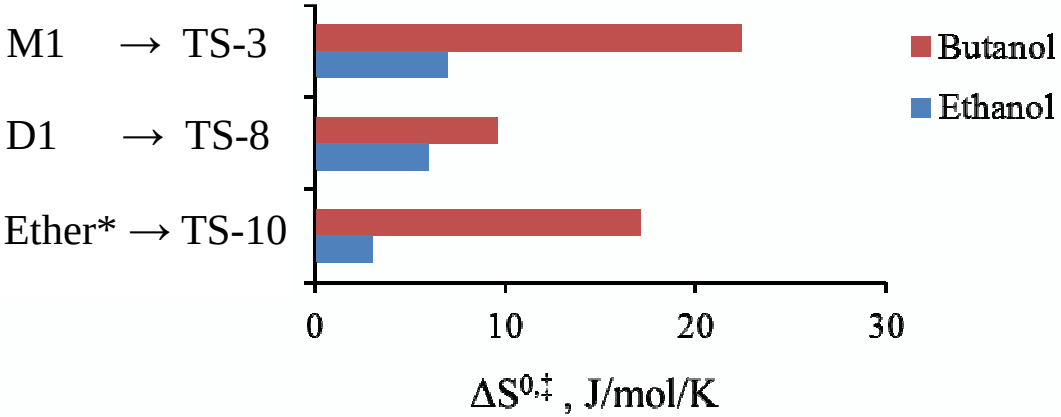
MARI's and Rate-Determining Steps

		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	$DBE_{(g)} \leftrightarrow Butene_{(g)} + BuOH_{(g)}$			

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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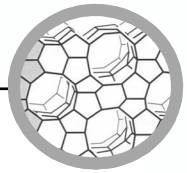
Experimental procedures and conditions

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:

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

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

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

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

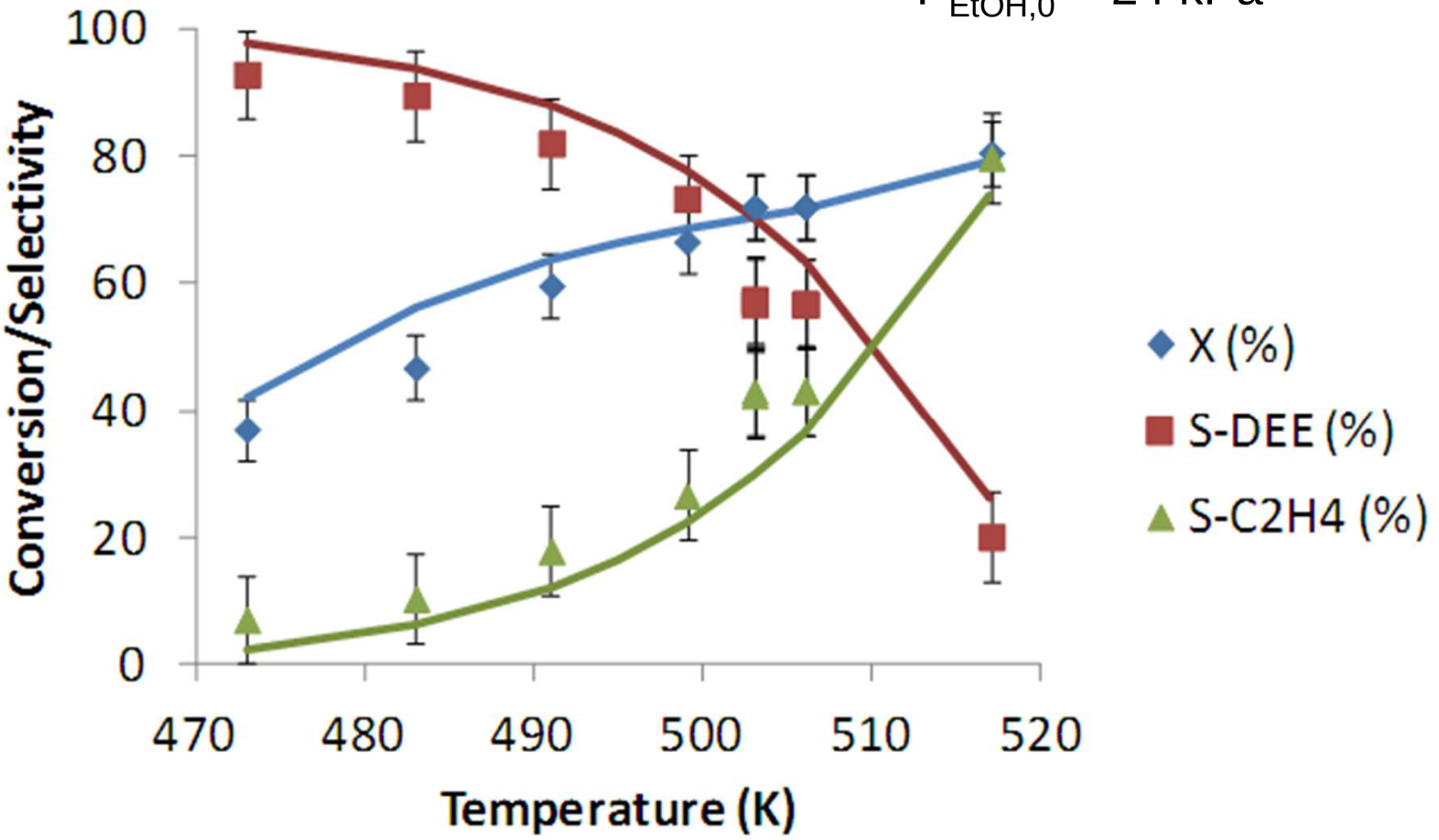
$F_i = F_{i,0}$ at $W = 0$

- 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*
- ν_{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

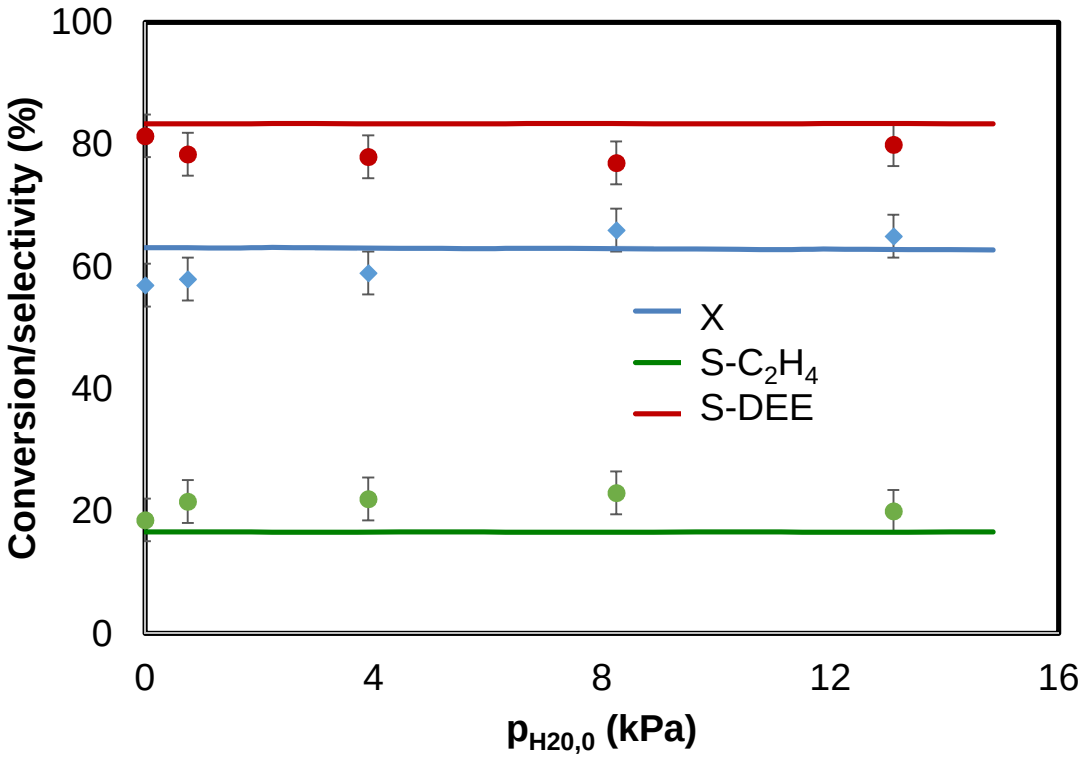


Effect of water

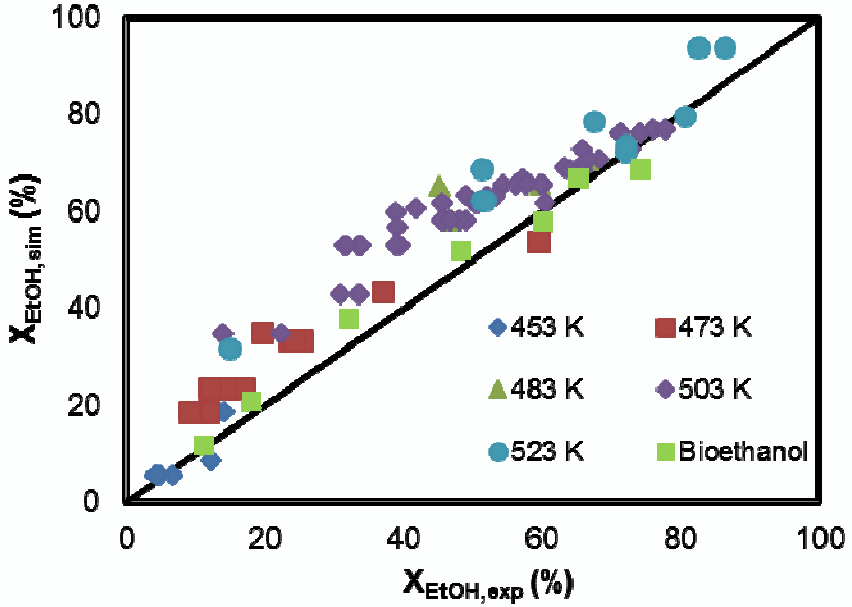
$W_{cat}/F_{EtOH,0}$ = 8.3 kg s / mol

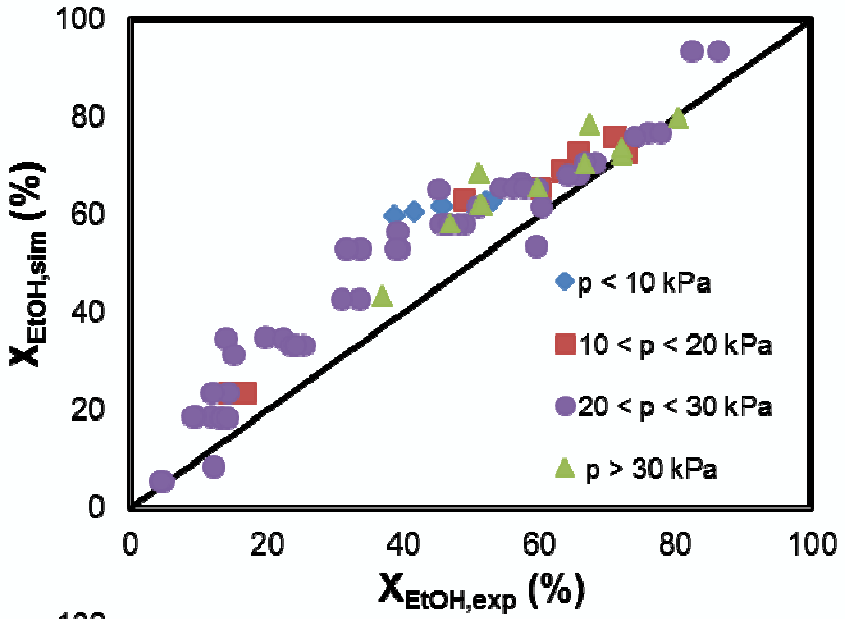
$P_{EtOH,0}$ = 29 kPa

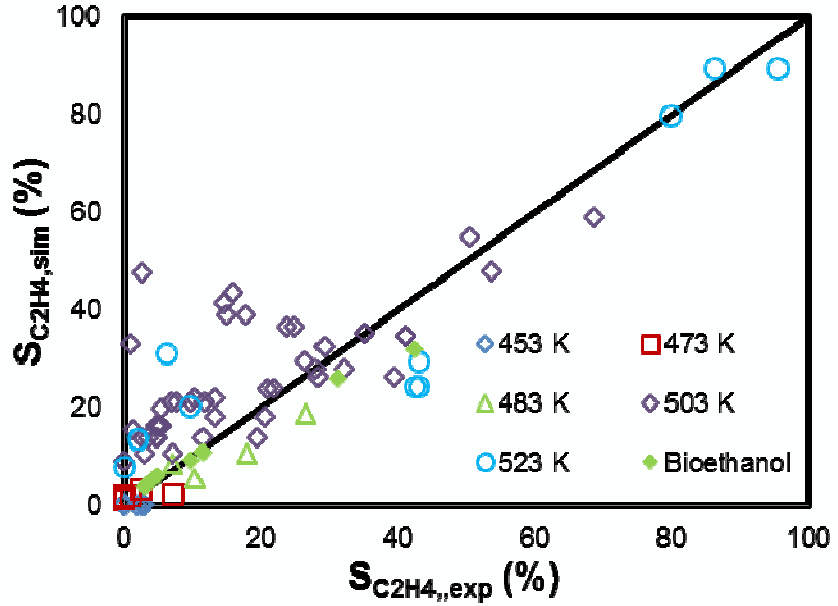
T = 503 K

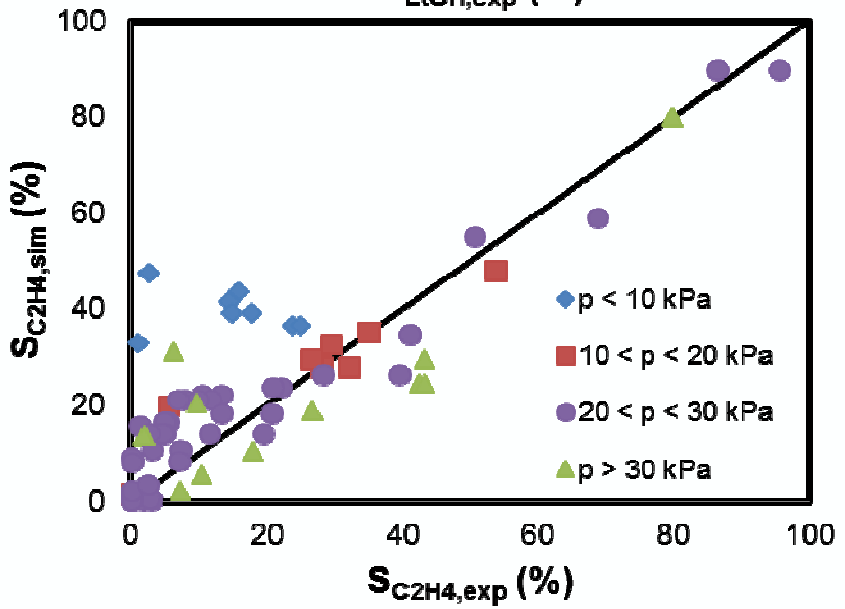


Parity diagrams









Overview

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  - Reaction-path analysis
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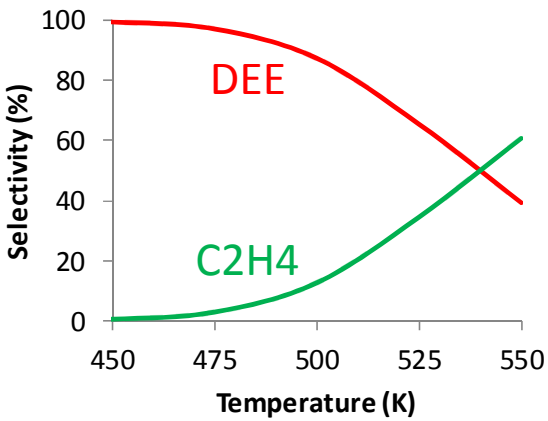
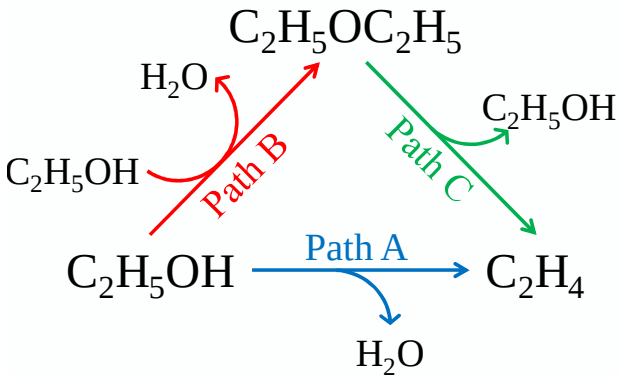
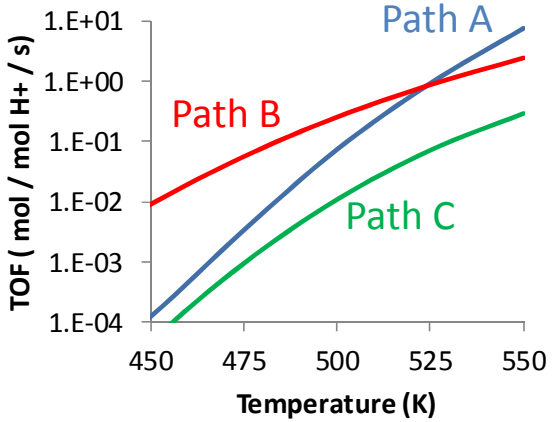
- Conclusions

Reaction path analysis: effect of T



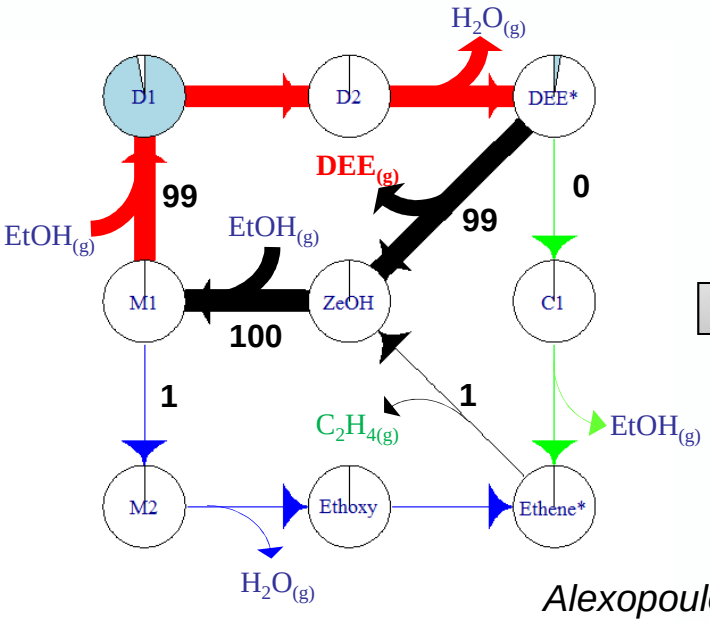


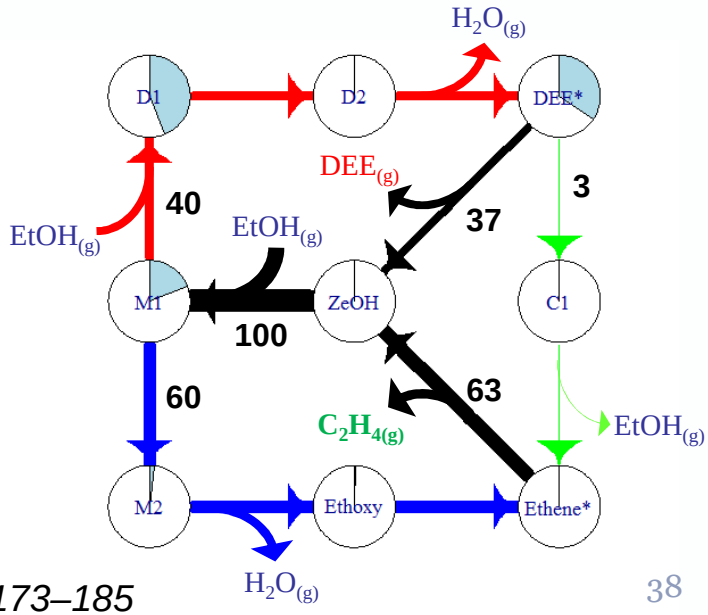


450 K

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

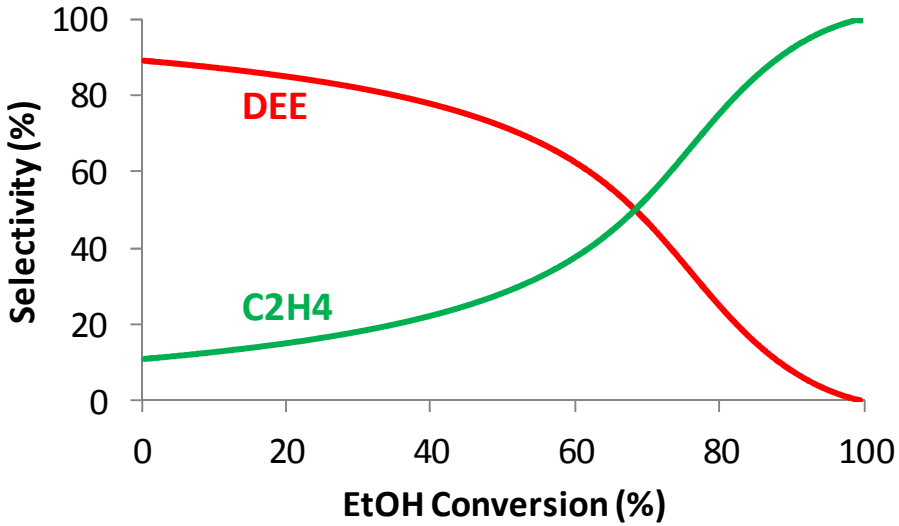
550 K

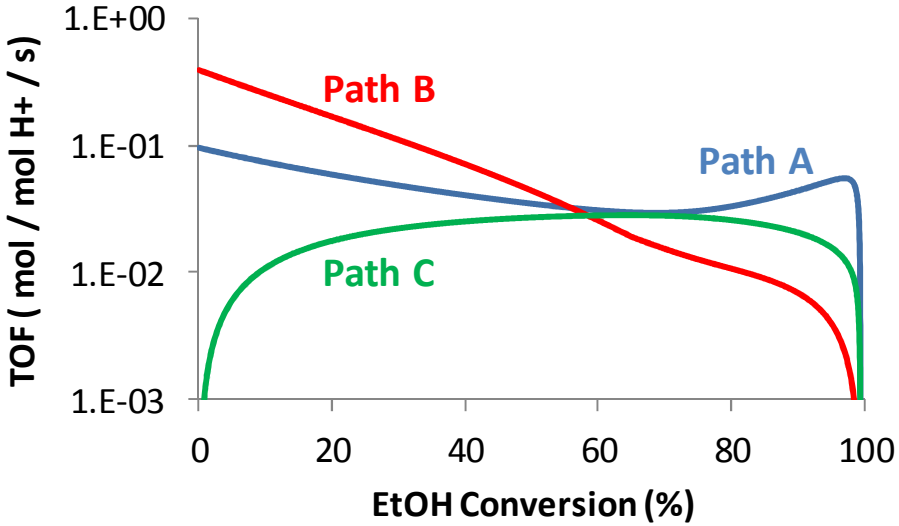


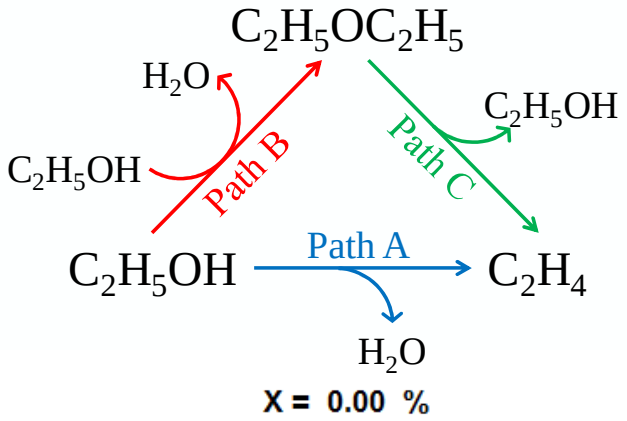


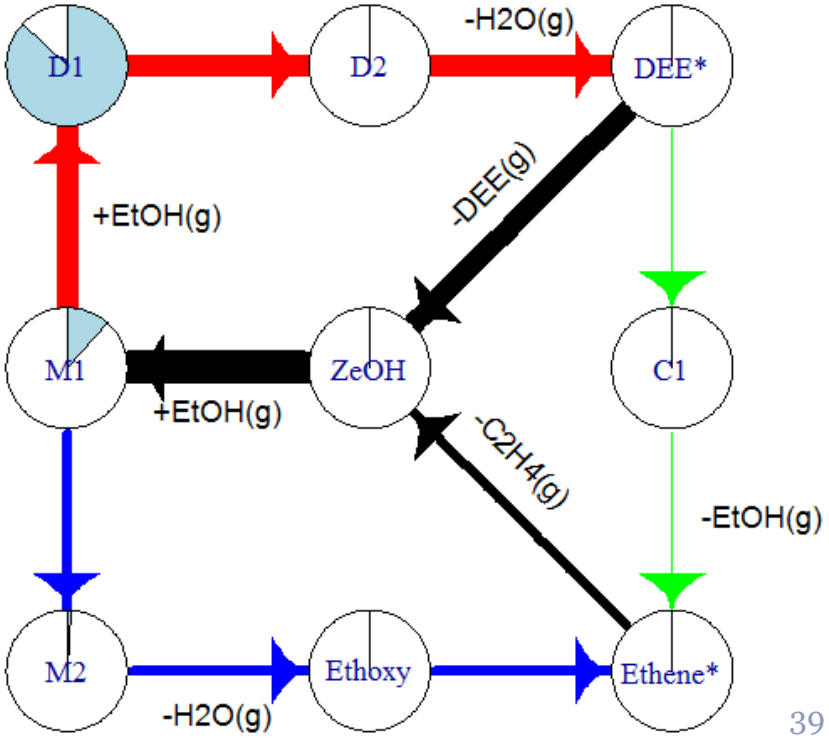
Alexopoulos et al., J Catal. (2016),339, 173–185

Reaction path analysis: effect of conversion





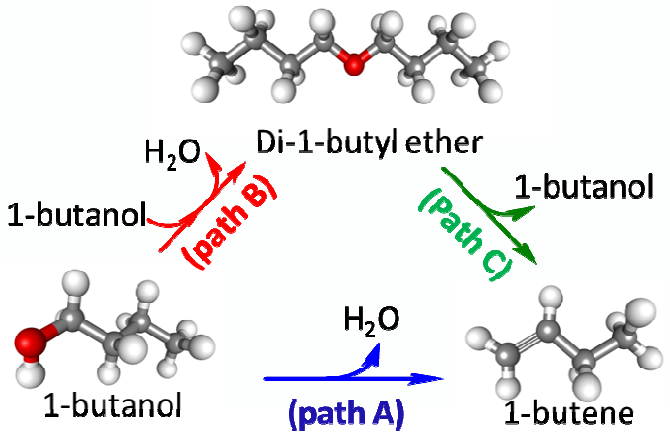


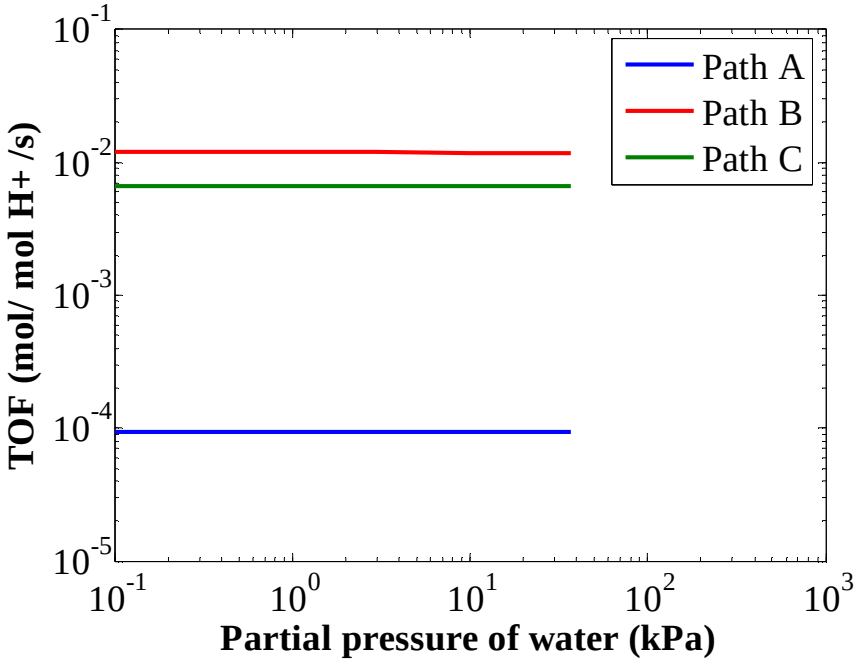


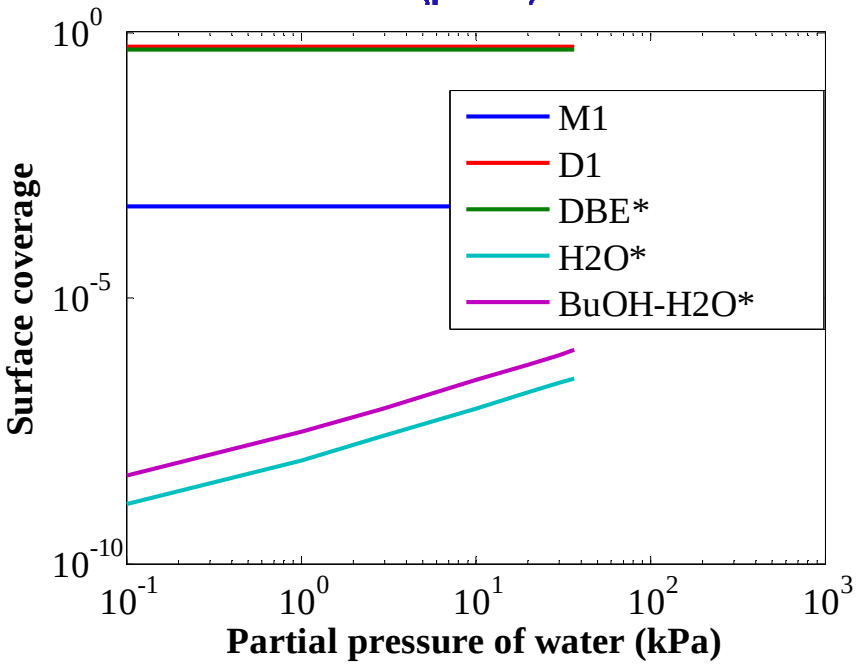
H-ZSM-5, $p_{EtOH,0}$ = 10kPa, T = 500 K

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%



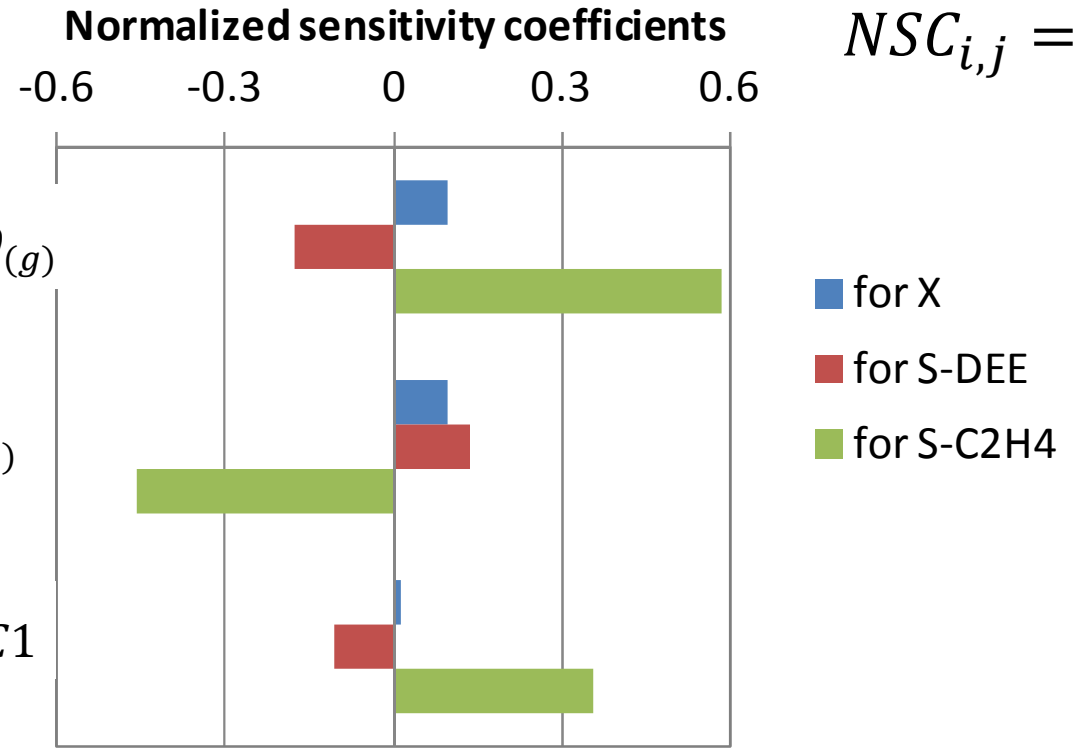




Sensitivity analysis for catalyst design

H-ZSM-5; T= 517 K; $p_{EtOH,0}$ = 24 kPa
$W_{cat}/F_{EtOH,0}$ = 6.5 kg s / mol

$$NSC_{i,j} = \frac{A_i dR_j}{R_j dA_i}$$



A: $M2 \overset{TS2}{\longleftrightarrow} Ethoxy + H_2O_{(g)}$

B: $D2 \overset{TS8}{\longleftrightarrow} DEE* + H_2O_{(g)}$

C: $DEE* \overset{TS10}{\longleftrightarrow} C1$

IF 

maximum selectivity for C_2H_4 at given conversion (60%)

C: $DEE* \overset{TS10}{\longleftrightarrow} C1$

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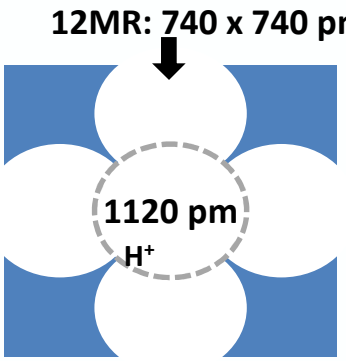
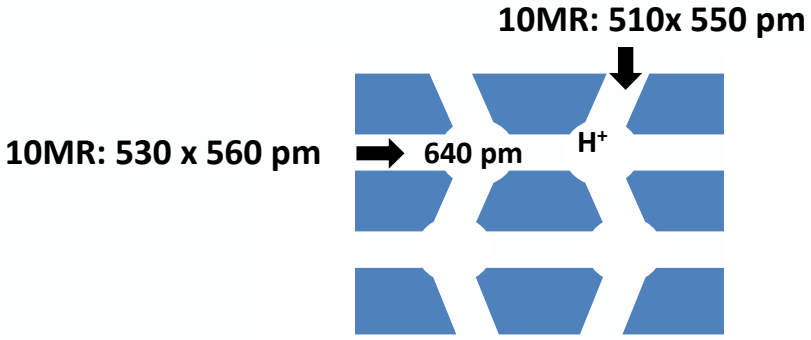
Zeolite Frameworks

3D zeolites

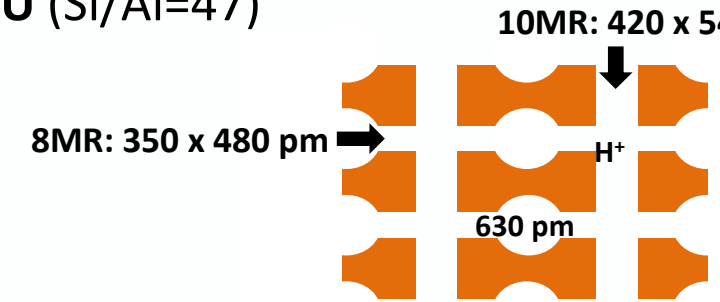


H-FAU (Si/Al=47)



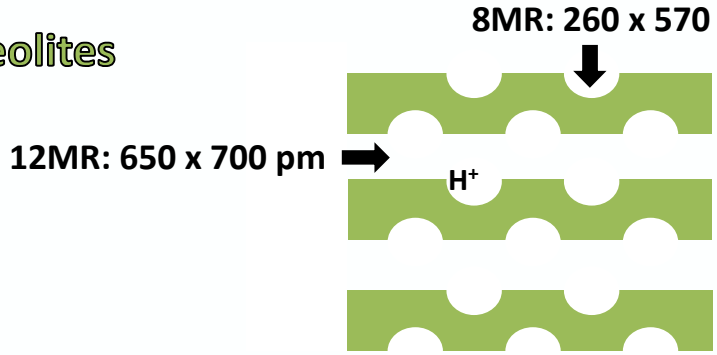
H-ZSM-5 (Si/Al=95)

2D zeolite

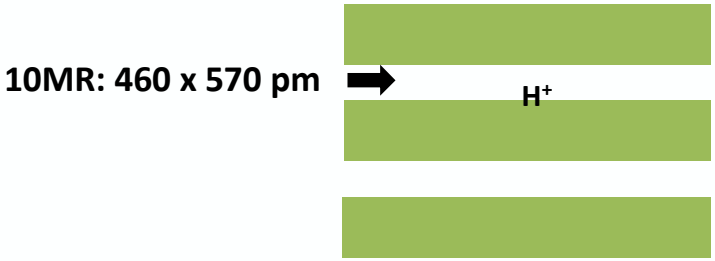


H-FER (Si/Al=71)

1D zeolites

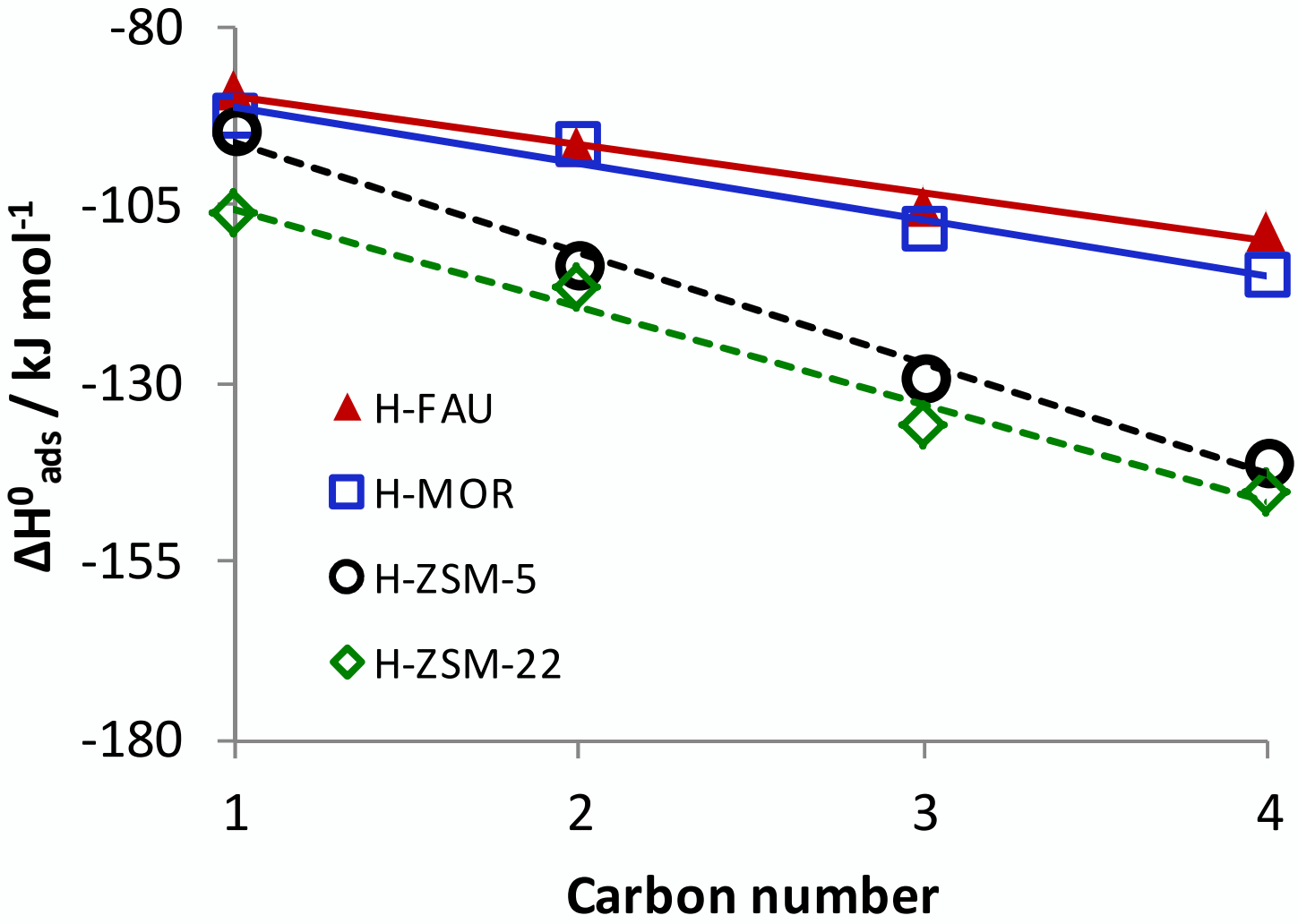


H-MOR (Si/Al=95)



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

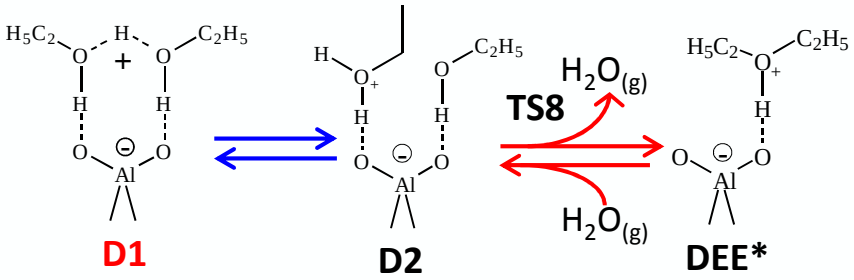
Chemisorption



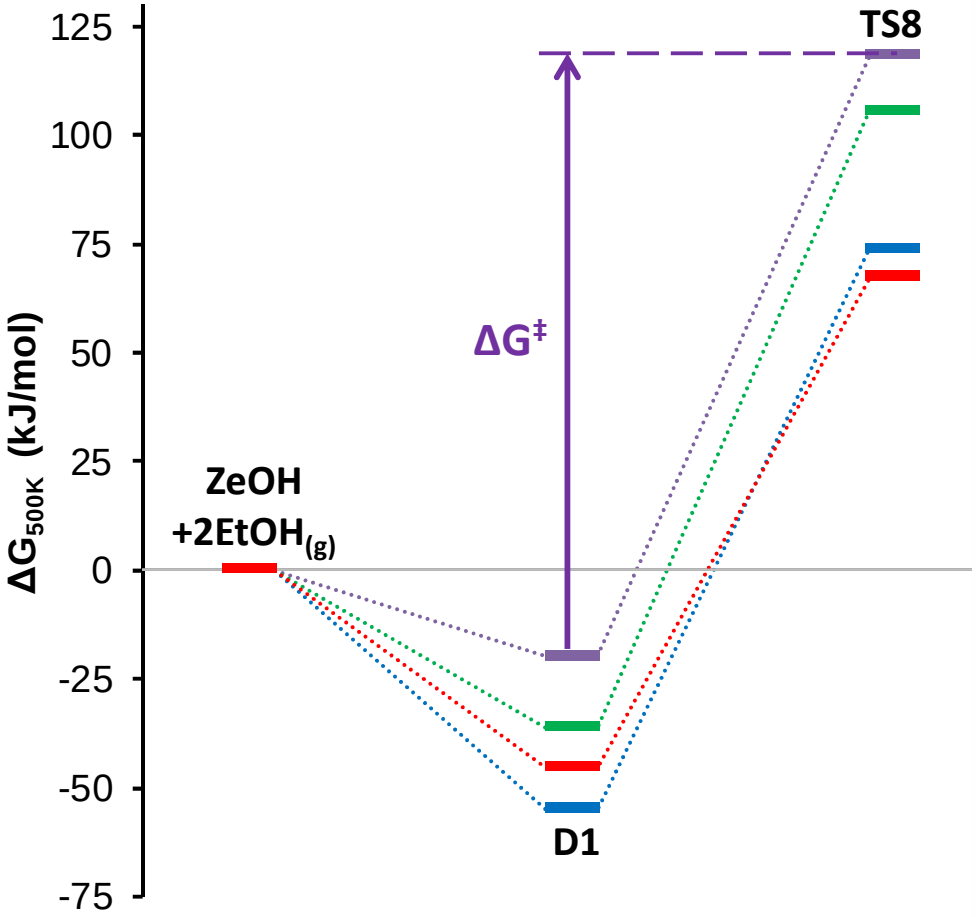
Nguyen et al., J. Catal. (2015) 322,91-103

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

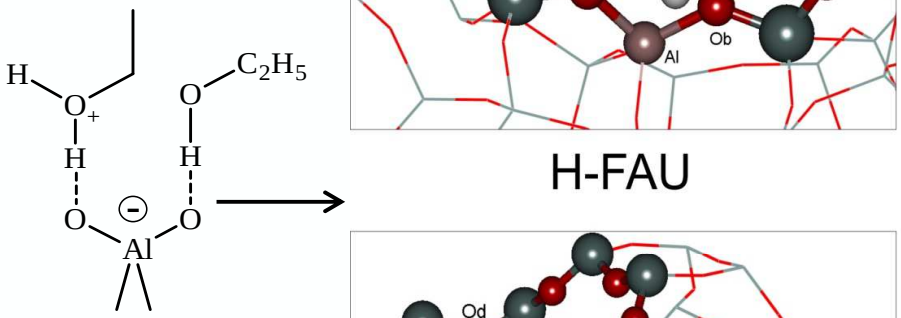


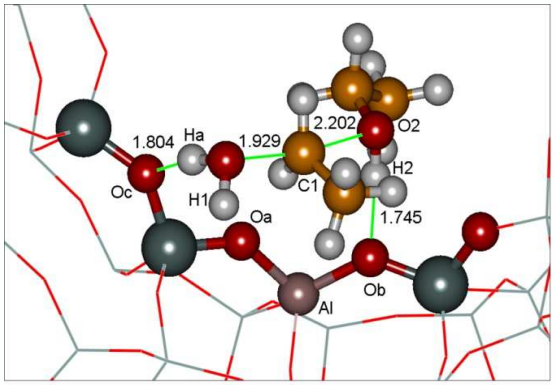
10-MR zeolites more active than 12-MR zeolites



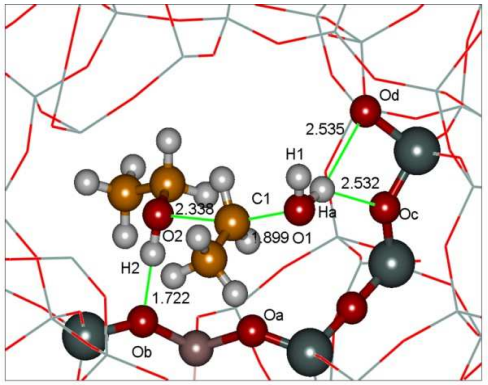
TS stabilization: vdW & hydrogen bonds

TS-8

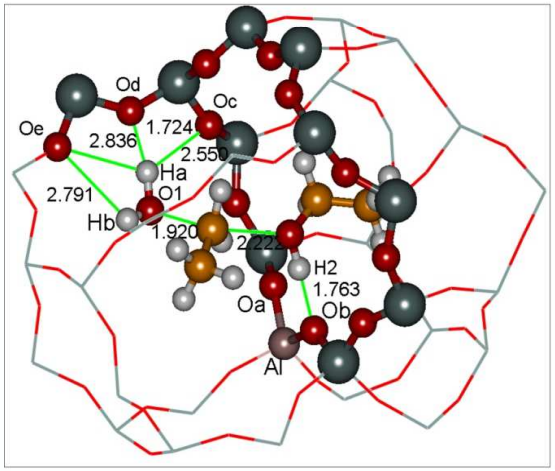




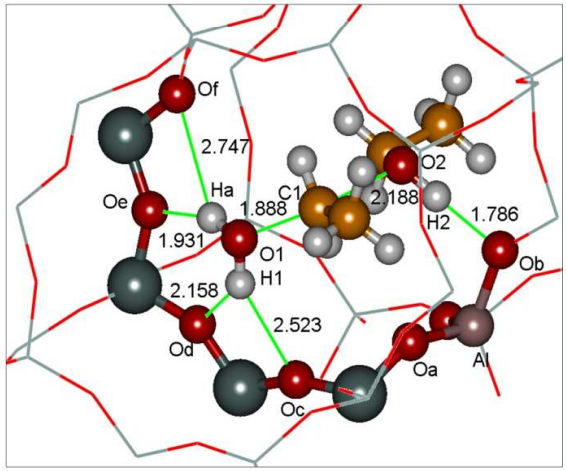
H-FAU



H-MOR (12-MR)

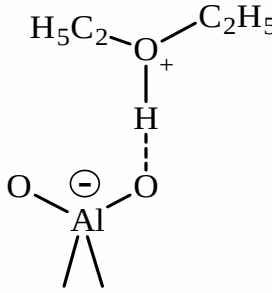


H-ZSM-5



H-ZSM-22

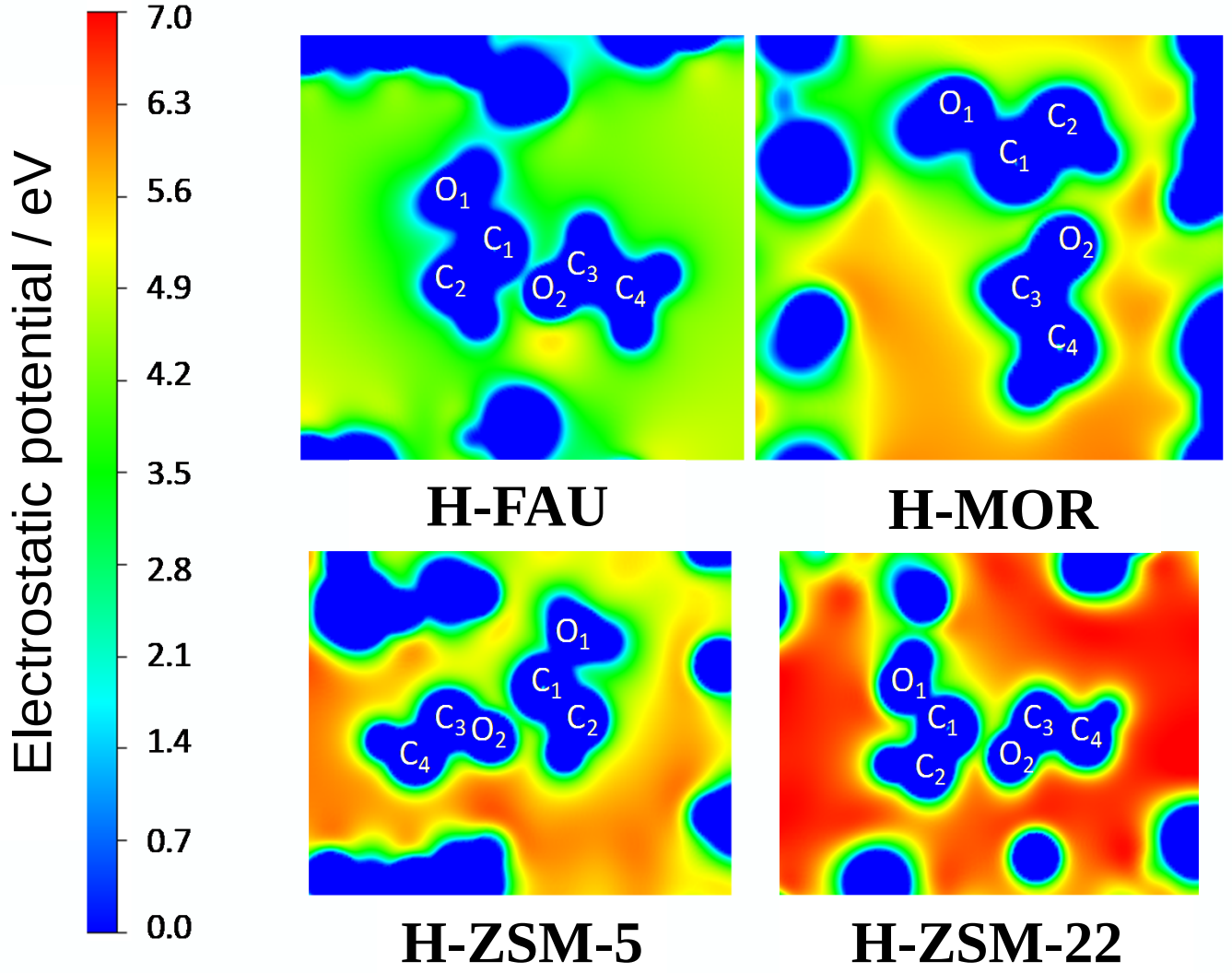
$H_2O_{(g)}$



DEE*

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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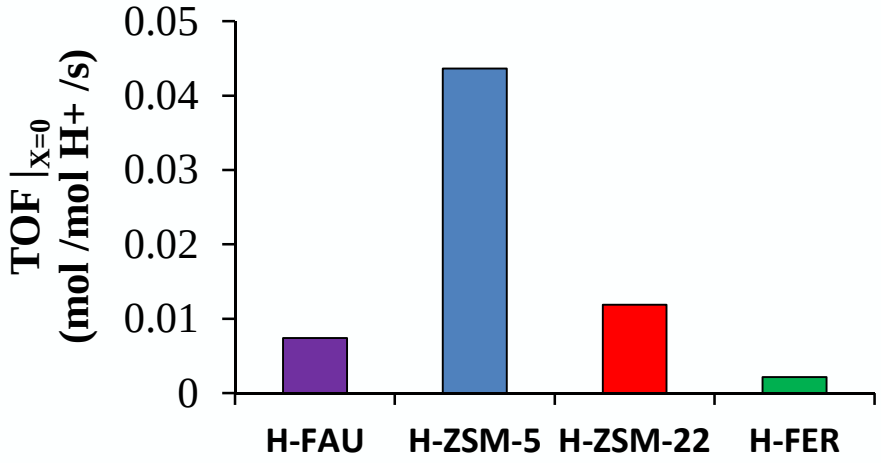
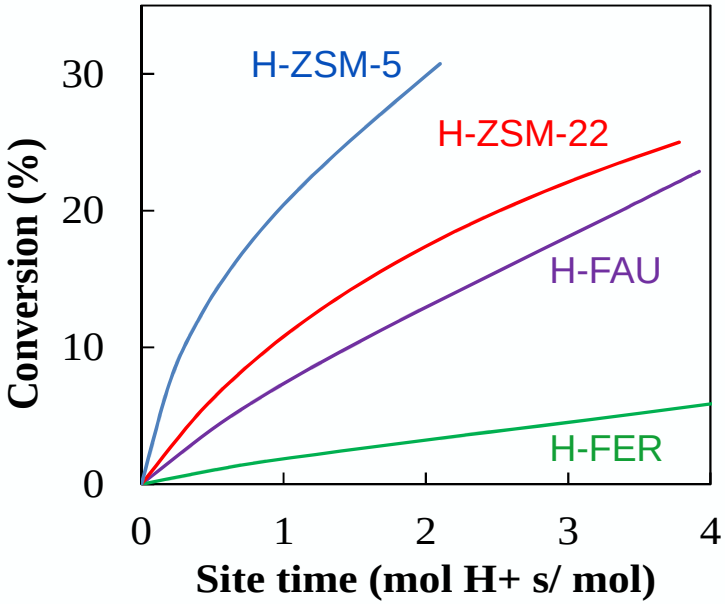
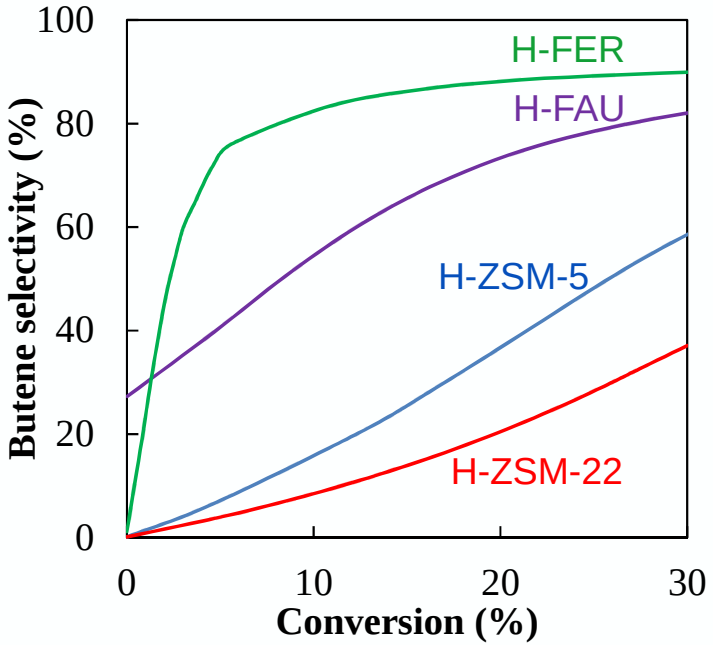
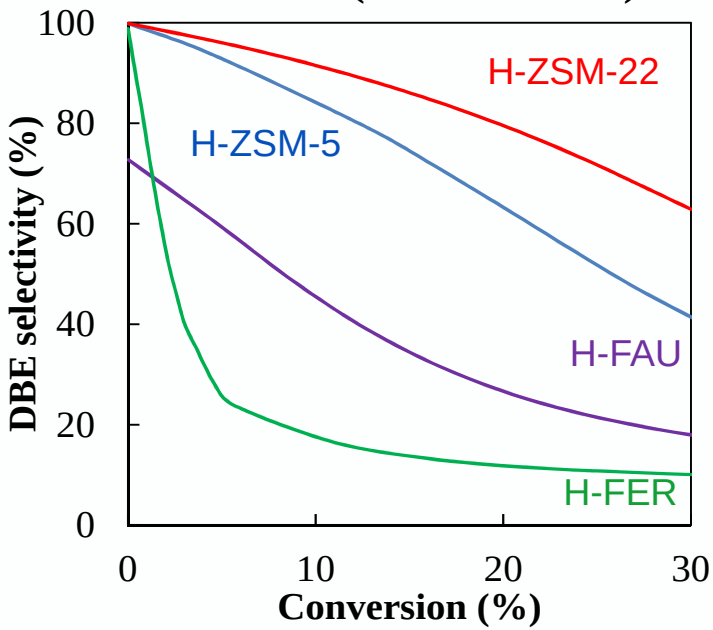
Butanol dehydration

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





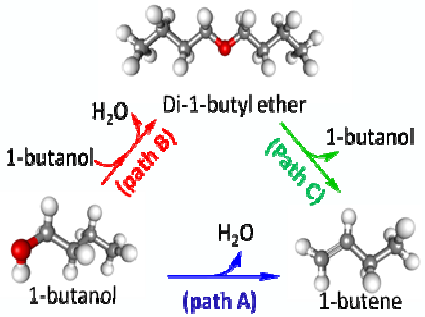




Effect of Zeolite: reaction path analysis

$P_{BuOH,0}$ = 10 kPa

Temperature= 450 K

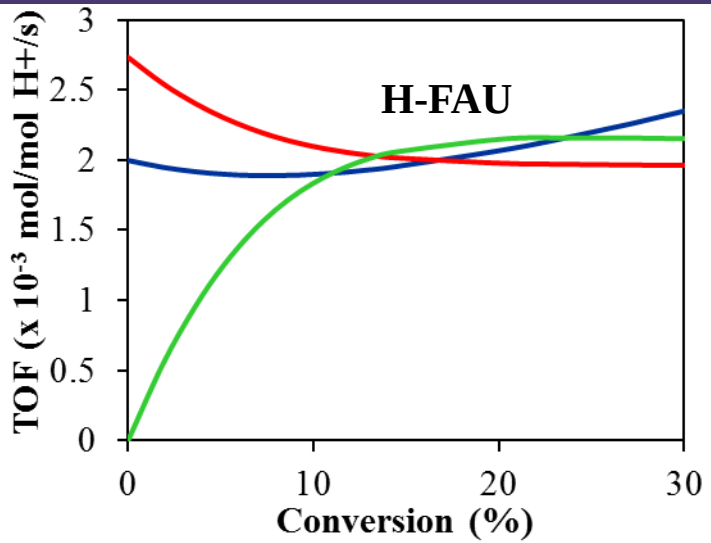


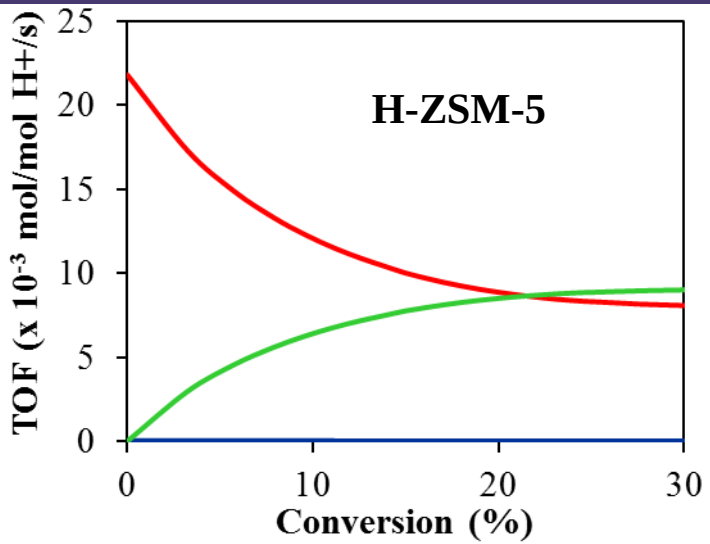
path A

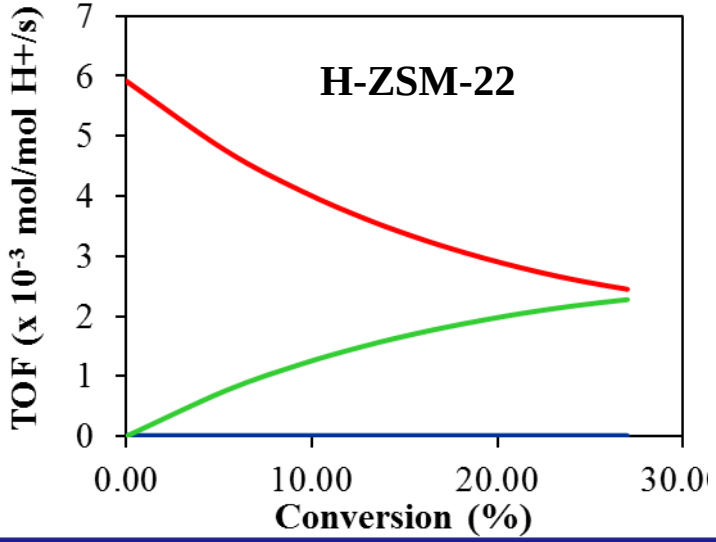
path B

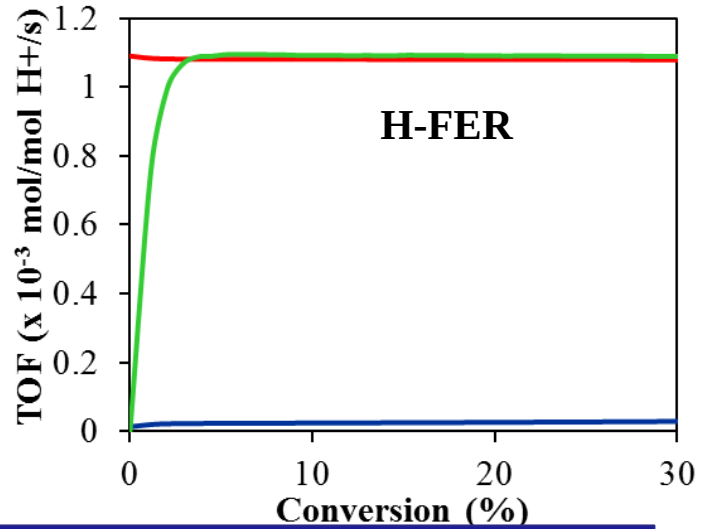
path C

H-FER and H-FAU: selective for butene







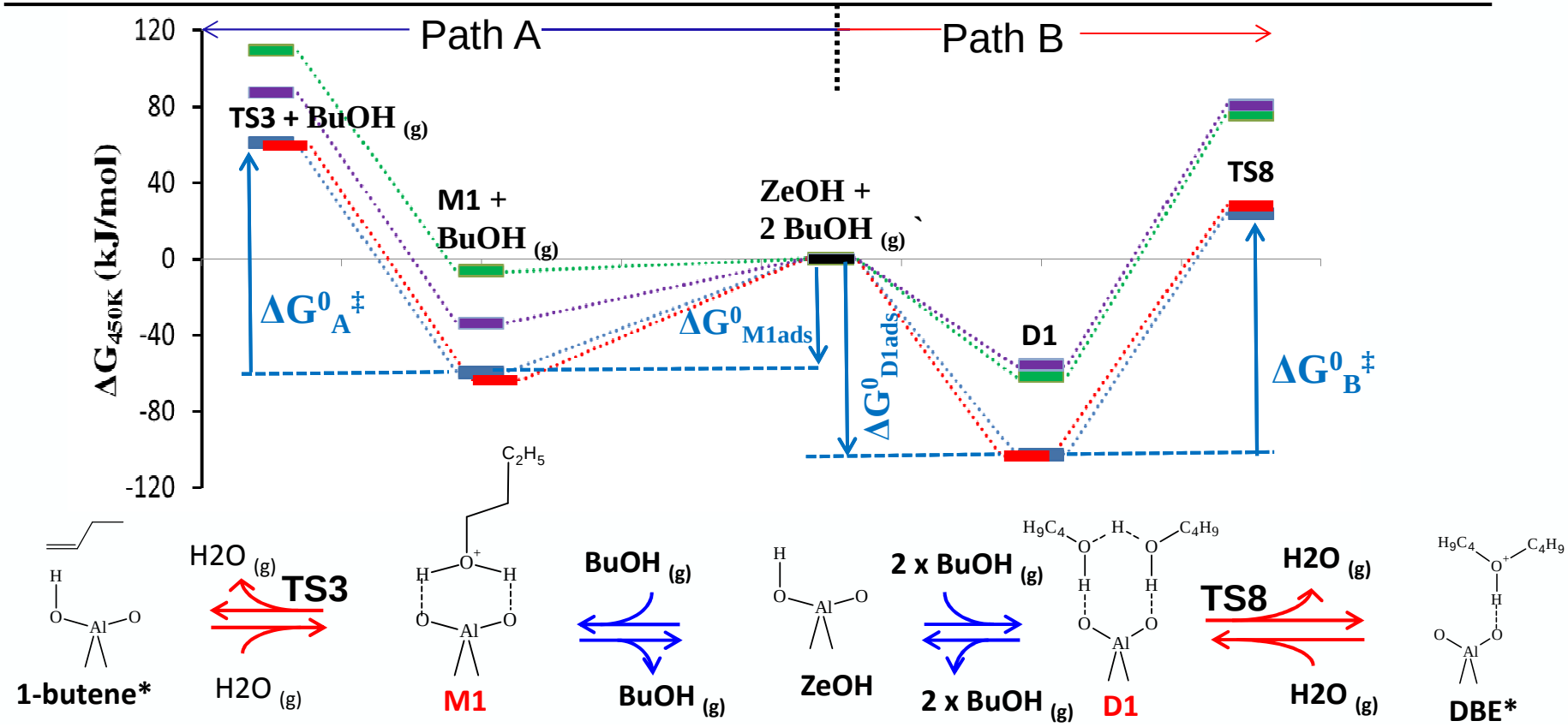


H-FER: ether-mediated route (path B followed by path C) favored to produce 1-butene

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

Effect of zeolite : path A versus path B

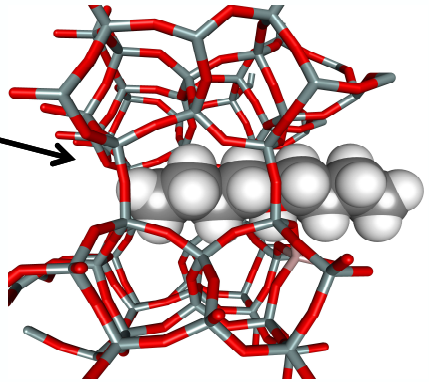
Zeolite	ΔG^0_{M1ads} (kJ/mol)	$\Delta G^0_A{}^{\ddagger} = G_{TS3} - G_{M1}$ (kJ/mol)	ΔG^0_{D1ads} (kJ/mol)	$\Delta G^0_B{}^{\ddagger} = G_{TS8} - G_{D1}$ (kJ/mol)
H-FAU	-34	121	-56	134
H-ZSM-5	-59	120	-103	127
H-ZSM-22	-64	123	-103	131
H-FER	-7	116	-62	137



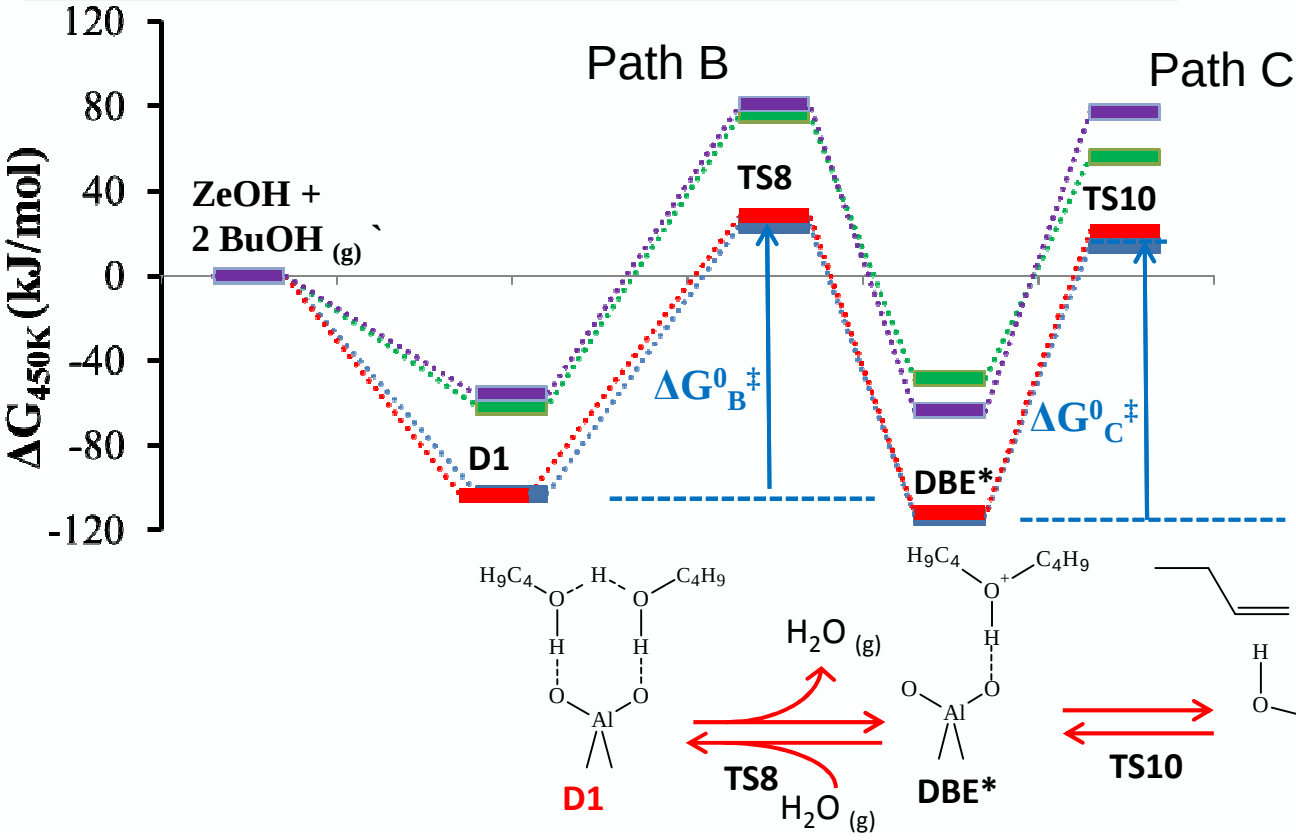
Effect of zeolite: path B and C

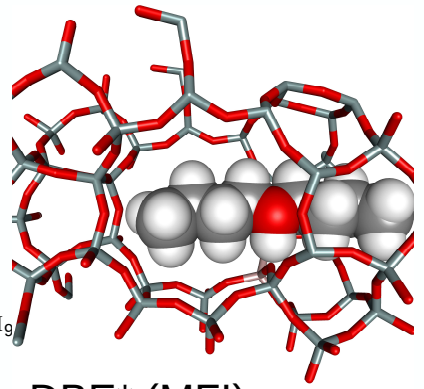
Zeolite	$\Delta G^{\ddagger}_{B} = G_{TS8} - G_{D1}$ (kJ/mol)	$\Delta G^{\ddagger}_{C} = G_{TS10} - G_{DBE*}$ (kJ/mol)
H-FAU	134	132
H-ZSM-5	127	128
H-ZSM-22	131	132
H-FER	137	105

Steric constraints



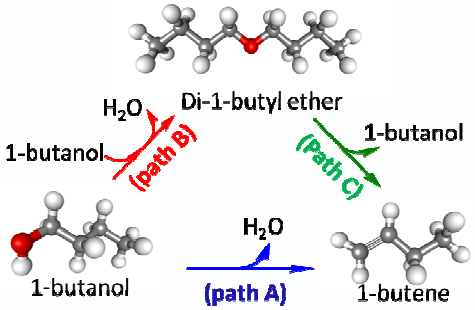
DBE* (FER)





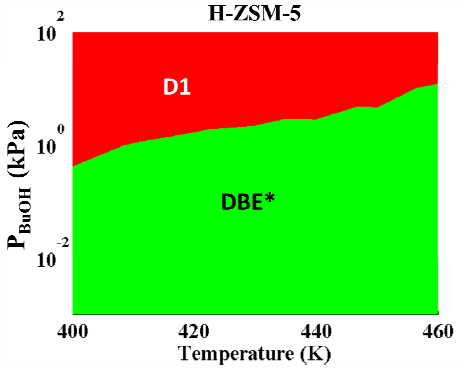
DBE* (MFI)

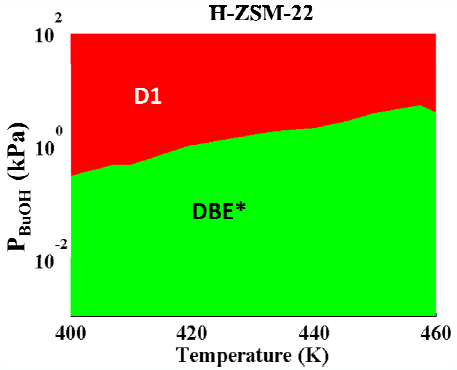
Caveat: effect of reaction conditions

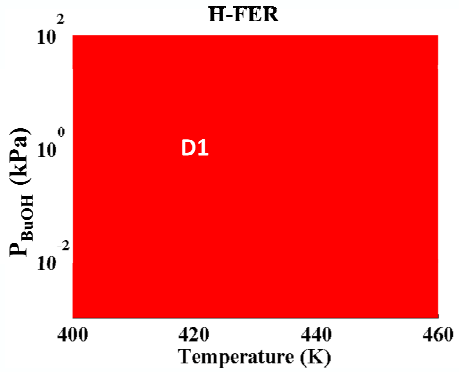


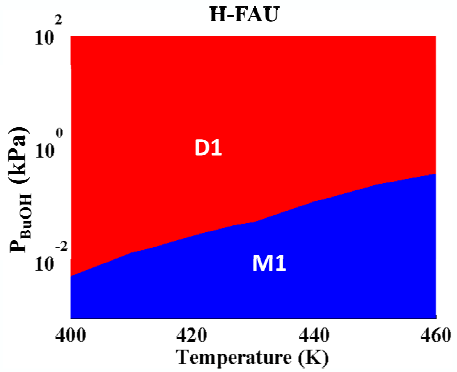
	Low	High
Temperature	B	A
P_{ROH}	A	B
Conversion (X)	A / B	A / C

MARI (at X= 10 %)

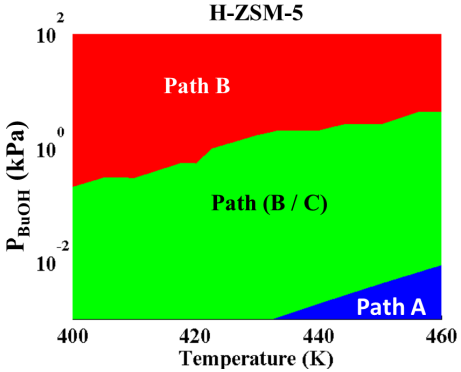


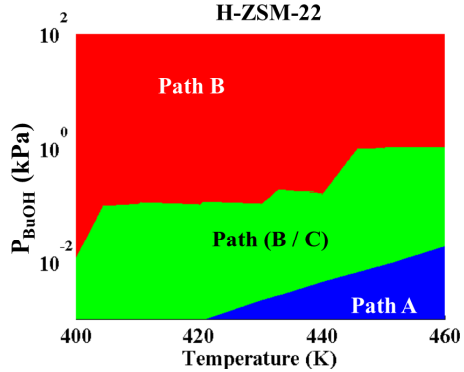


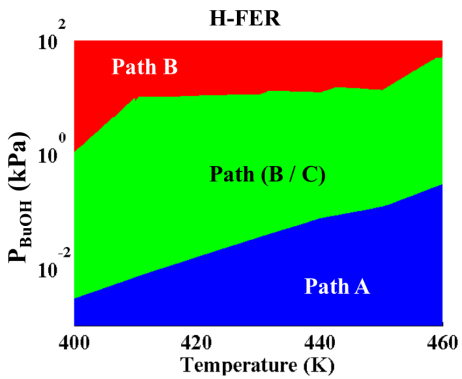


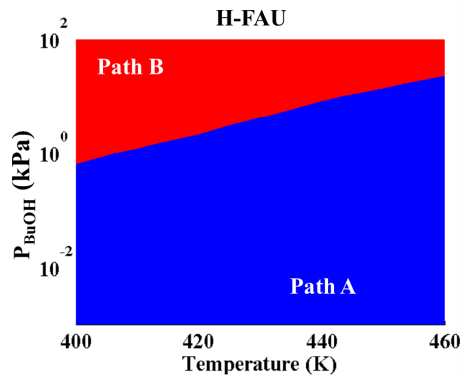


dominant path (at X= 10 %)

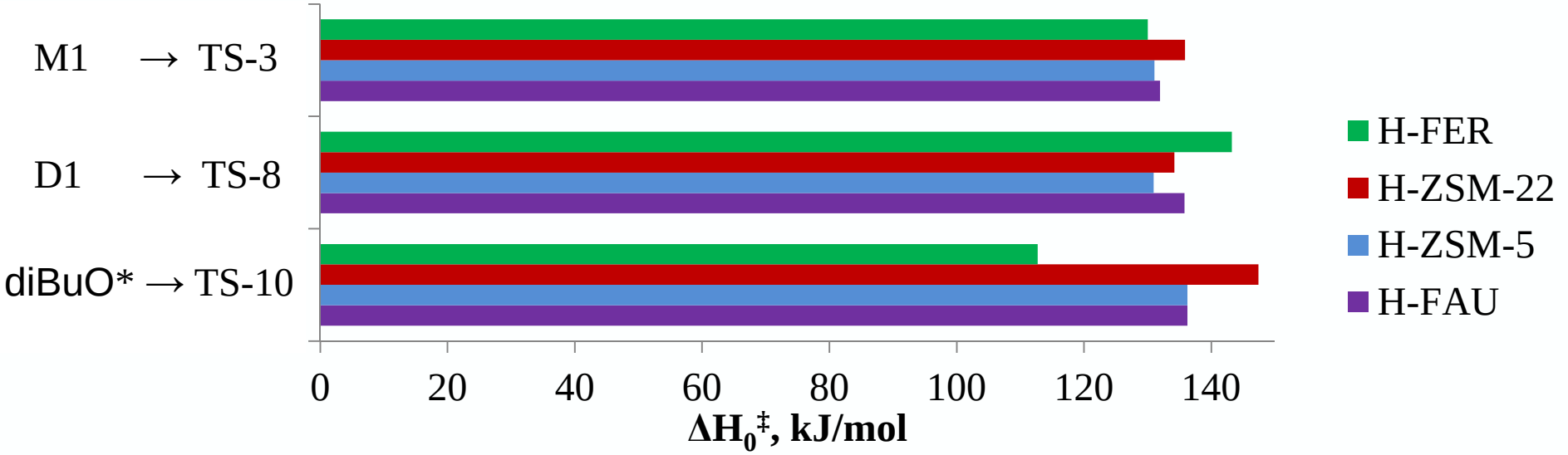


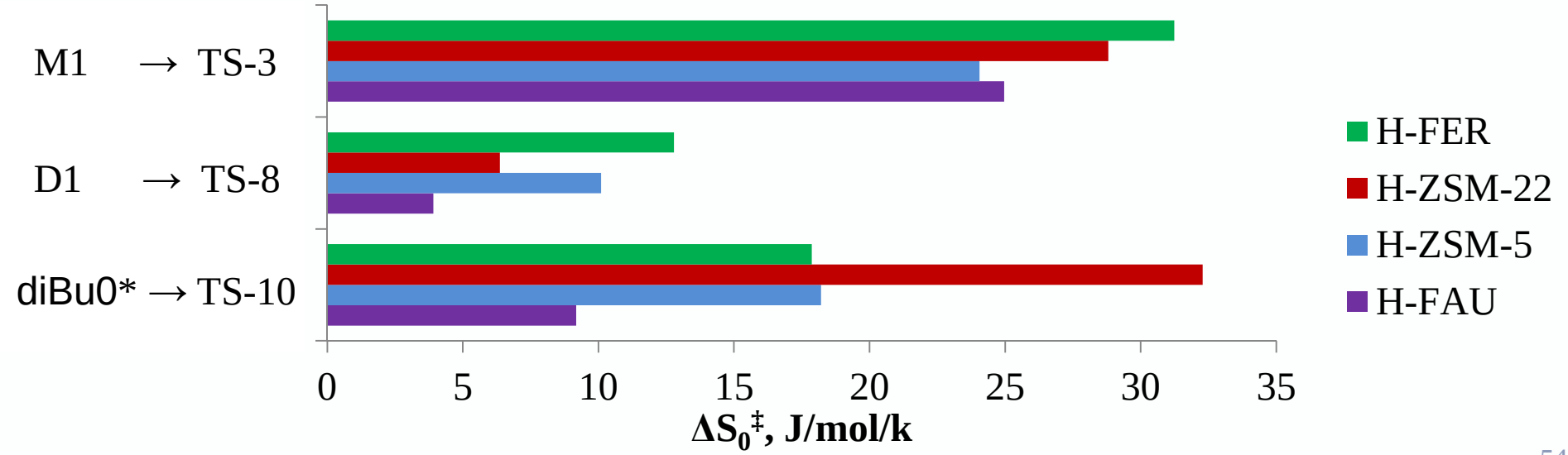






Effect of zeolites on Arrhenius parameters





Overview

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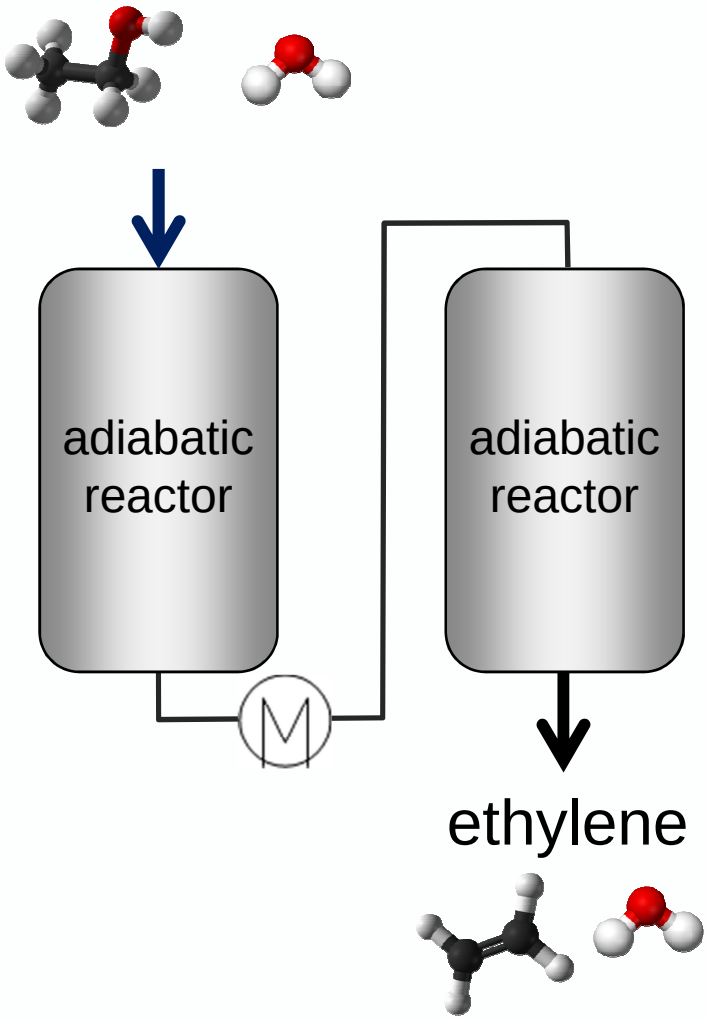
Industrial dehydration reactor

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

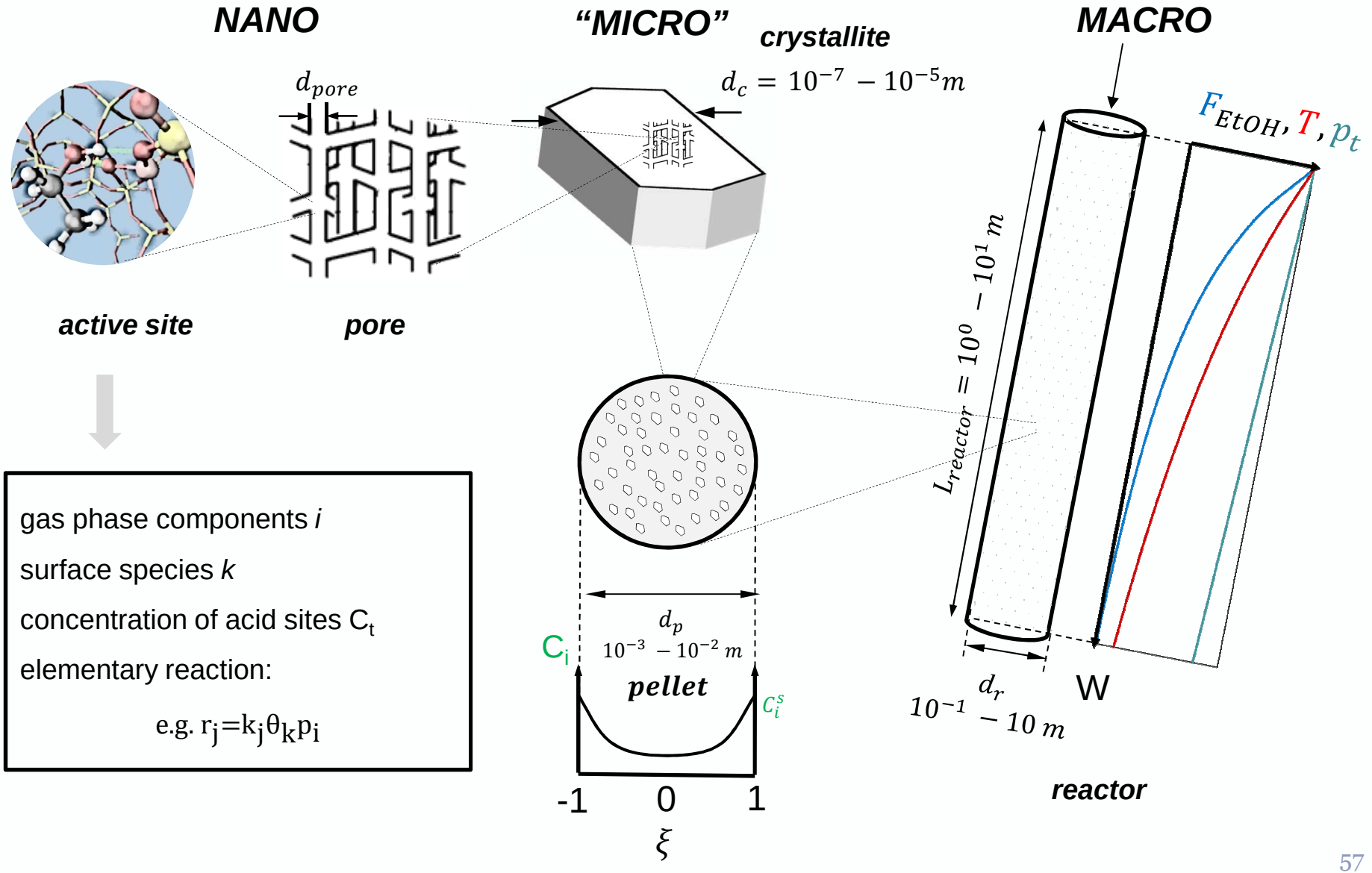
$C_2H_5OH \rightarrow C_2H_4 + H_2O$ $\quad \Delta H = 46$ kJ/mol$_{EtOH}$

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

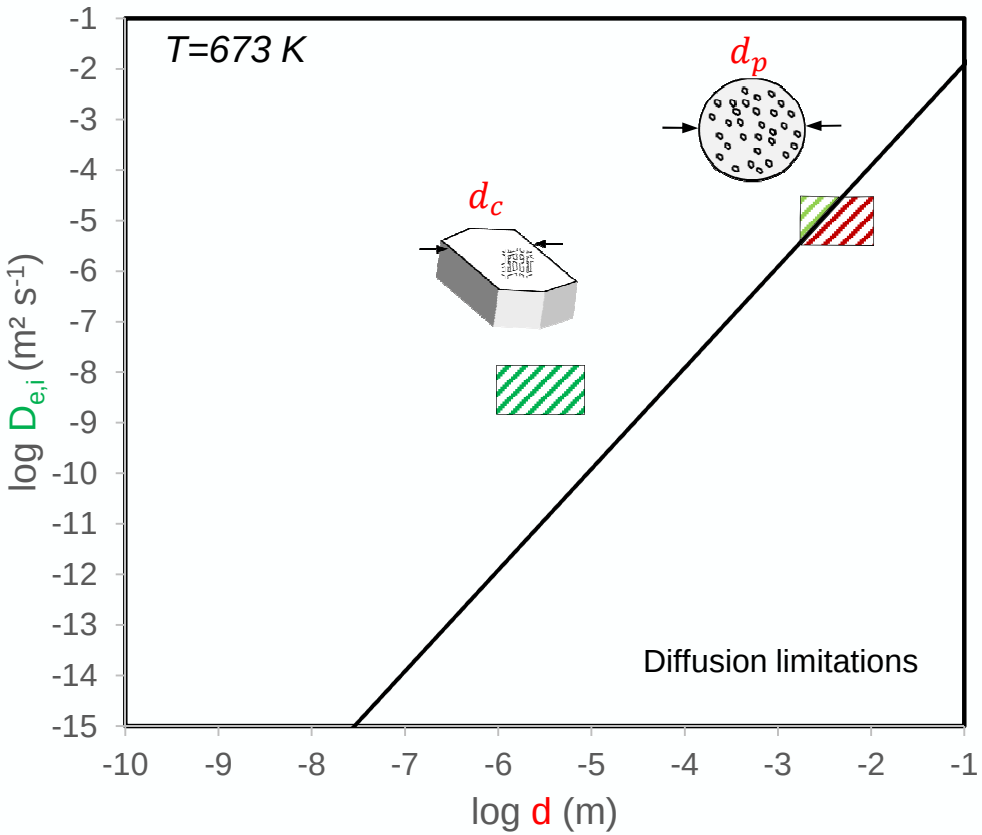
$(C_2H_5)_2O \rightarrow C_2H_4 + C_2H_5OH$ $\quad \Delta H = 70$ kJ/mol$_{EtOH}$

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

Multiscale modeling of an industrial reactor



Microscale: possible diffusion limitations



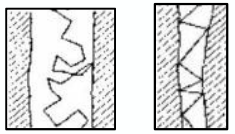
Weisz-Prater criterion:

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

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

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

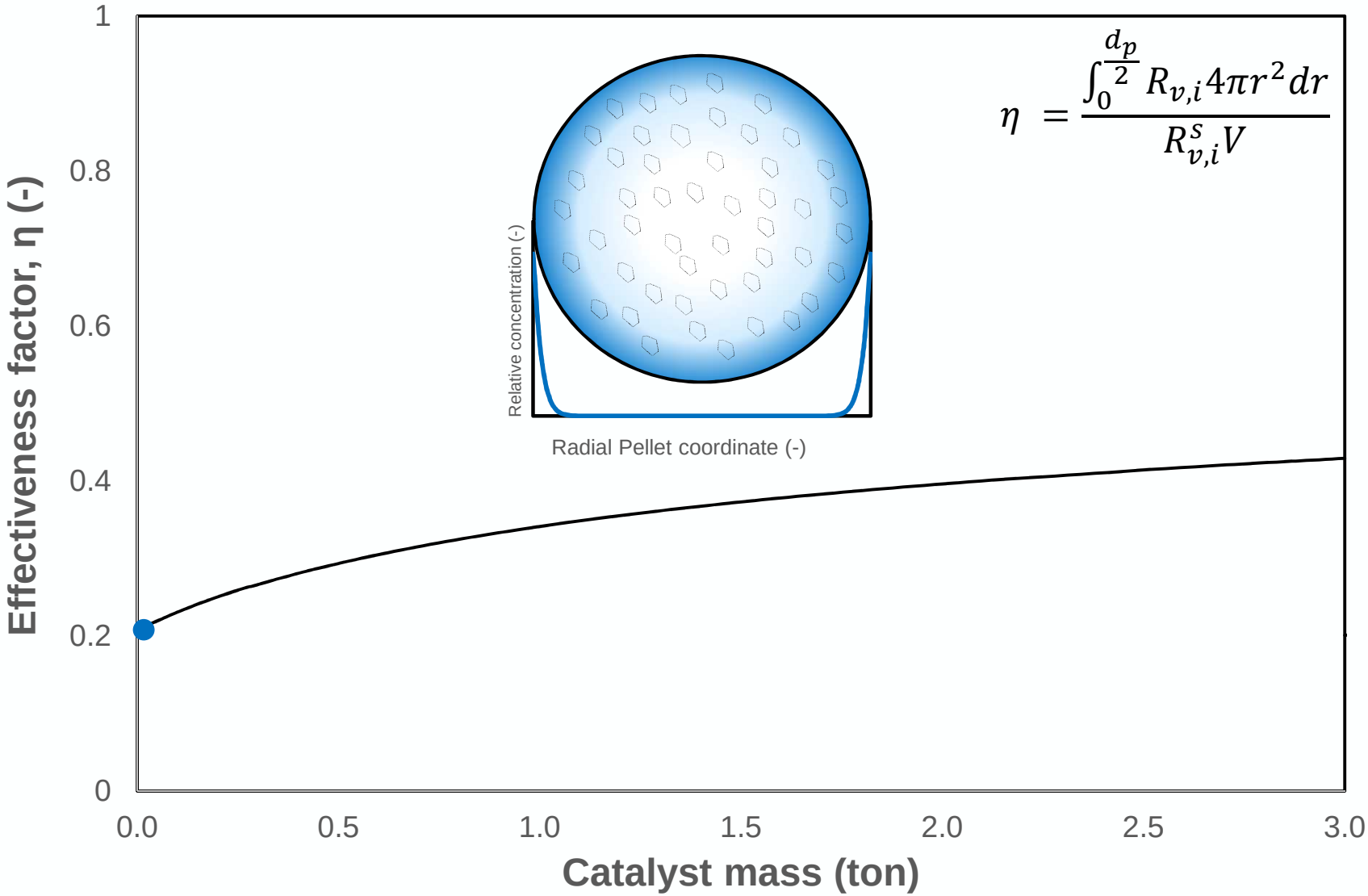
$$\frac{dF_i}{dW} = C_t \overline{R_i} \qquad F_i = F_{i,0} \text{ at } W=0$$

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

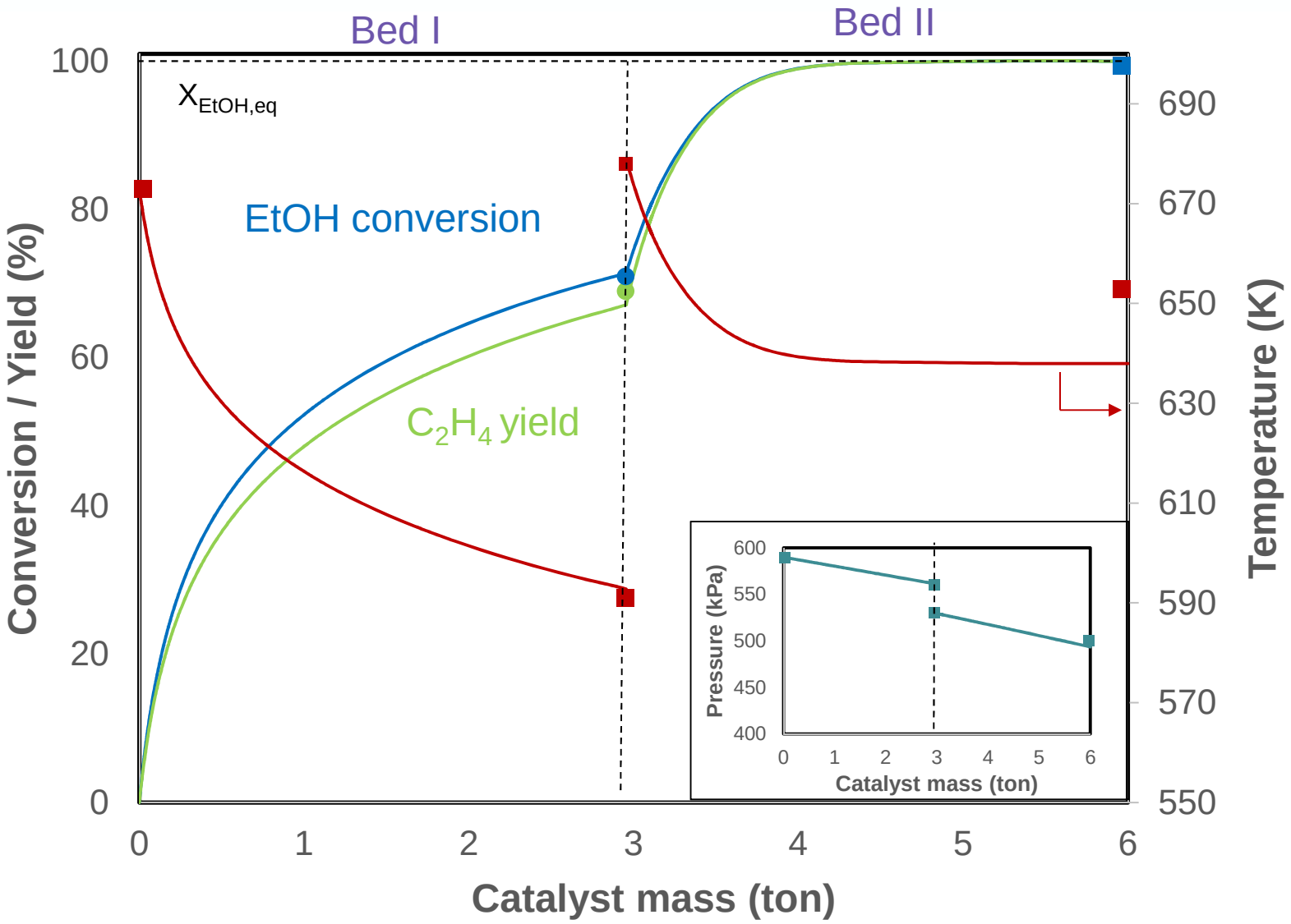
$$\frac{dp_t}{dW} = -f \frac{G^2}{\rho_b \rho_f A_r^3 d_p} \qquad p = p^0 \text{ at } W=0$$

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

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)

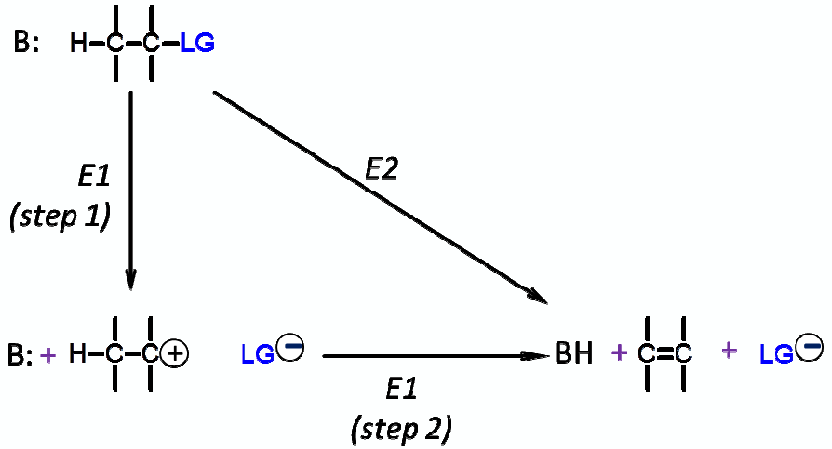
Glossary

- ***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

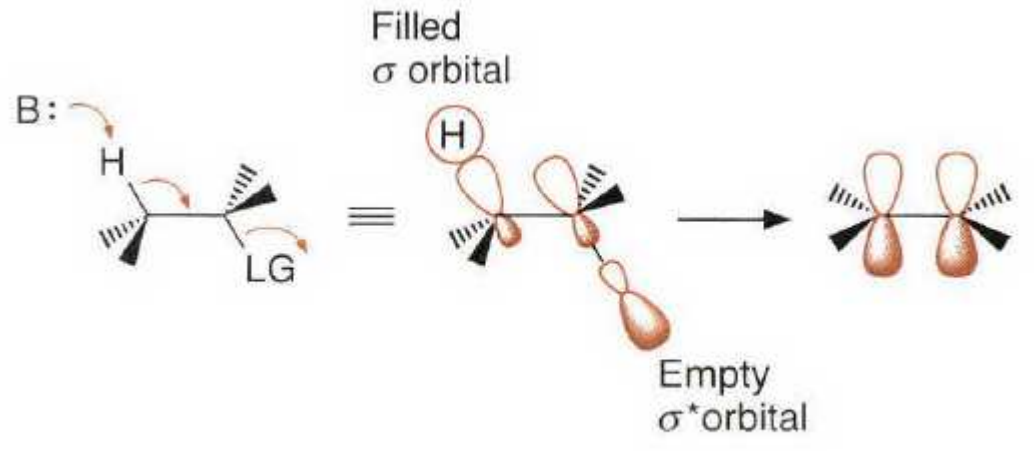
Glossary

- ***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.



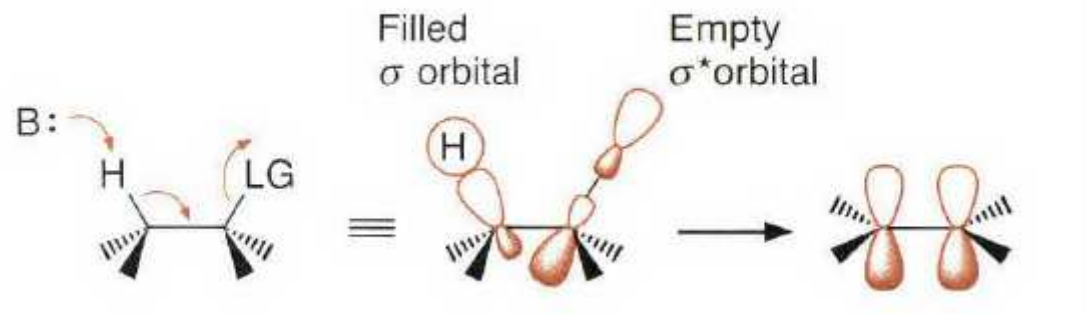
Glossary

- ***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)

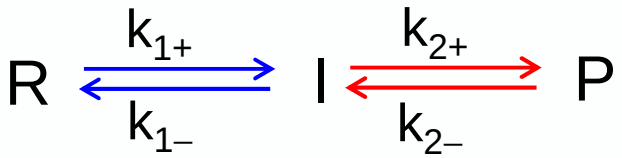


Glossary

- ***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.

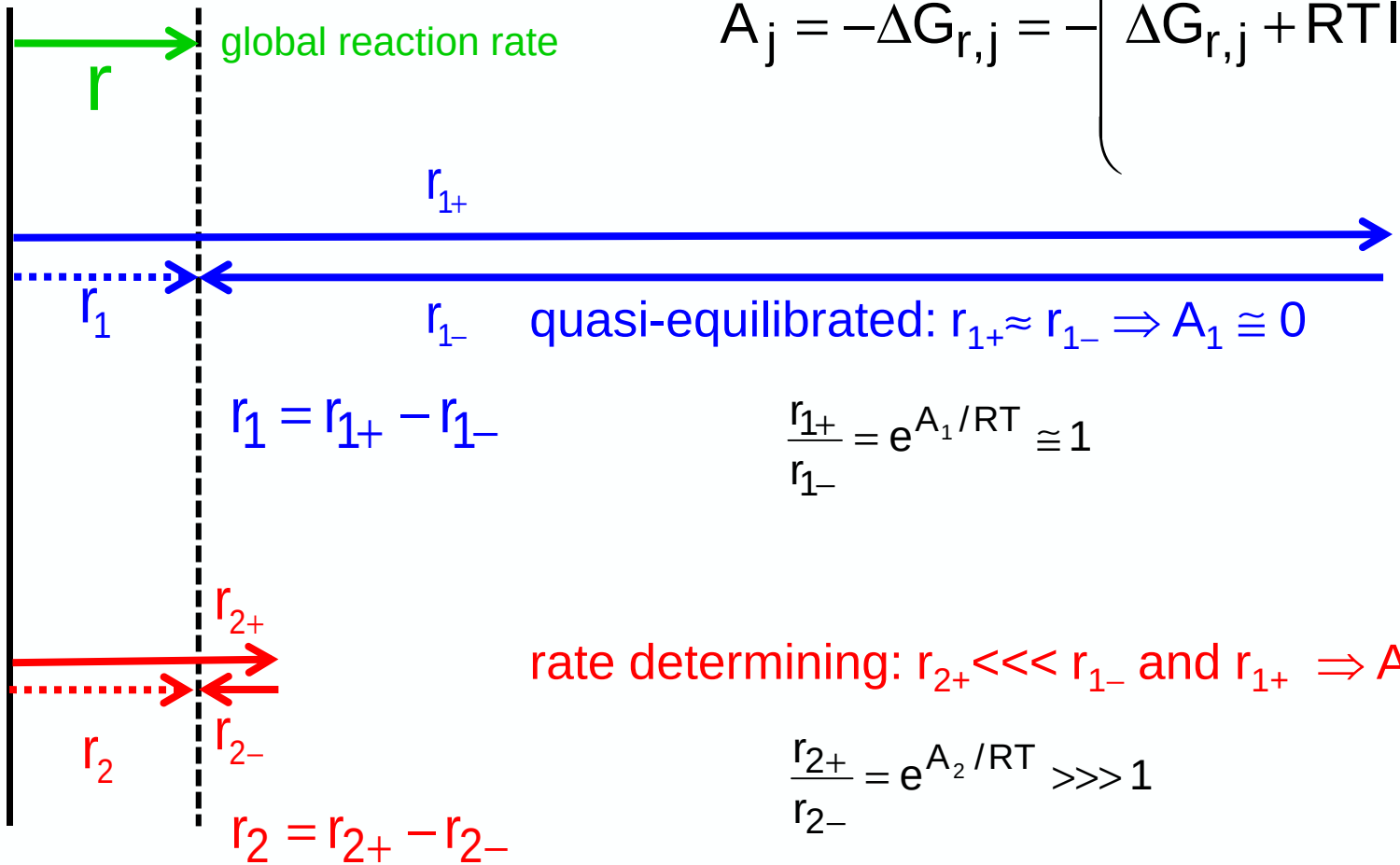
- ***SN2 (substitution, bimolecular)*** is a concerted reaction involving simultaneous bond breaking (between the carbon atom and leaving group) and bond formation(between carbon atom and the attacking nucleophile). The transition state for a SN2 type substitution involves a penta-coordinated carbon 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

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



quasi-equilibrated: $r_{1+} \approx r_{1-} \Rightarrow A_1 \cong 0$

$$\frac{r_{1+}}{r_{1-}} = e^{A_1/RT} \cong 1$$

rate determining: $r_{2+} <<< r_{1-}$ and $r_{1+} \Rightarrow A_2 >>> A_1$

$$\frac{r_{2+}}{r_{2-}} = e^{A_2/RT} >>> 1$$

Glossary

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

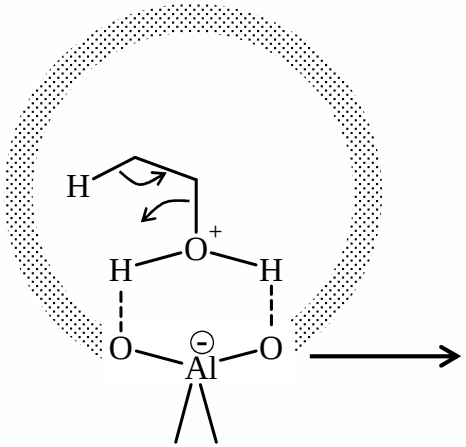
$$NSC_{i,j} = \frac{d(lnR_j)}{d(lnA_i)} = \frac{A_i dR_j}{R_j dA_i}$$

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

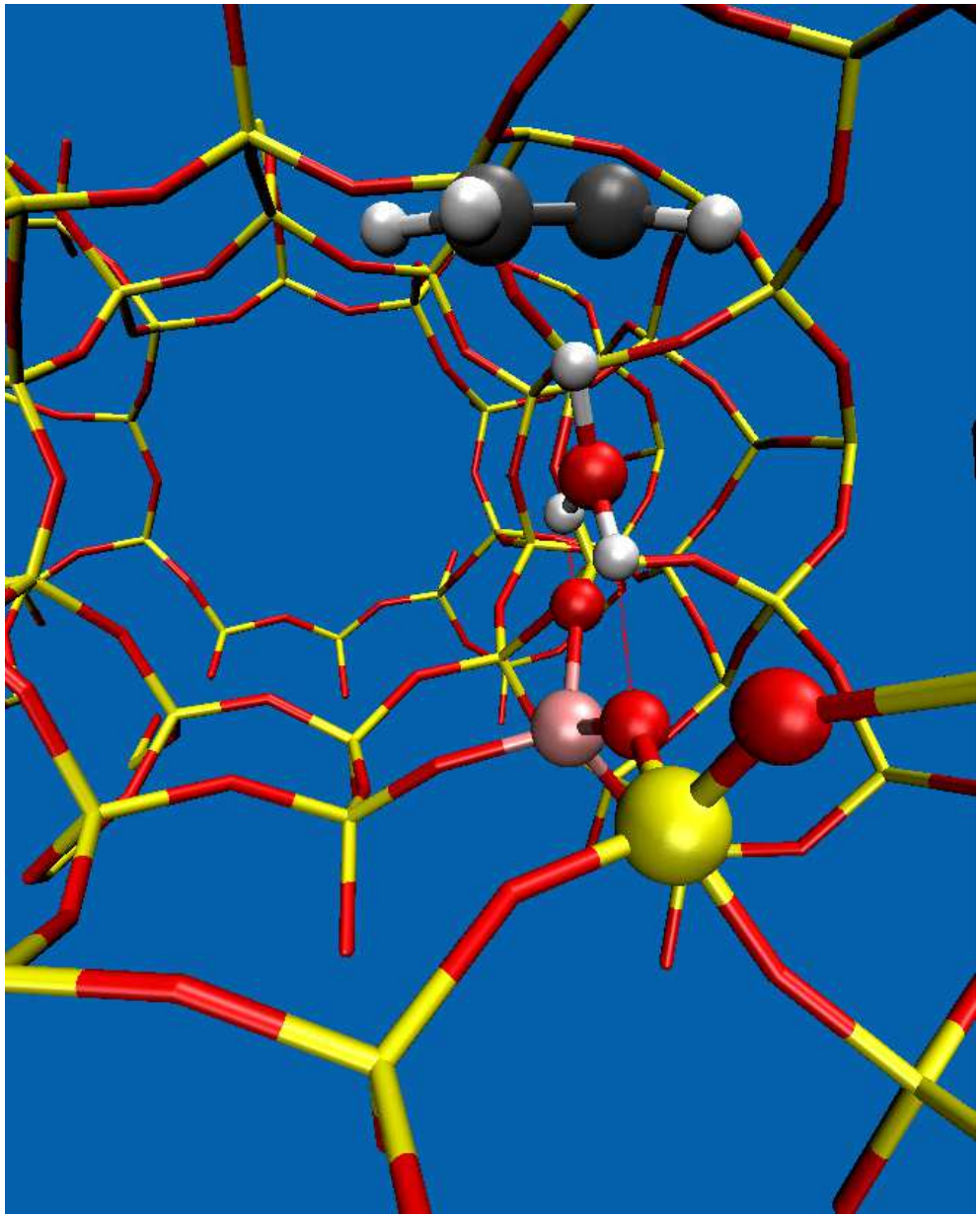
- **Reaction-path analysis:** analyzes the reaction rates that contribute to the rate of production or disappearance of a selected species, which allows to determine actual reaction path to form intermediates and products

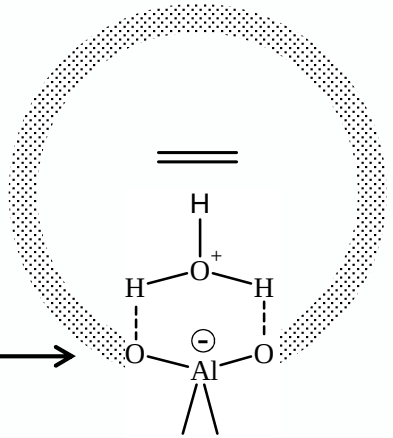
E1 like

TS1



M1

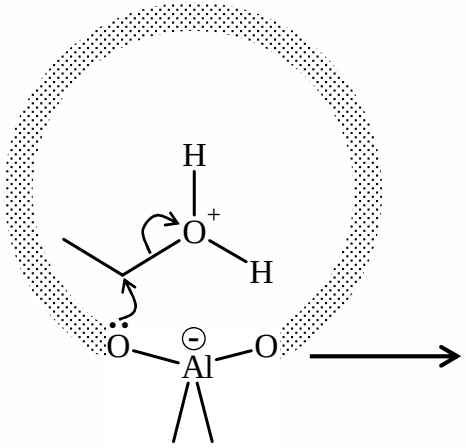




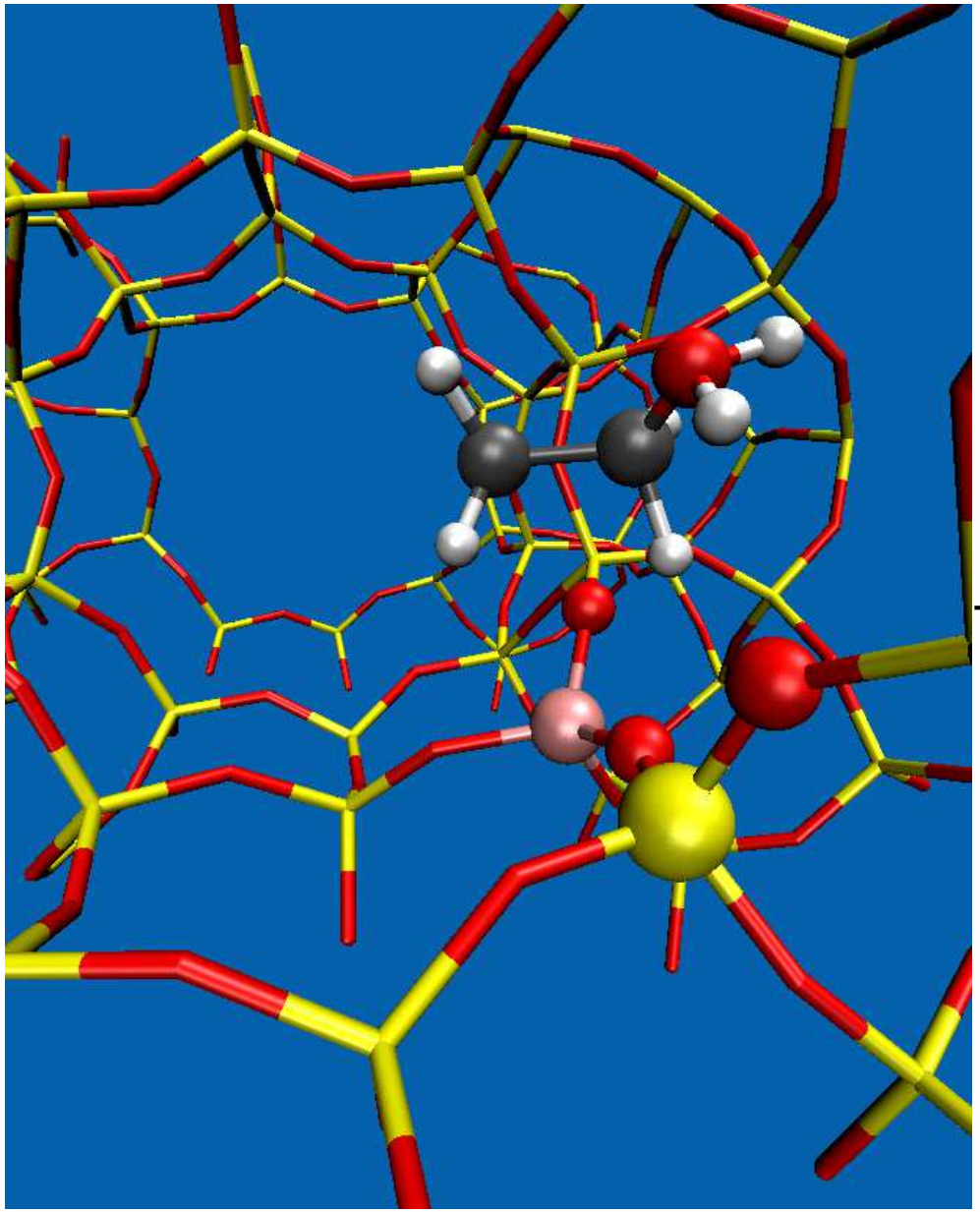
W

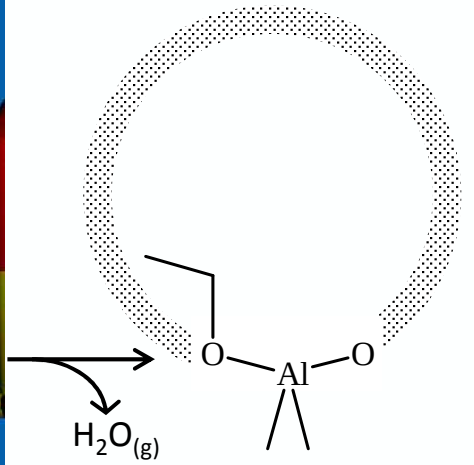
SN2

TS2



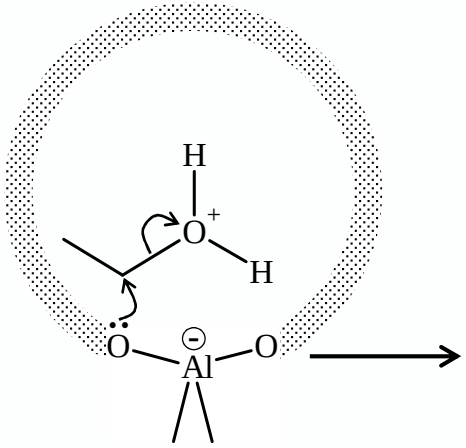
M2



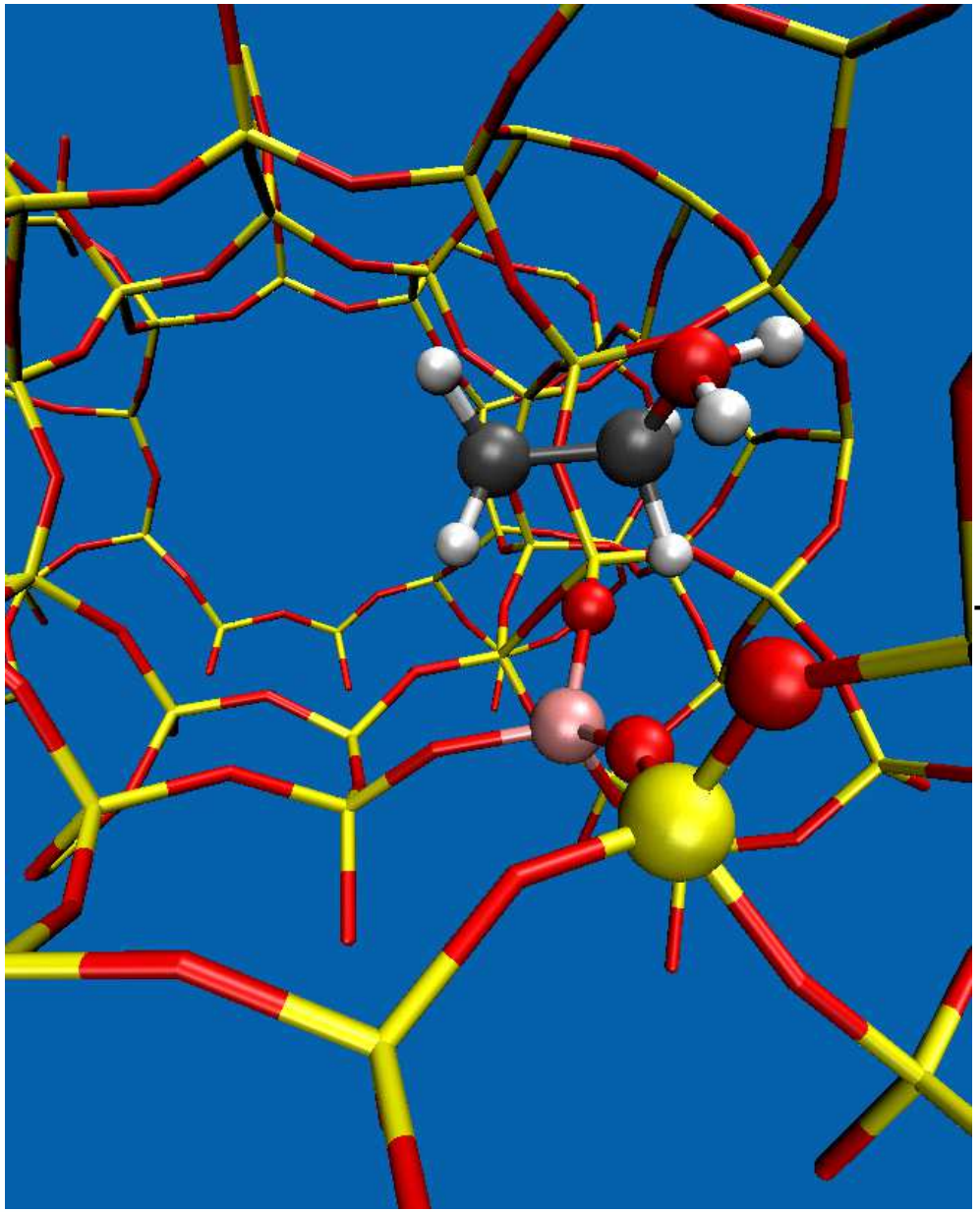


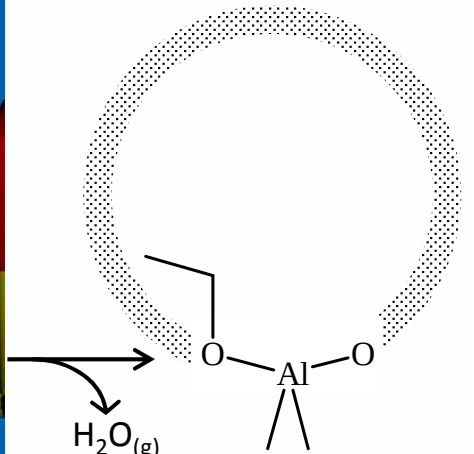
Ethoxy

SN2 TS2



M2



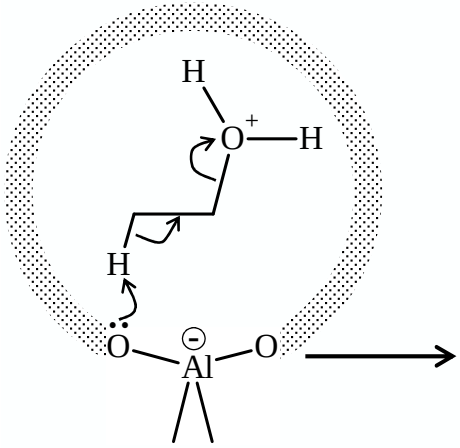


$H_2O_{(g)}$

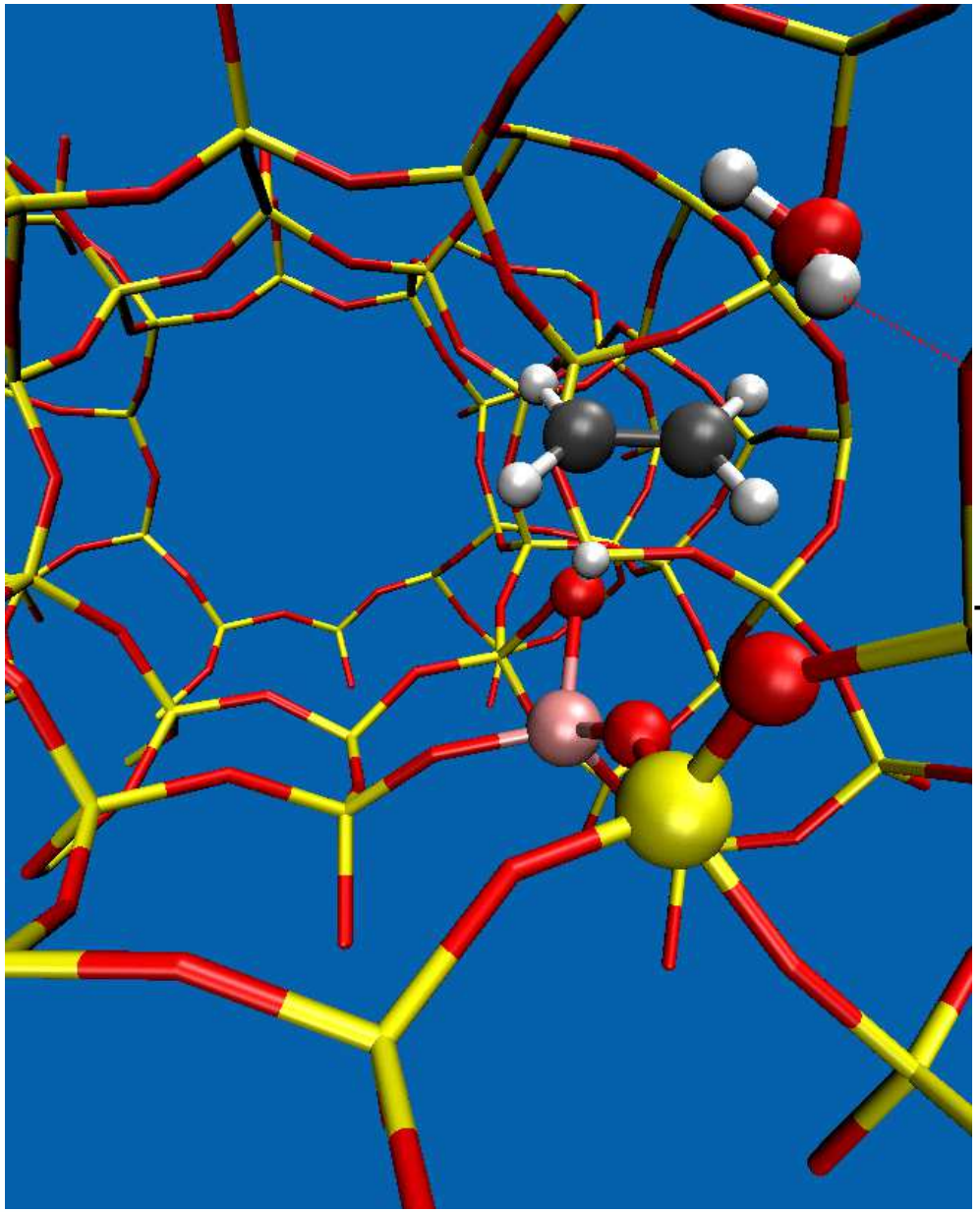
Ethoxy

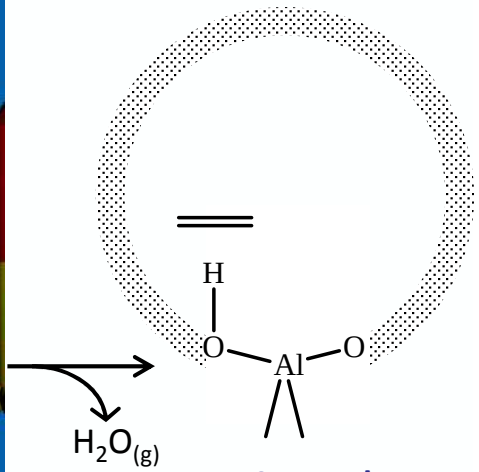
E2 (anti elimination)

TS3



M2



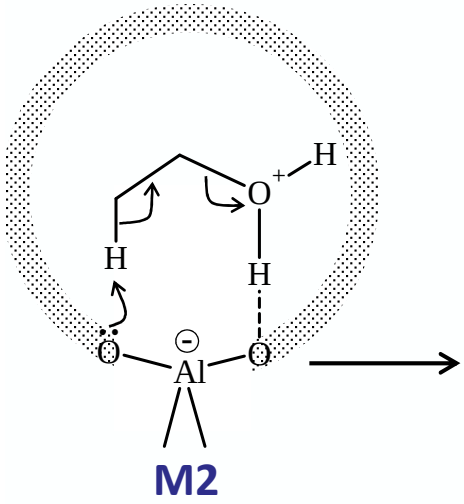


$H_2O_{(g)}$

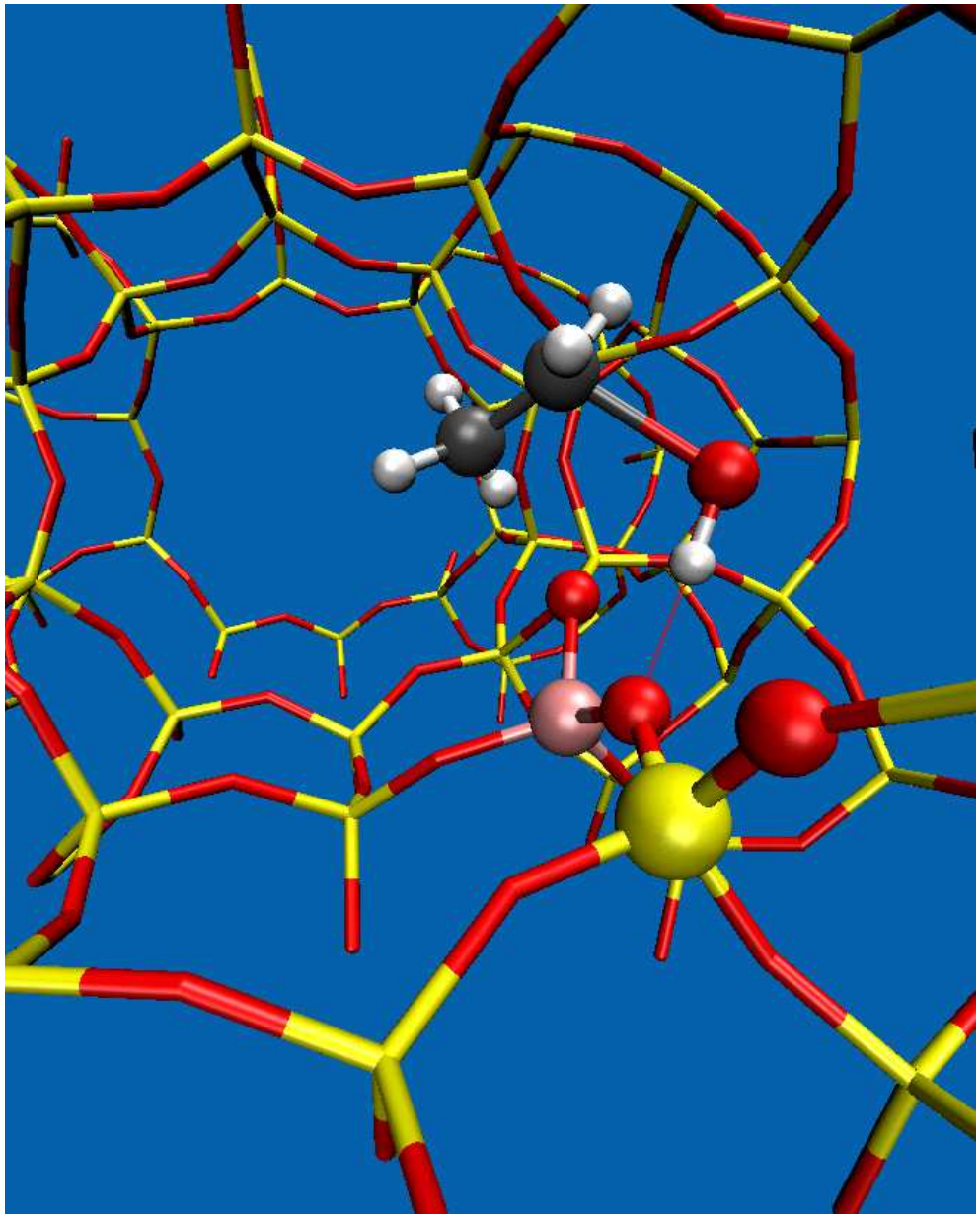
Ethene*

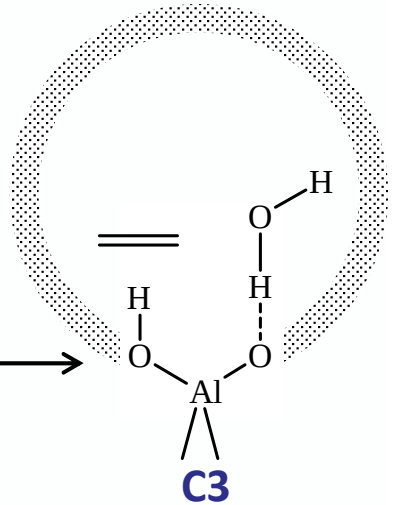
Syn elimination

TS4



M2

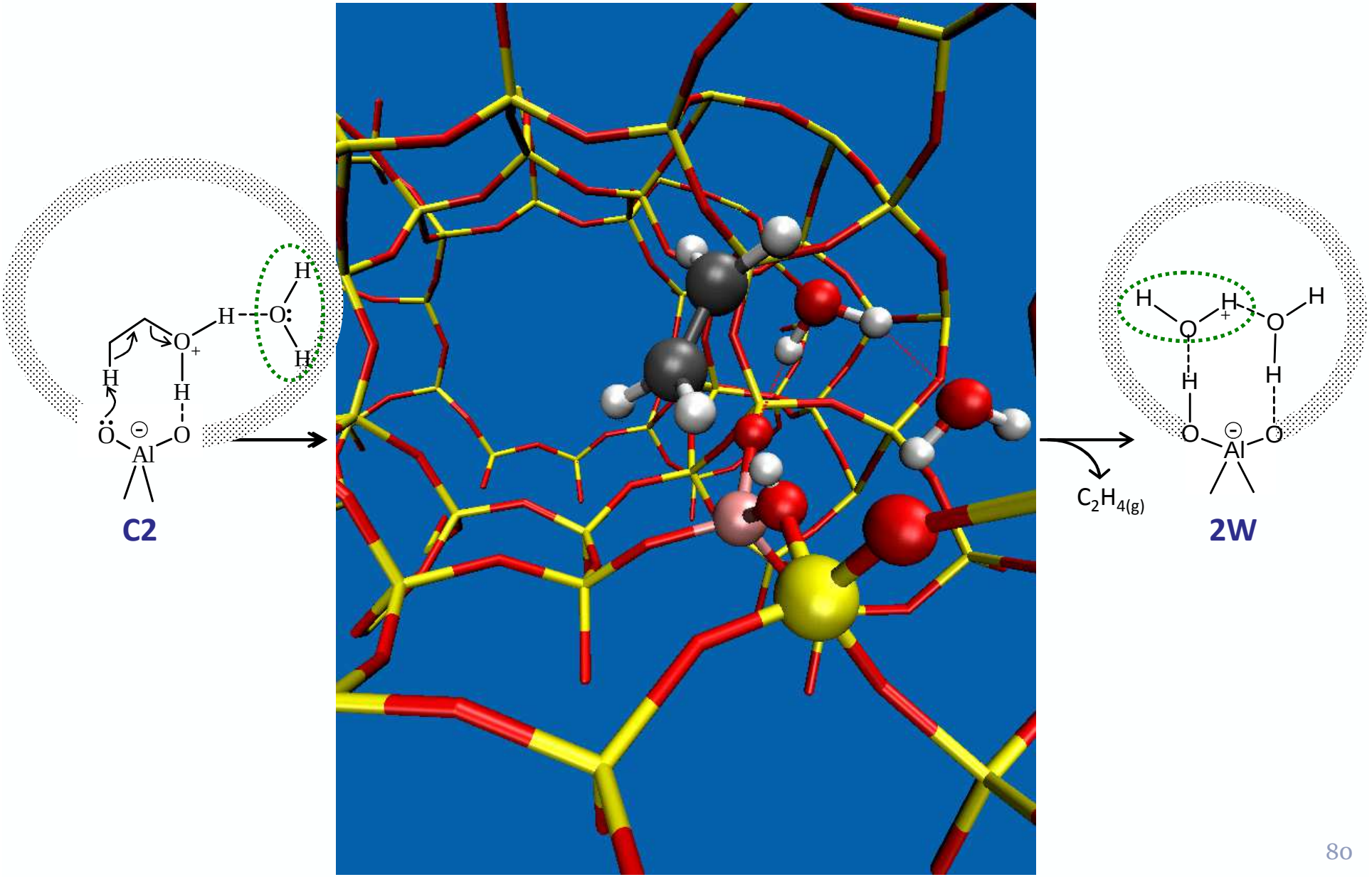




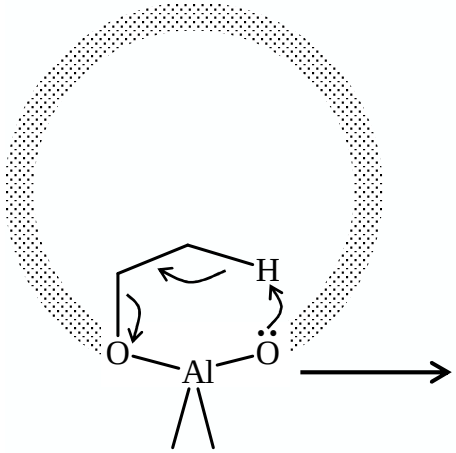
C3

Syn elimination

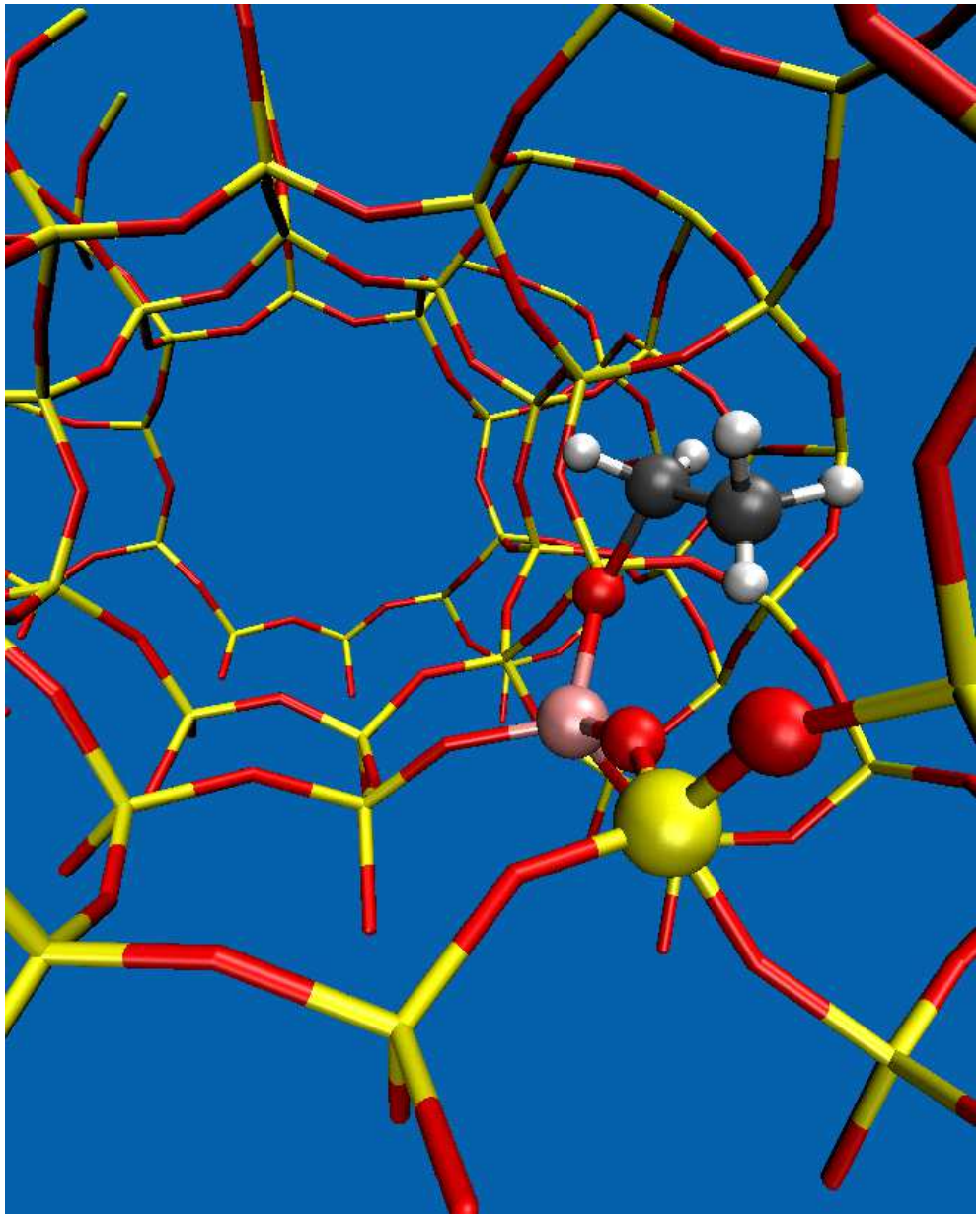
TS5

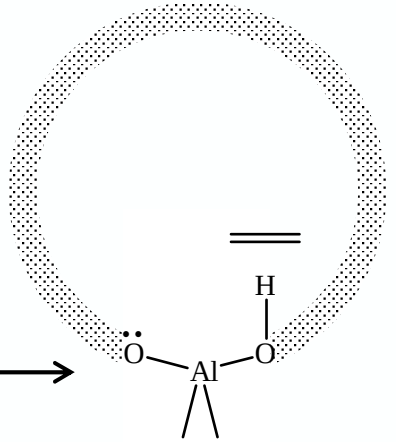


TS6



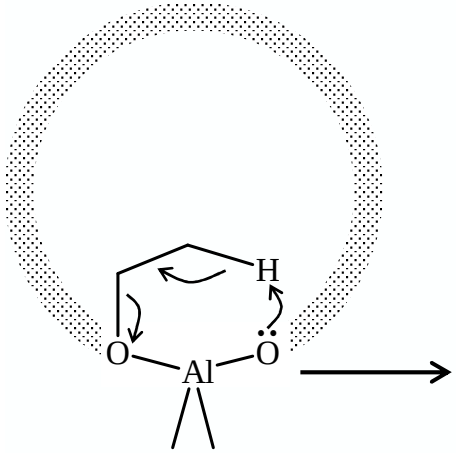
Ethoxy



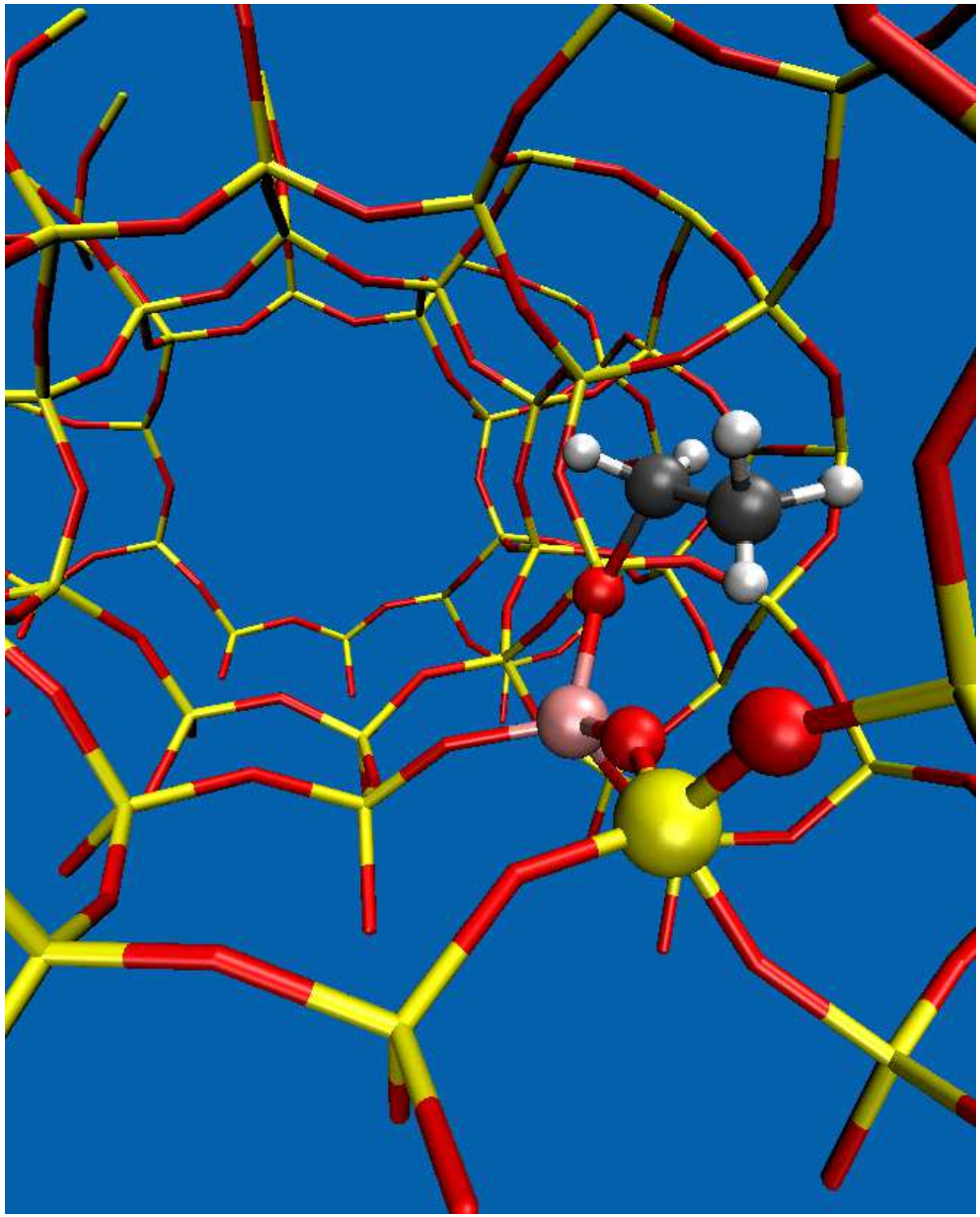


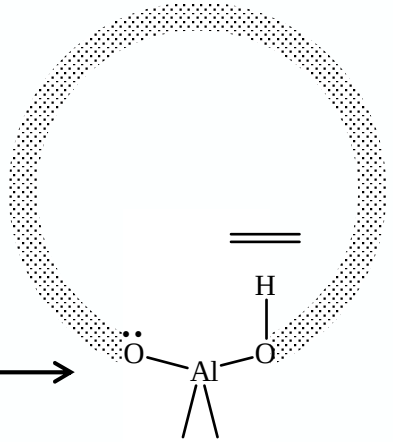
Ethene*

TS6



Ethoxy

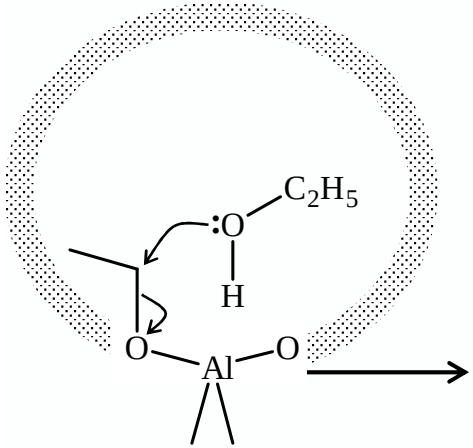




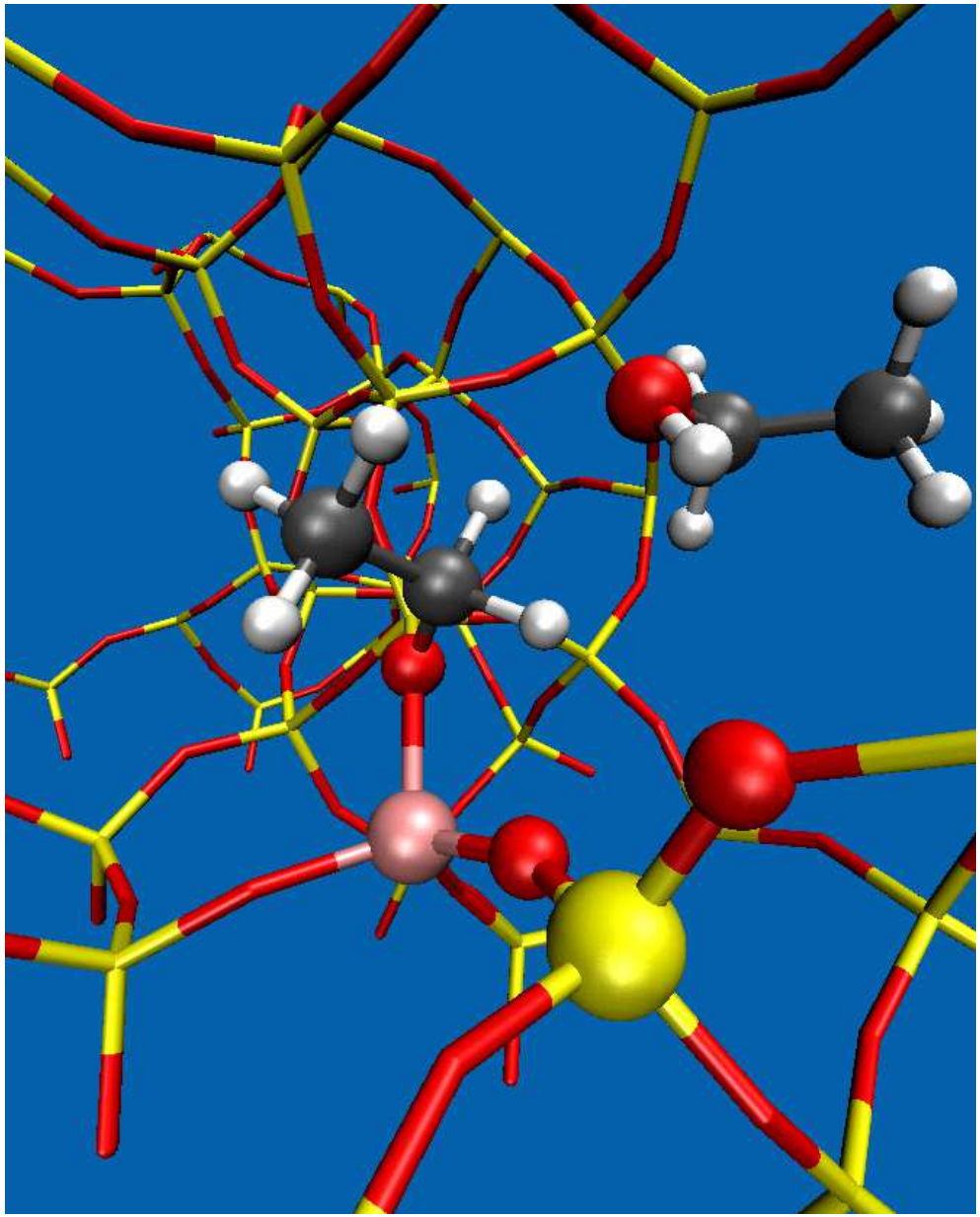
Ethene*

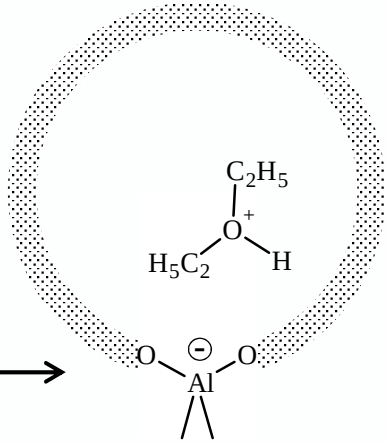
SN2

TS7



Ethoxy

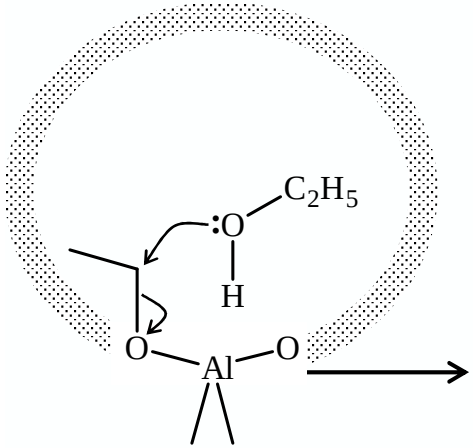




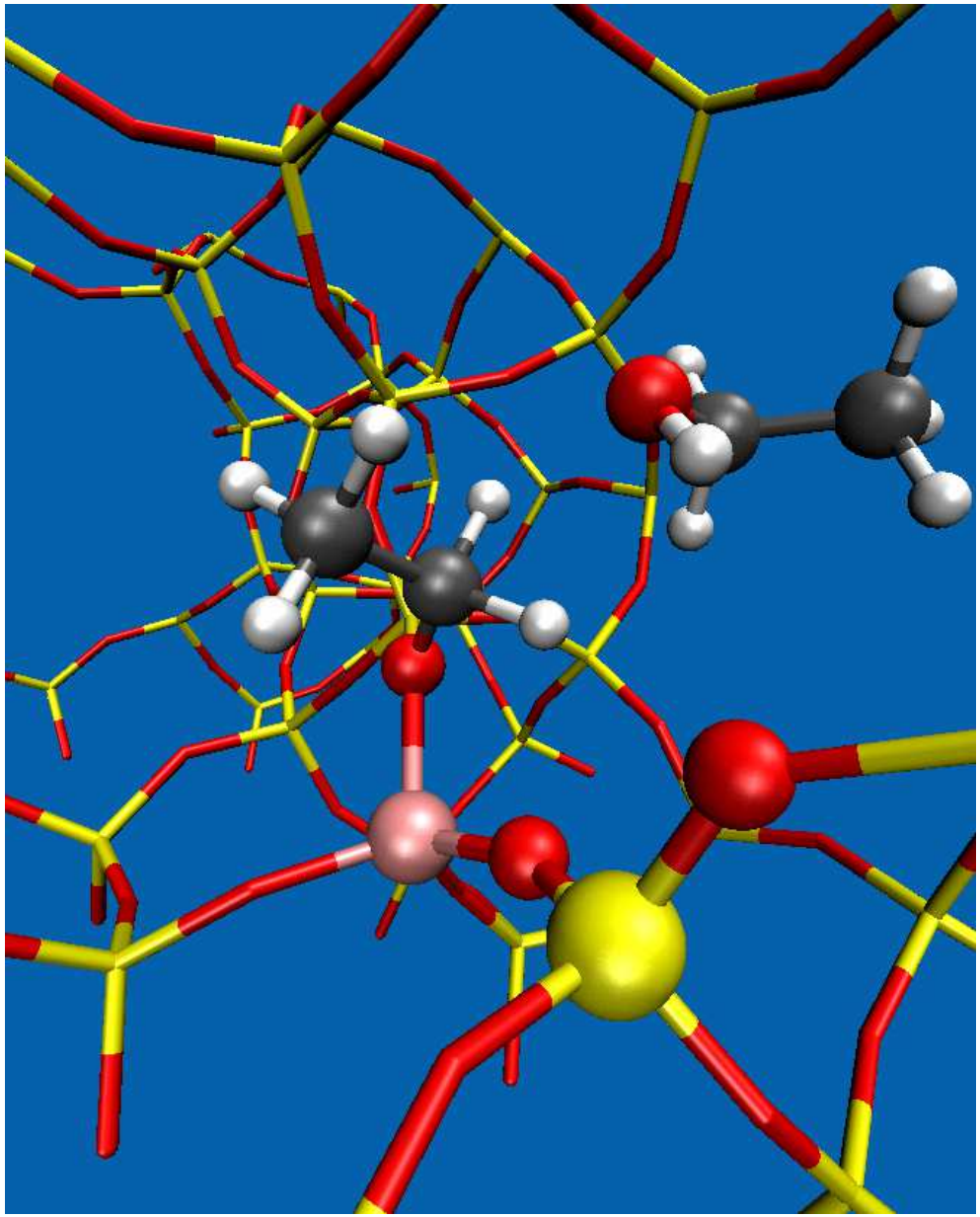
DEE*

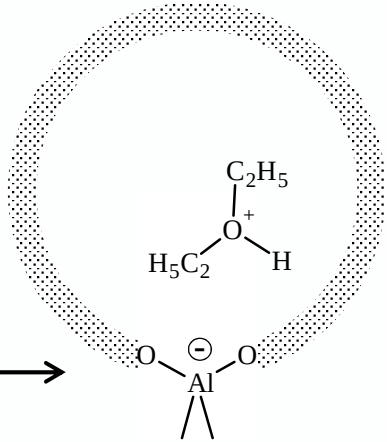
SN2

TS7



Ethoxy

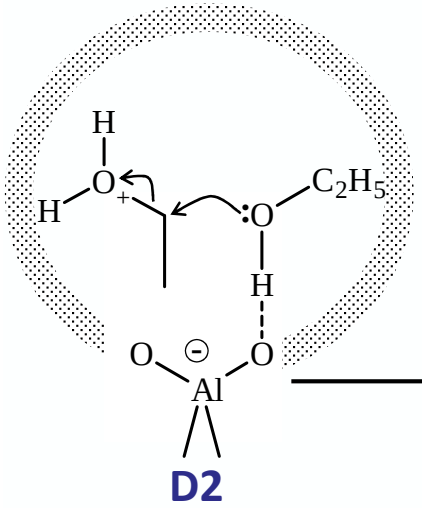




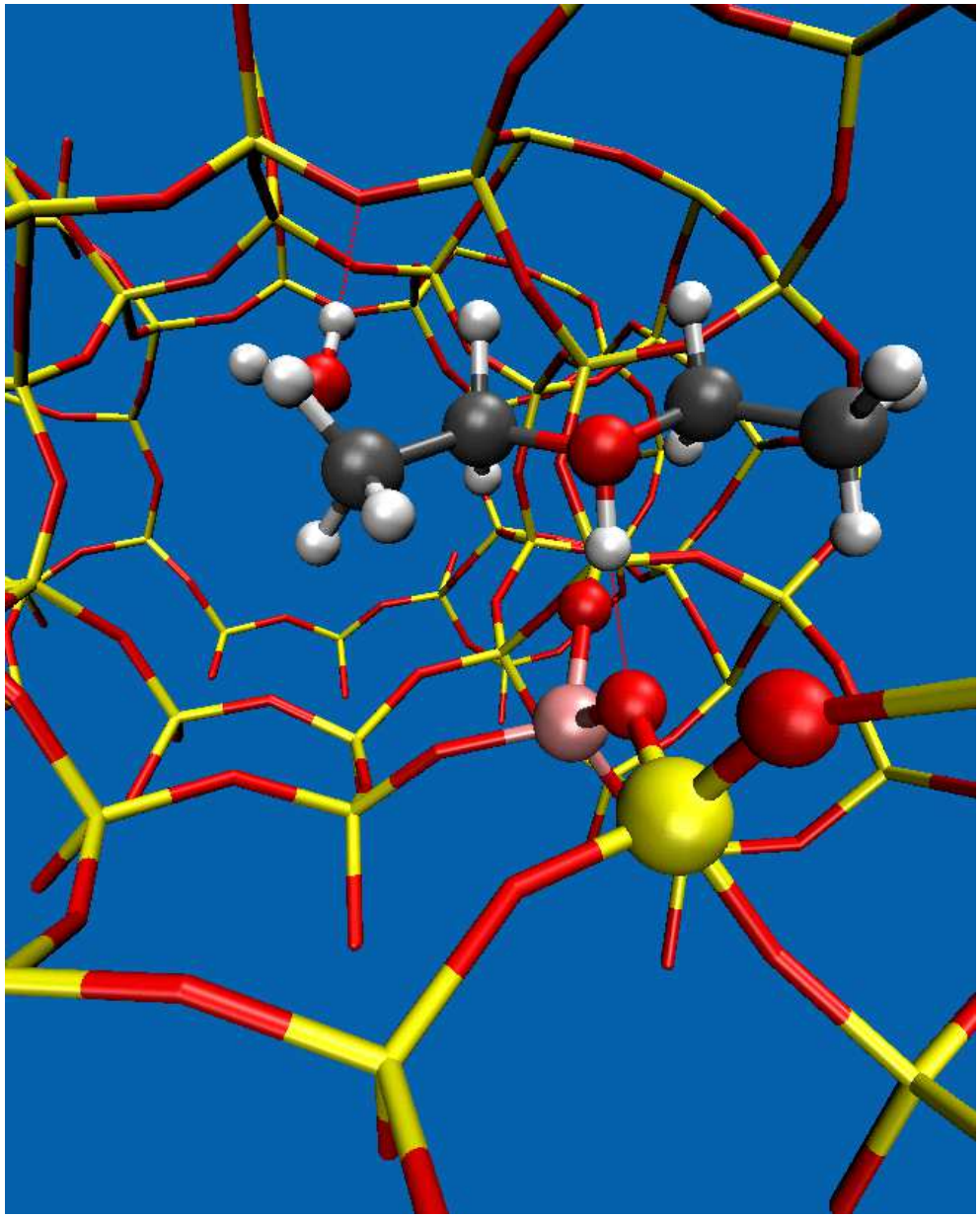
DEE*

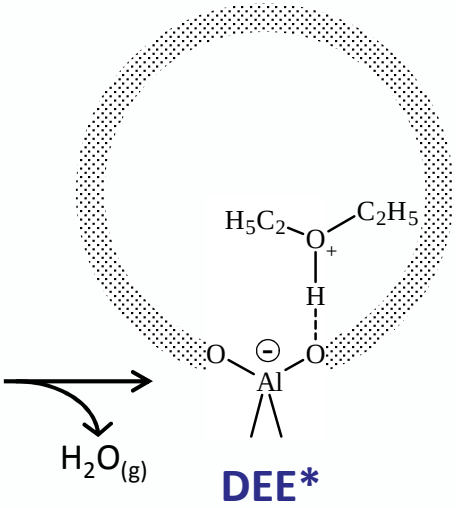
SN2

TS8



D2



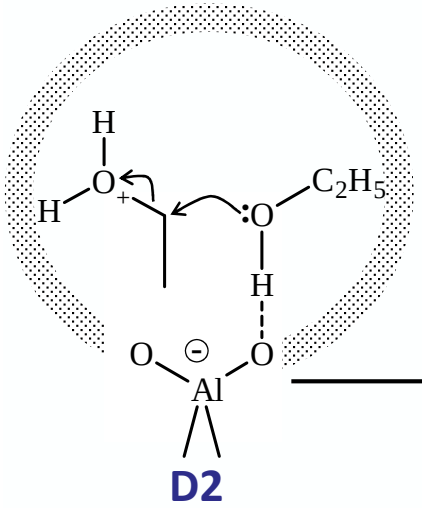


$H_2O_{(g)}$

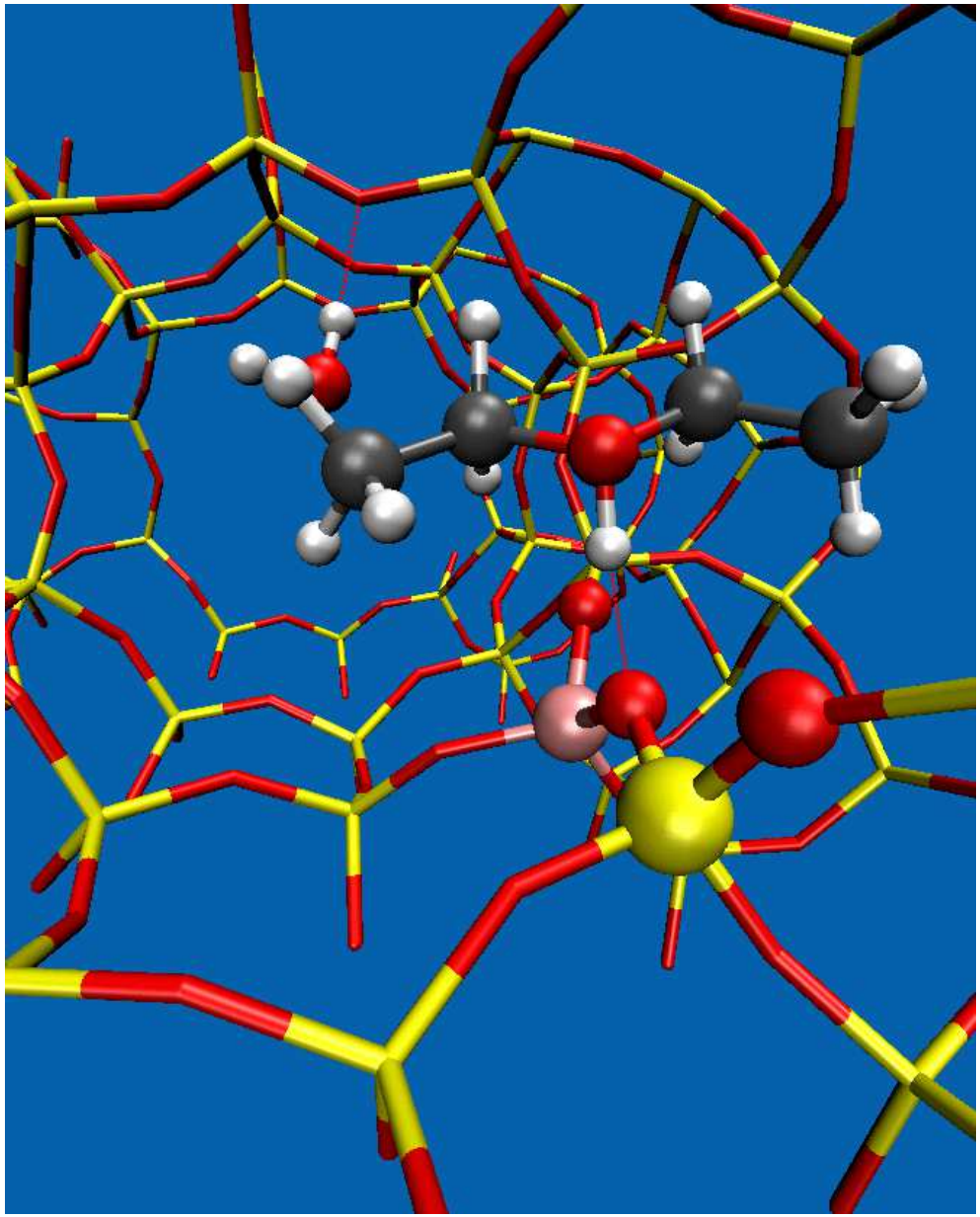
DEE*

SN2

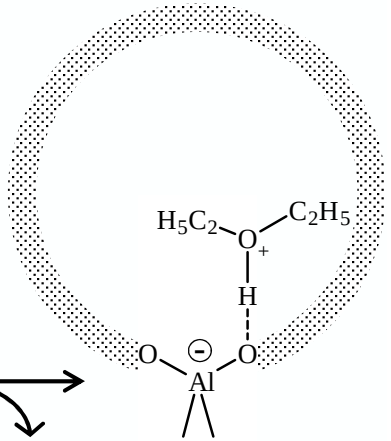
TS8



D2

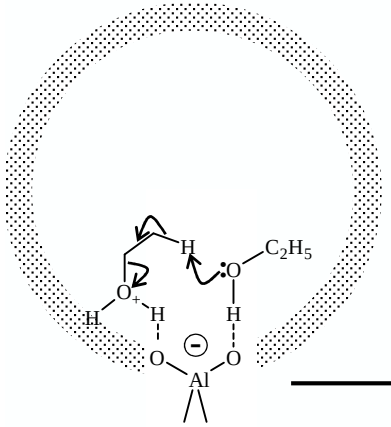


$H_2O_{(g)}$

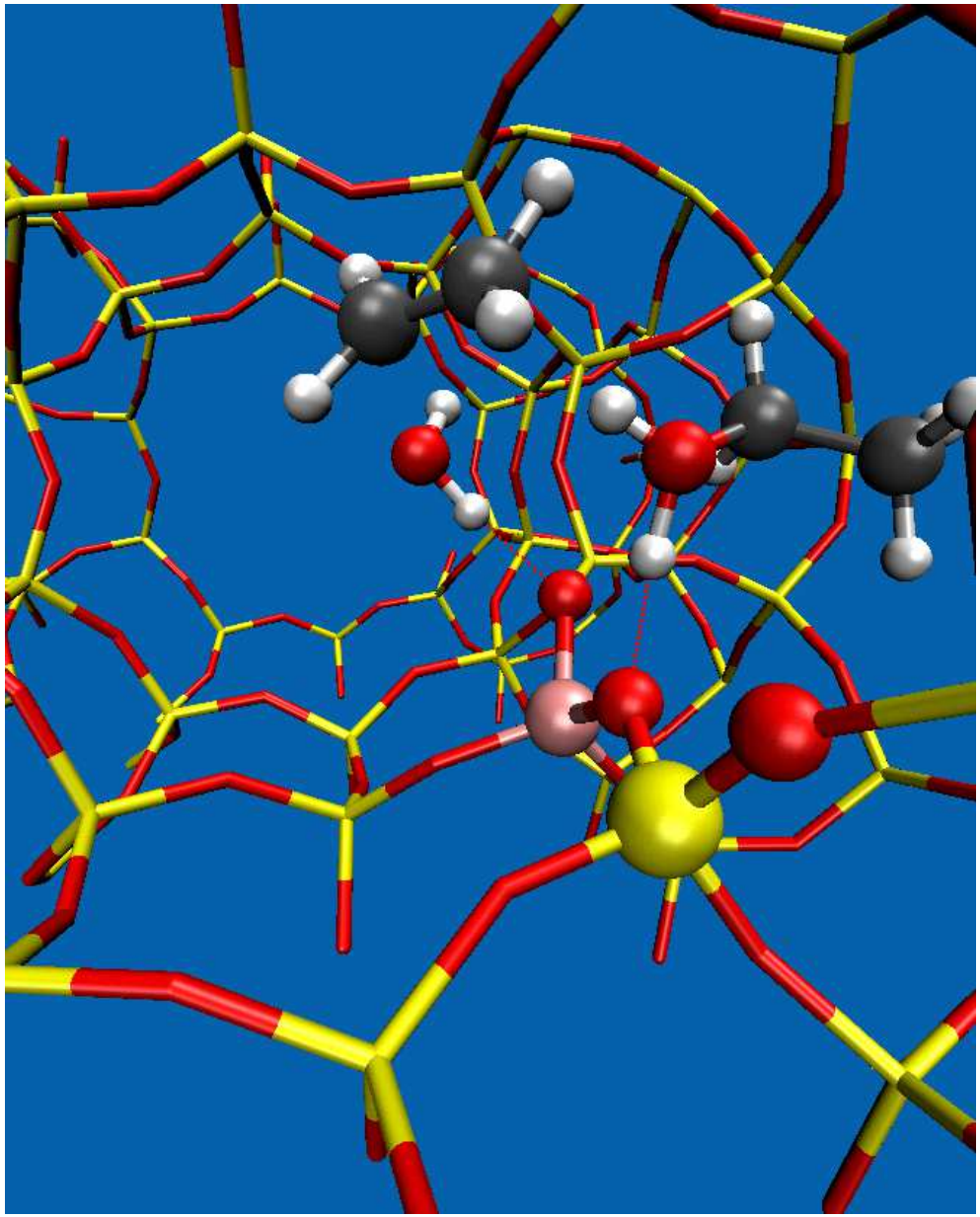


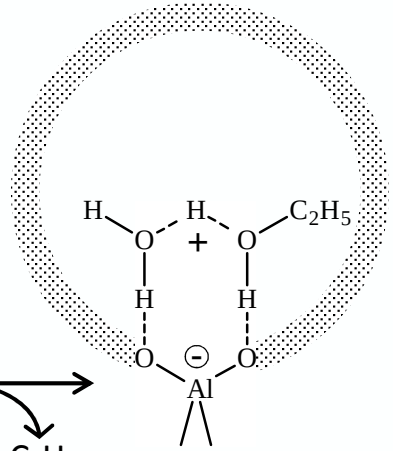
DEE*

Ethanol-assisted syn-elimination TS9



D2



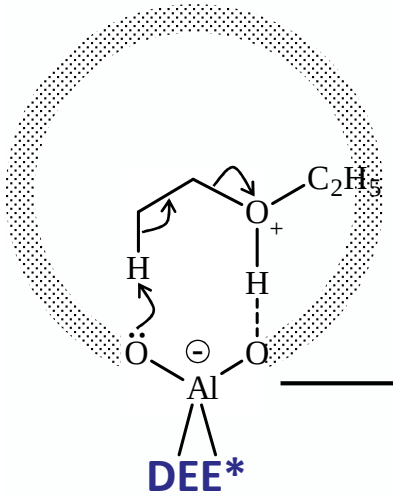


$C_2H_{4(g)}$

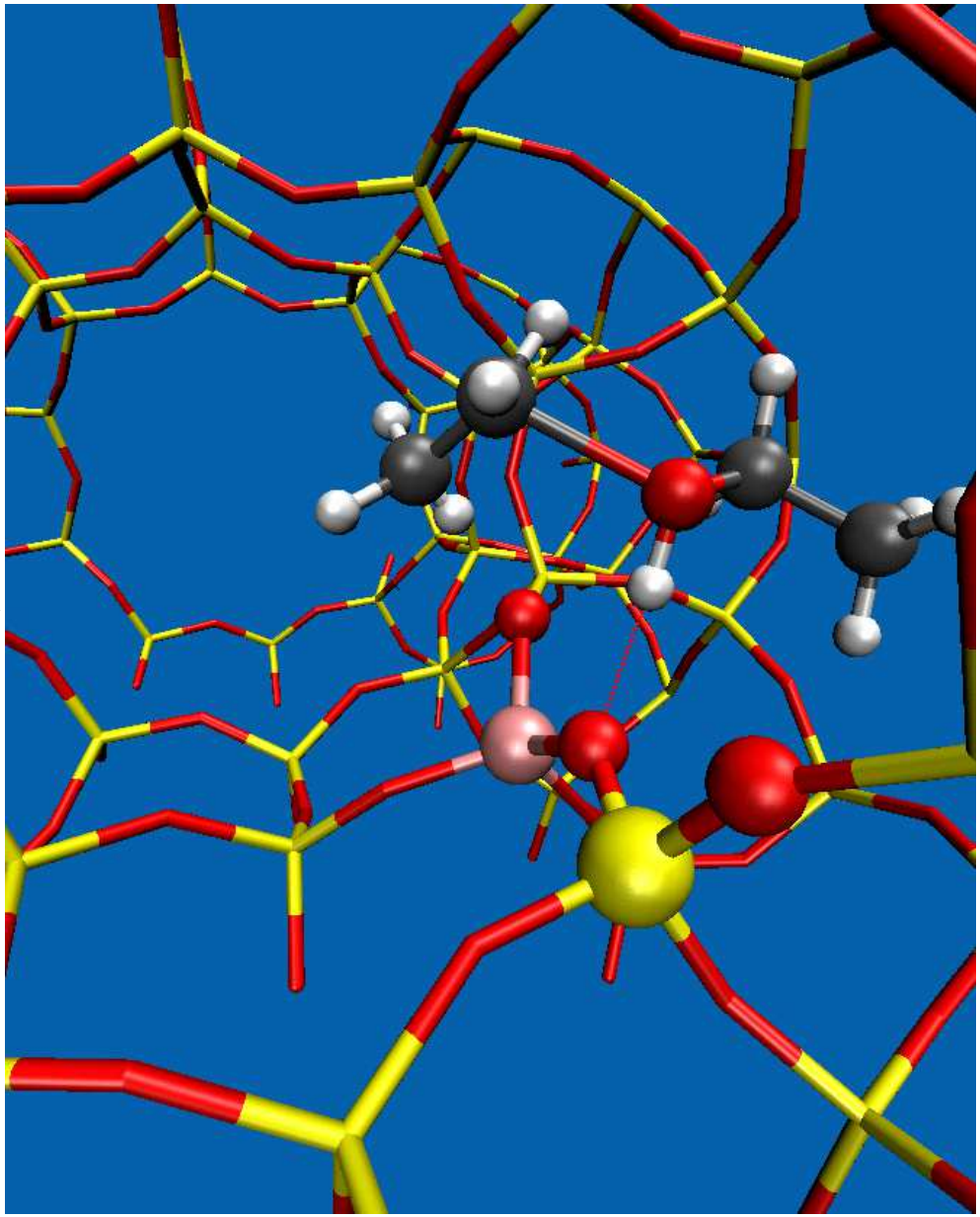
C2

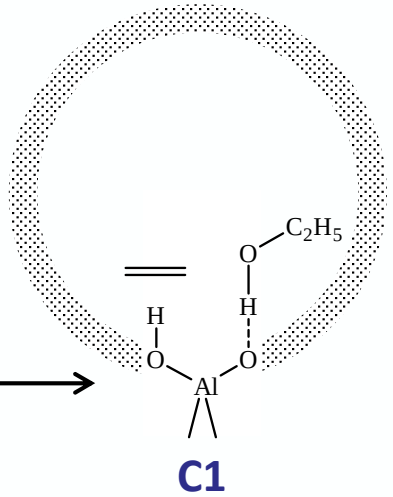
Syn elimination

TS10



DEE*

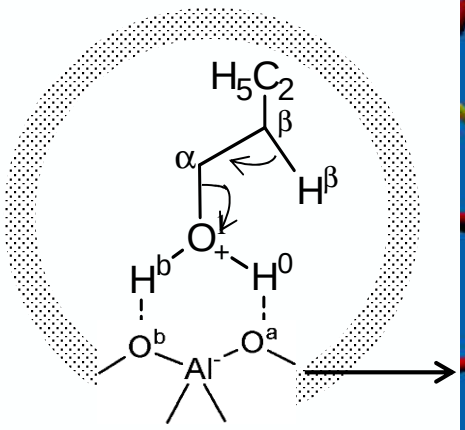




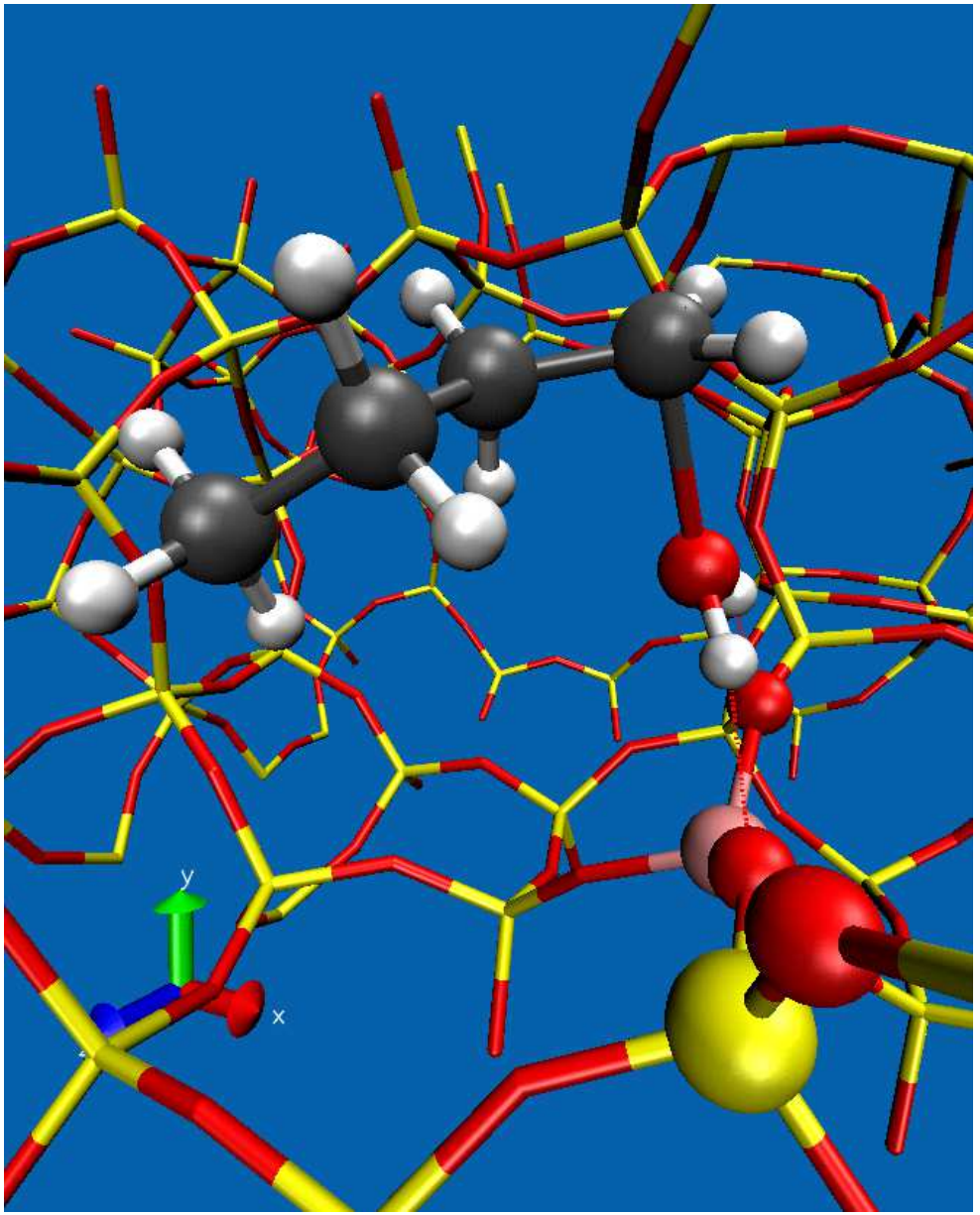
C1

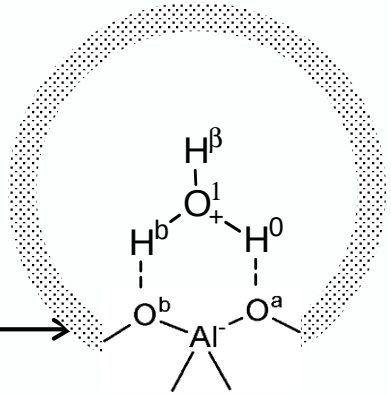
E1 like

TS1



M1

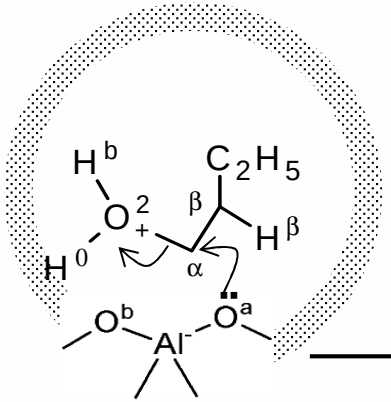




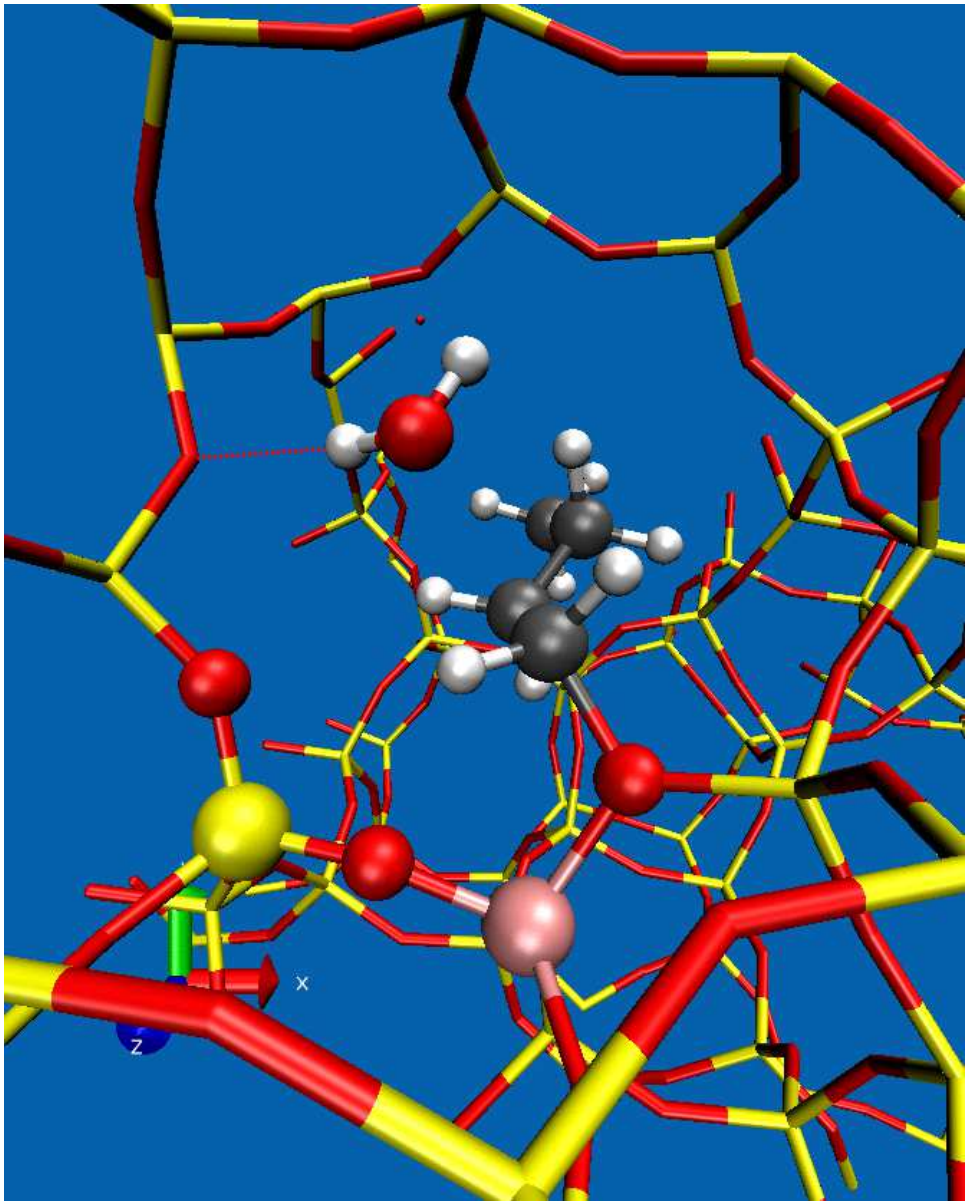
W

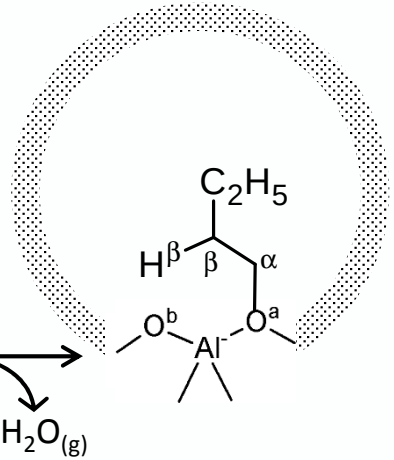
SN2

TS2



M2



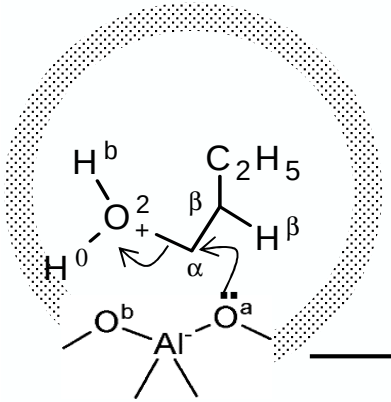


$H_2O_{(g)}$

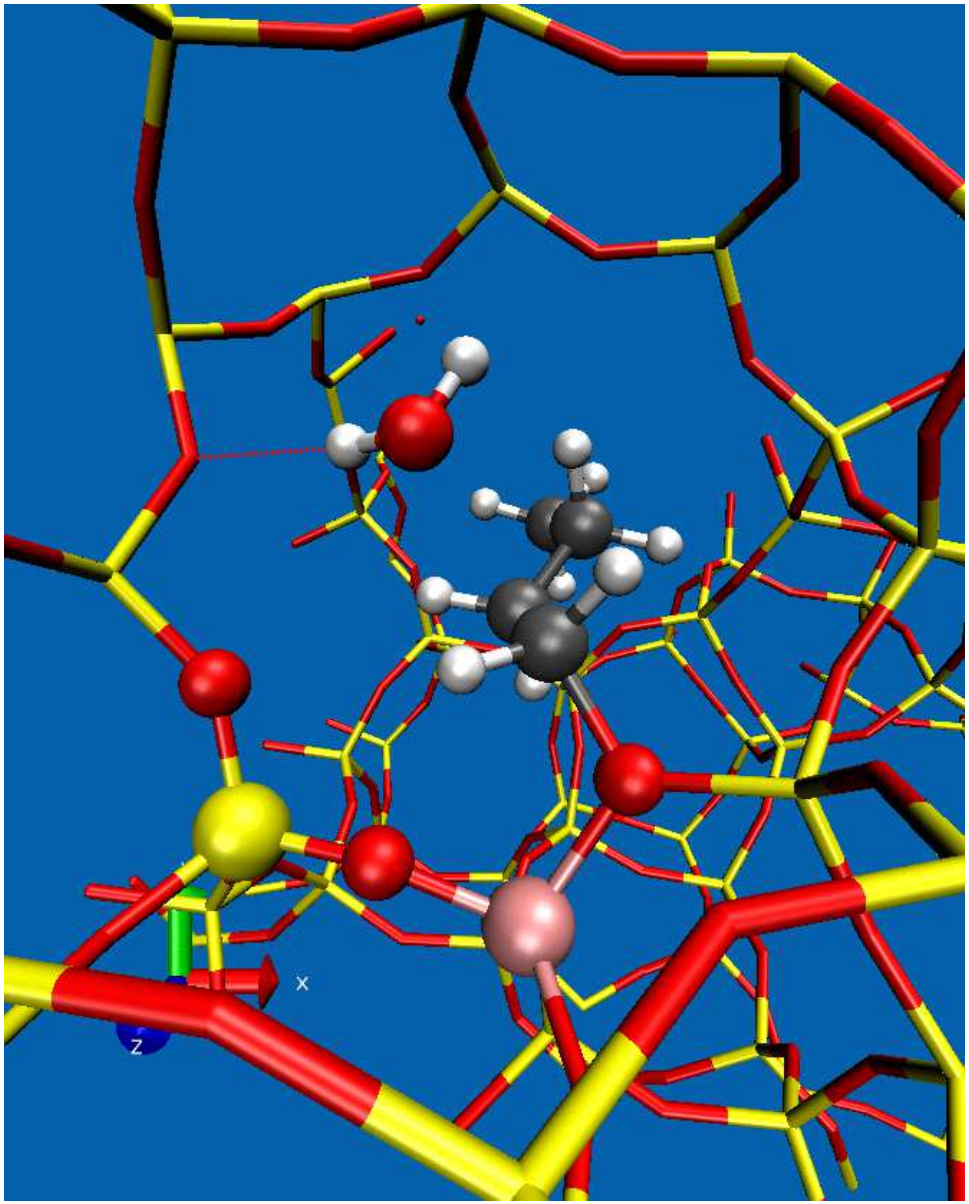
1-butoxide

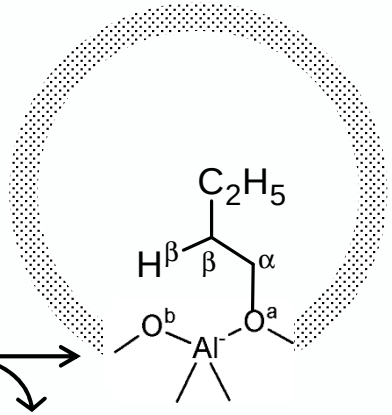
SN2

TS2



M2



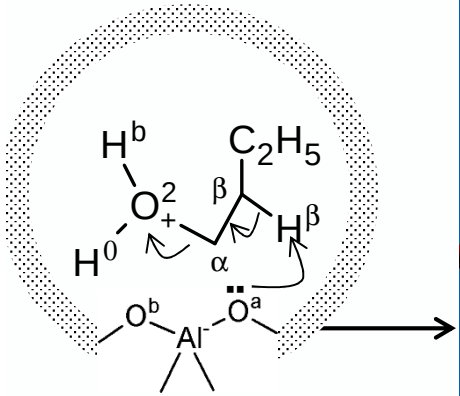


$H_2O_{(g)}$

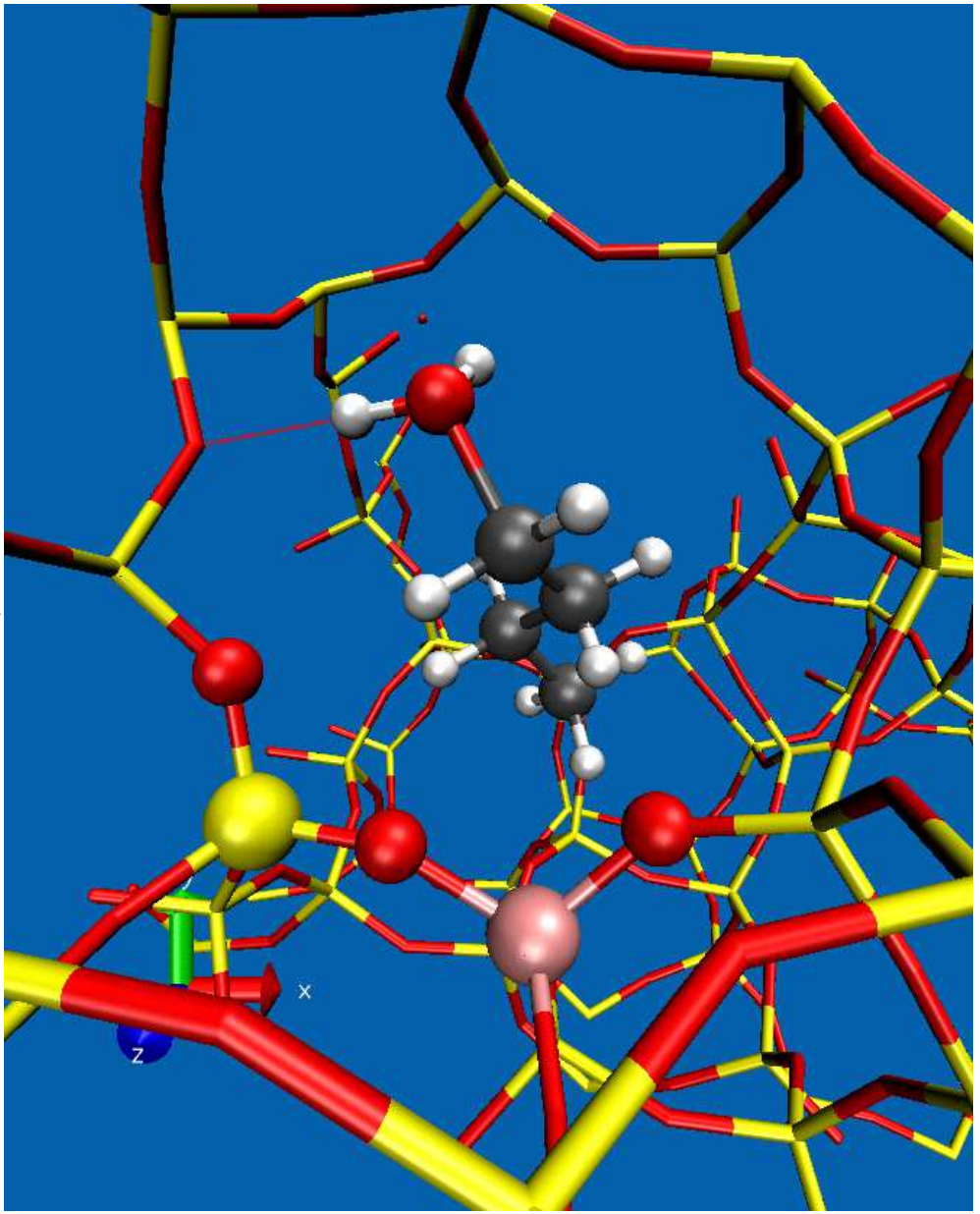
1-butoxide

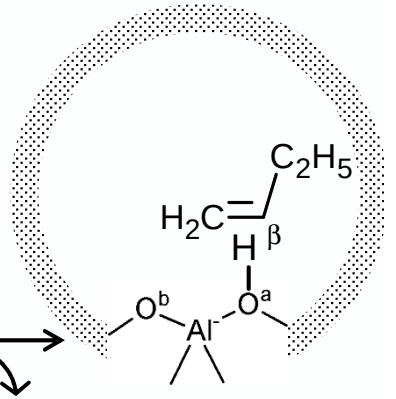
E2 (anti elimination)

TS3



M2



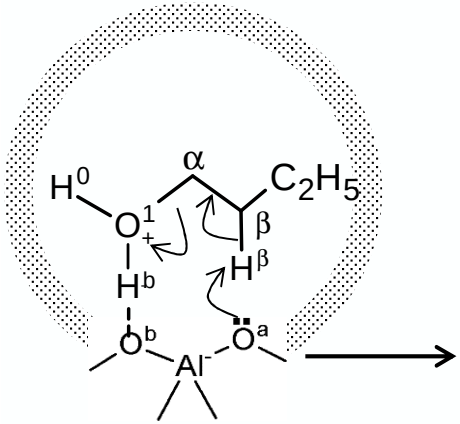


$H_2O_{(g)}$

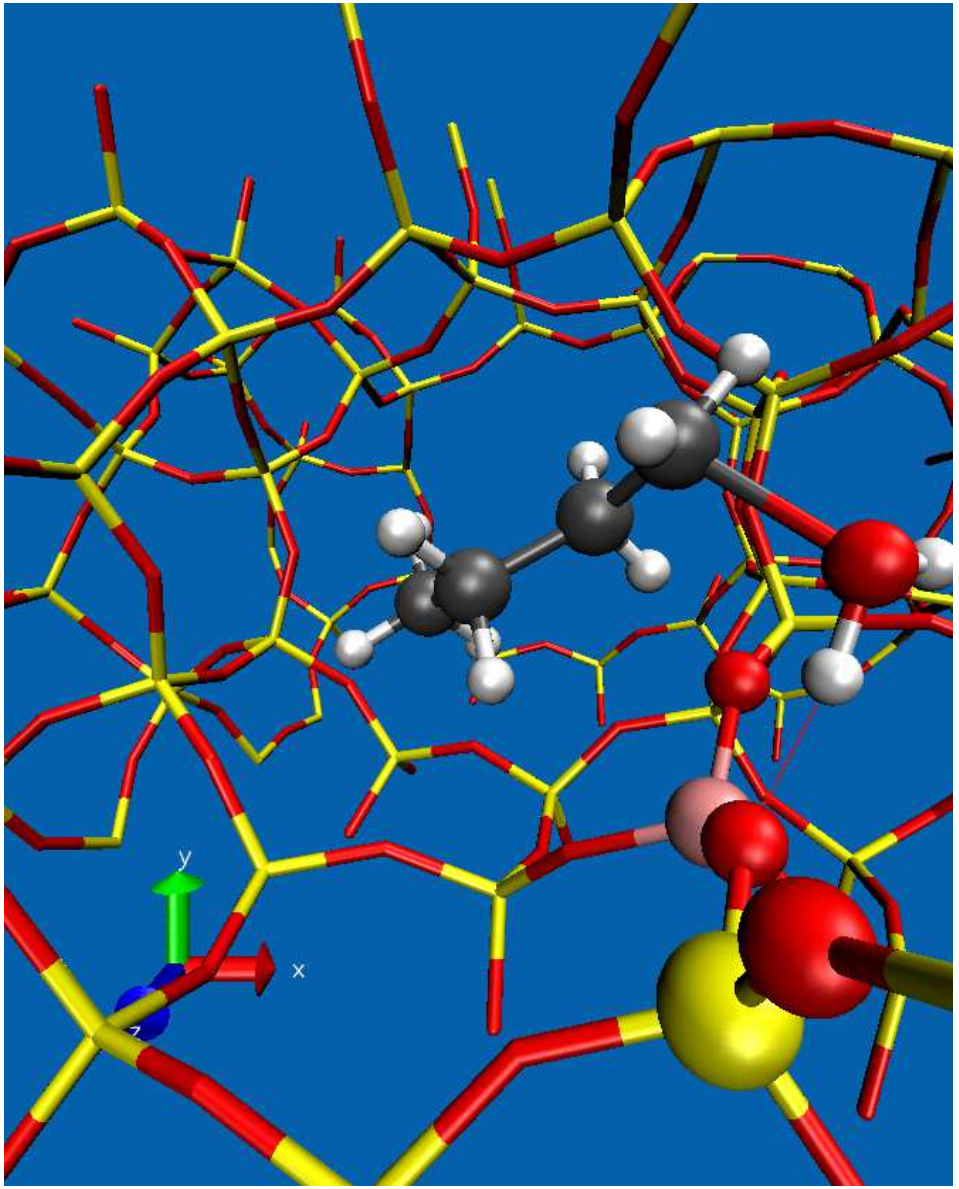
1-butene

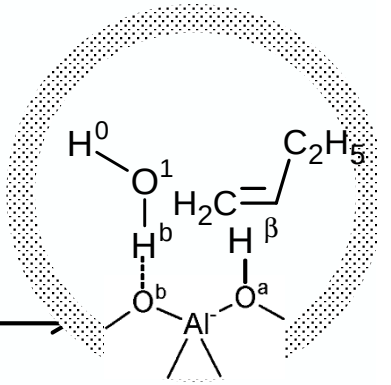
Syn elimination

TS4



M2

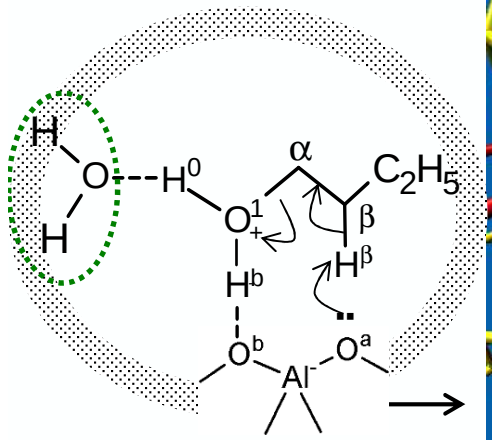




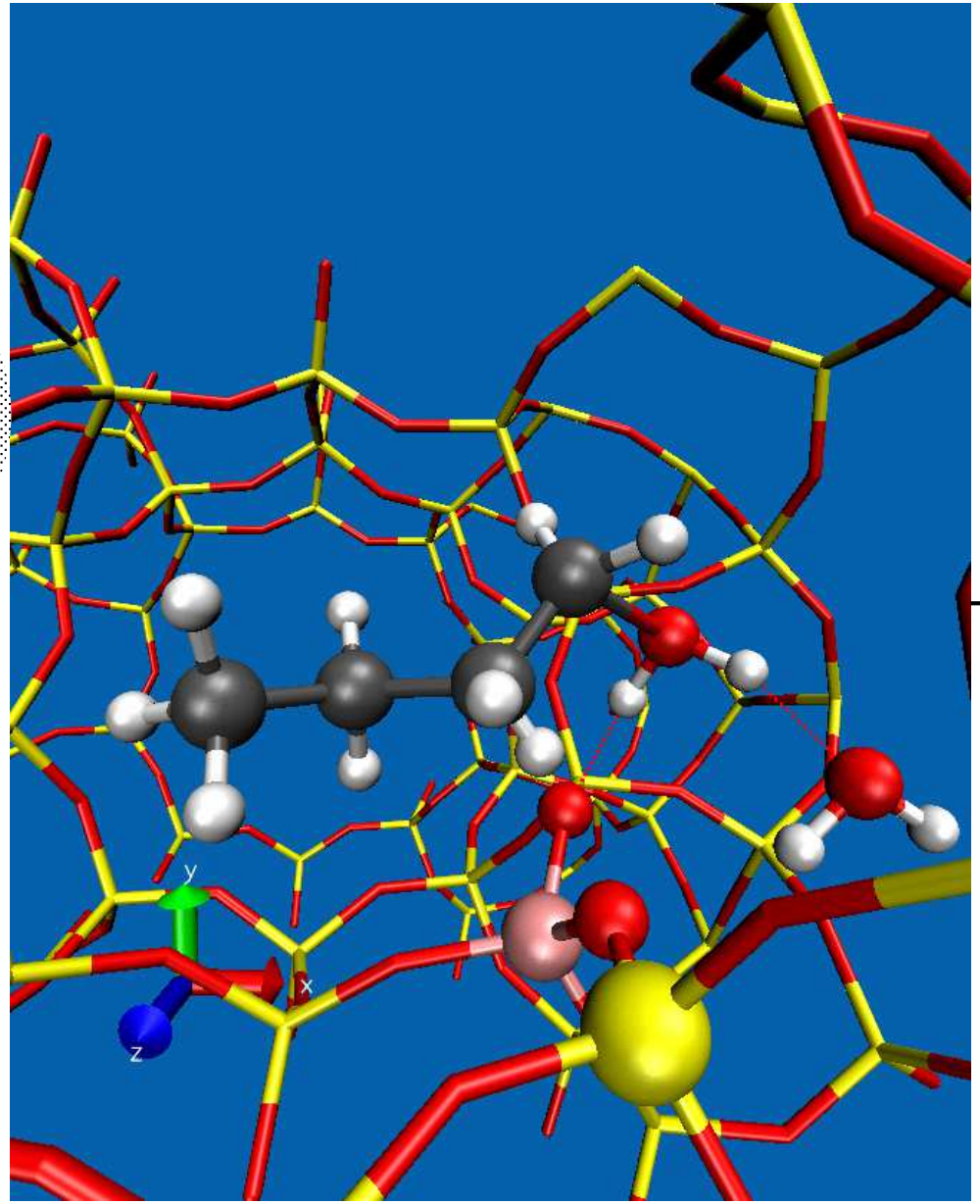
C3

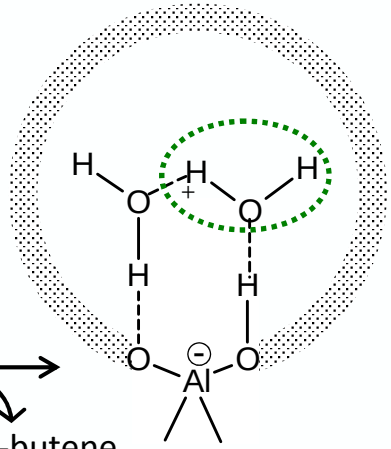
Syn elimination

TS5



C2

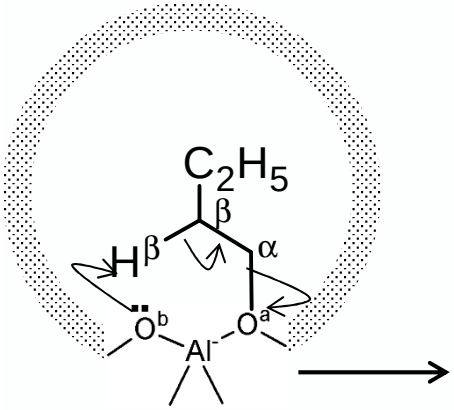




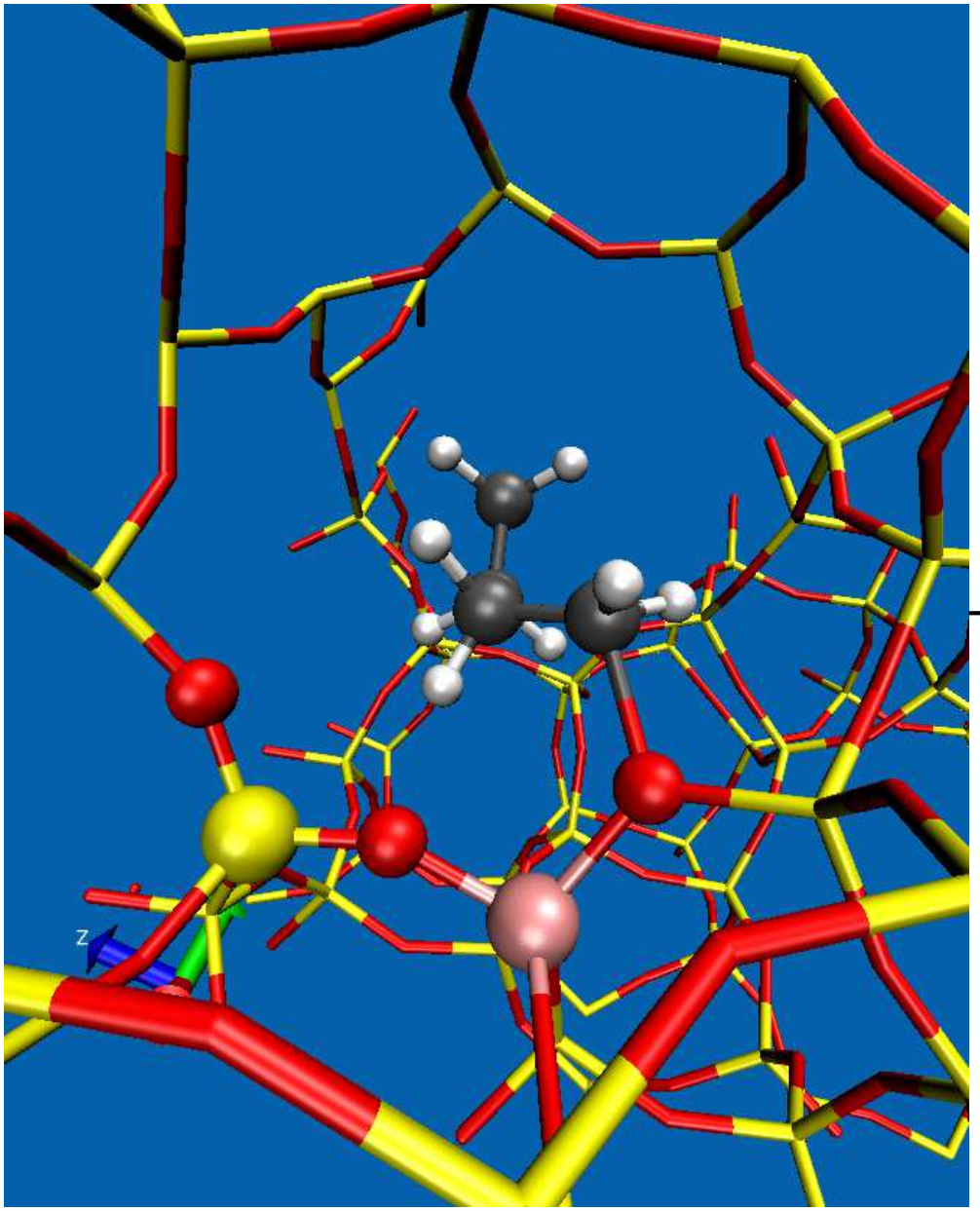
1-butene$_{(g)}$

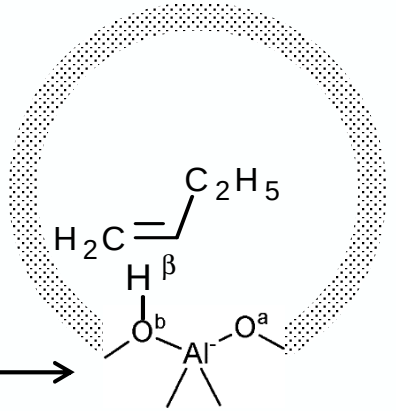
2W

TS6



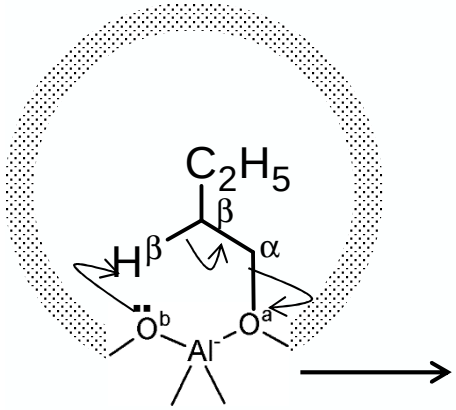
1-butoxide



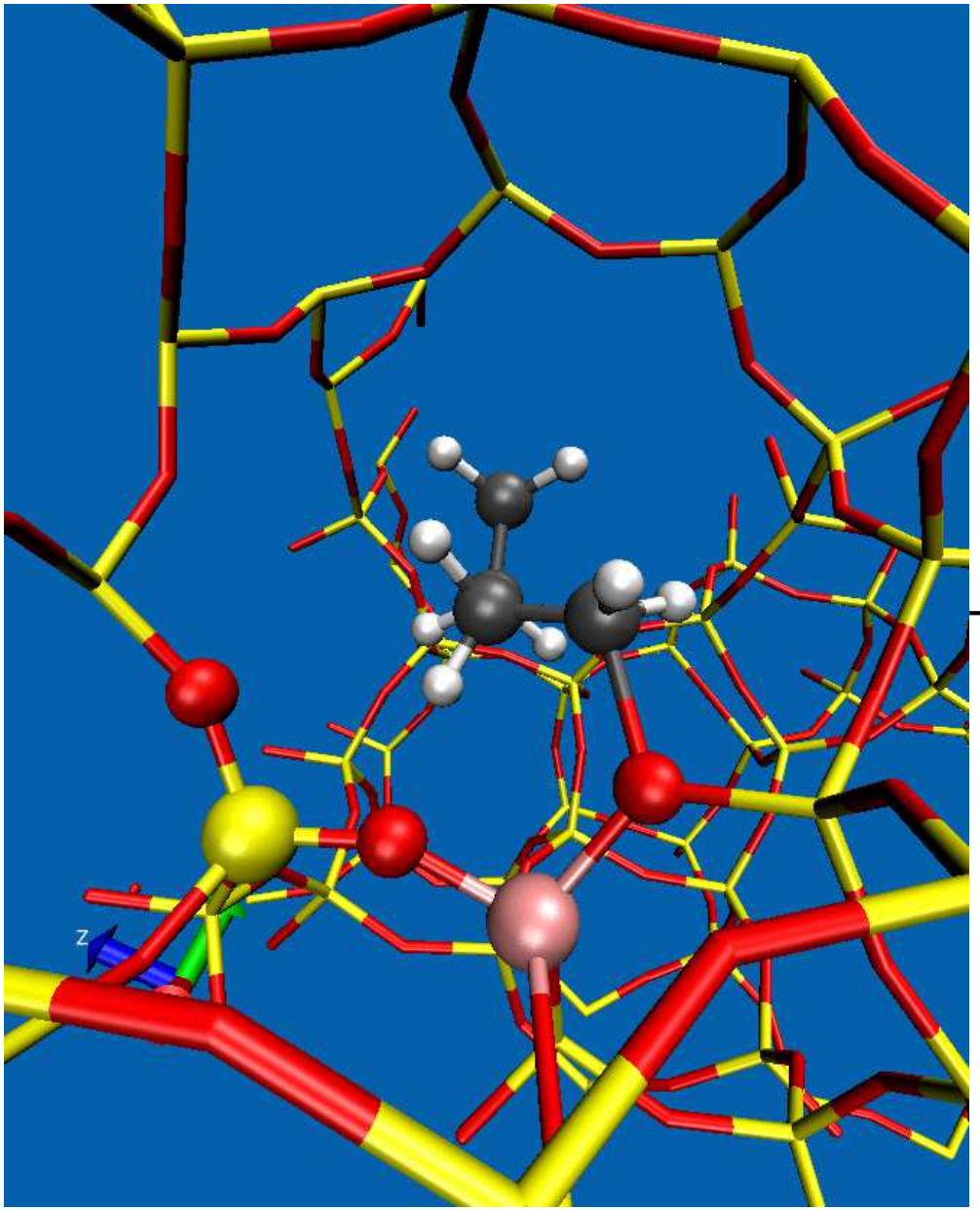


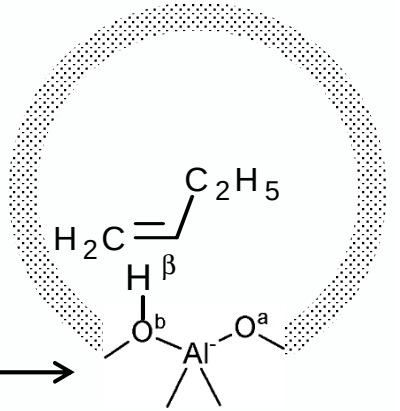
1-butene*

TS6



1-butoxide

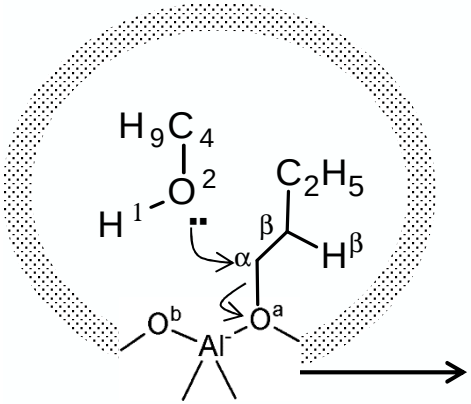




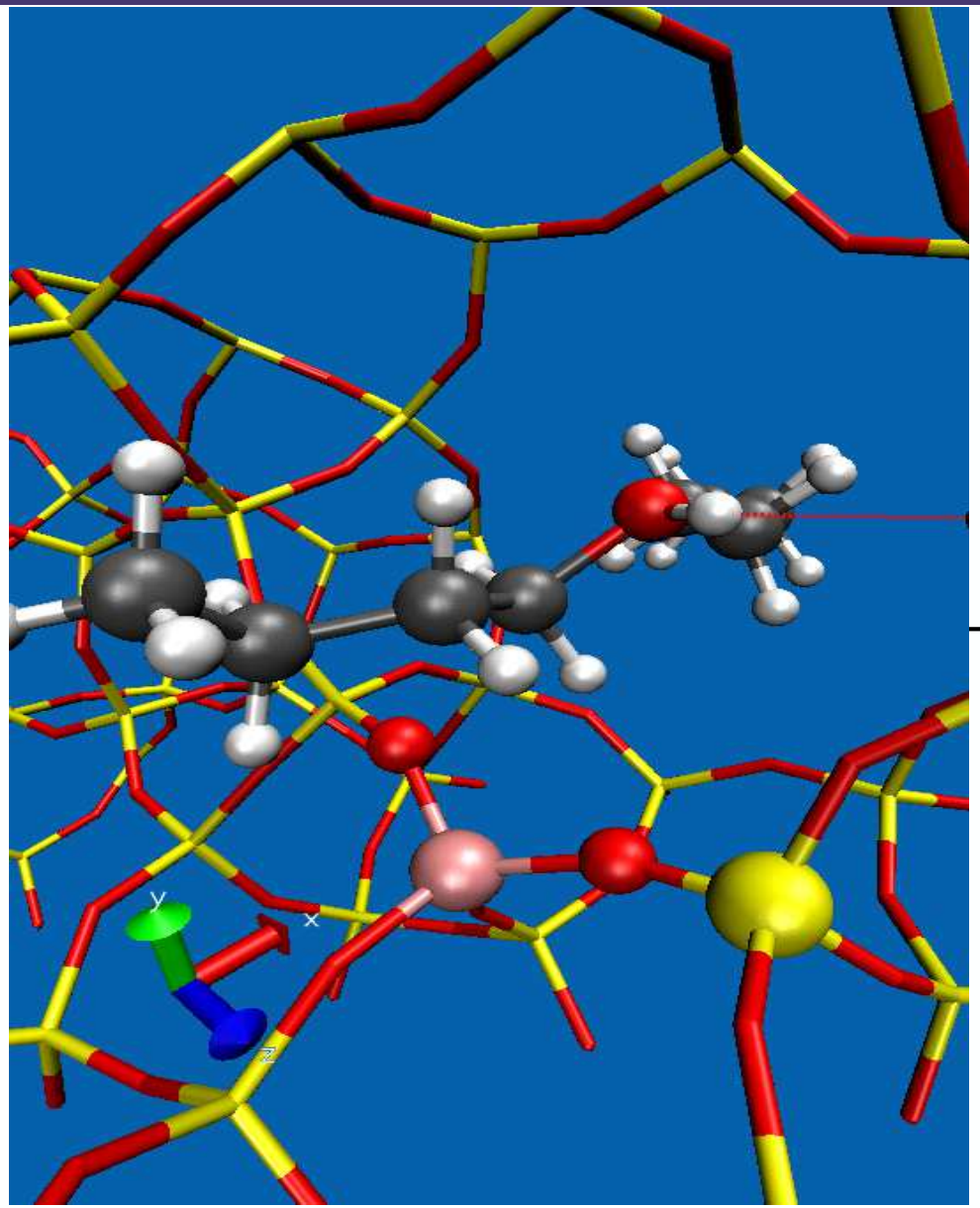
1-butene*

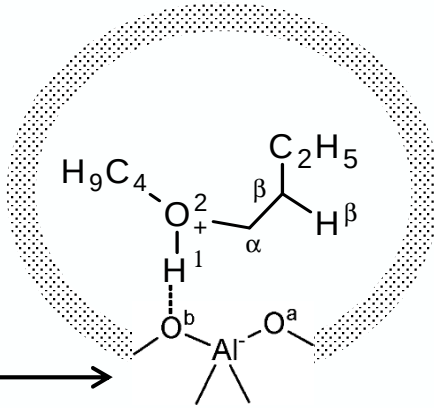
SN2

TS7



1-butoxide +
1-butanol (g)

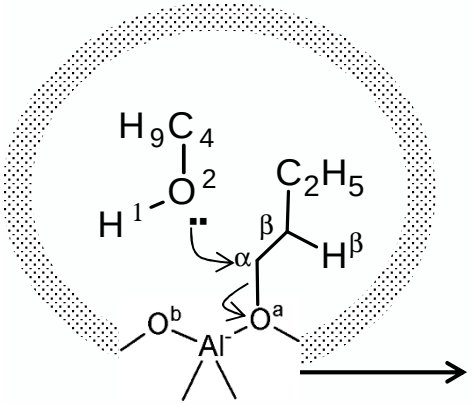




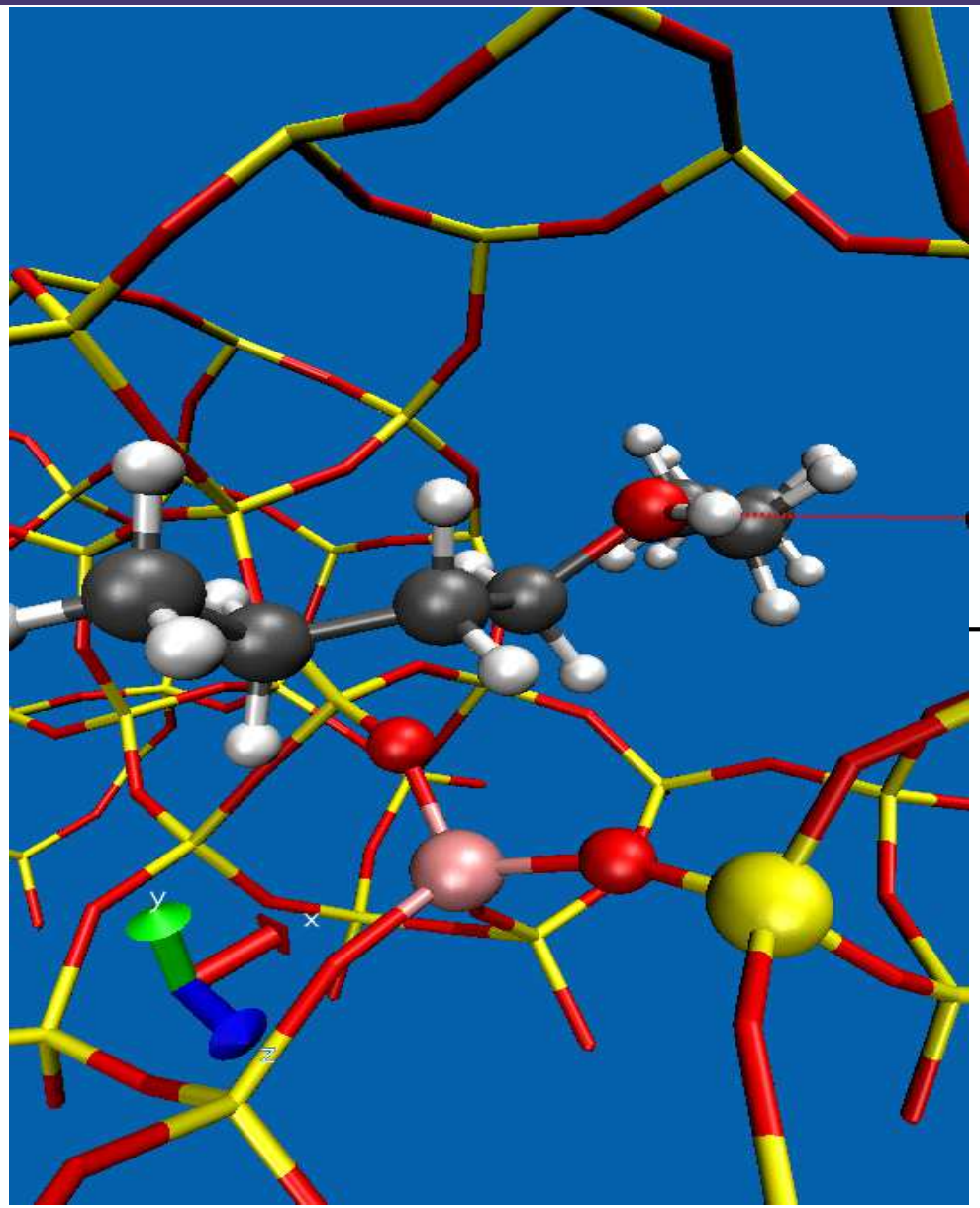
DBE*

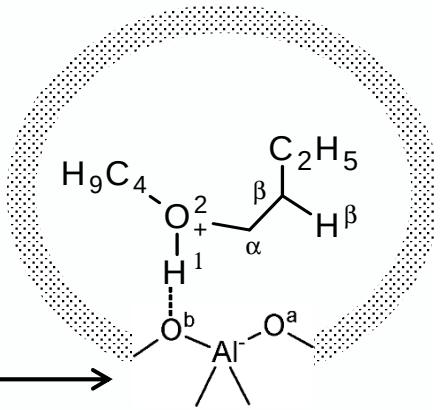
SN2

TS7



1-butoxide +
1-butanol (g)

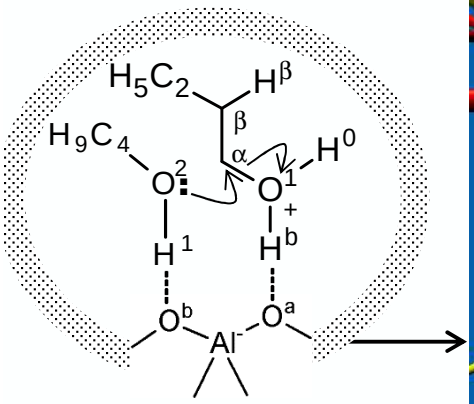




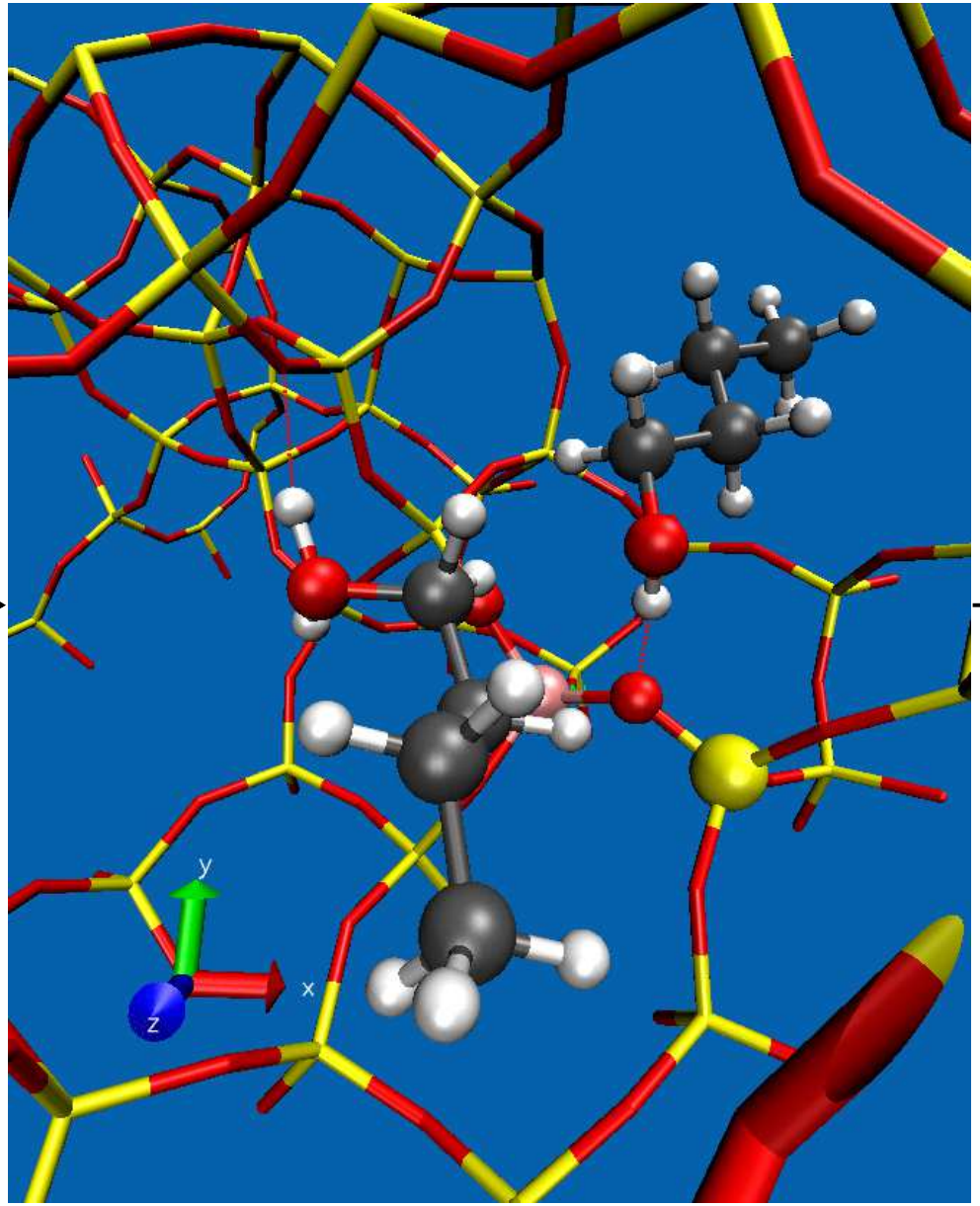
DBE*

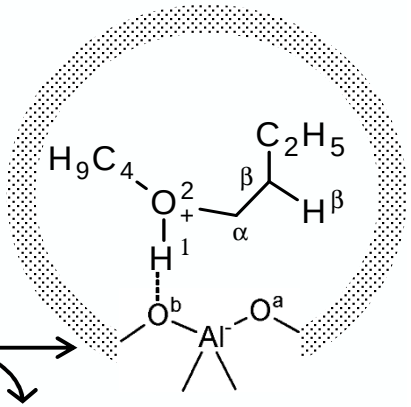
SN2

TS8



D2



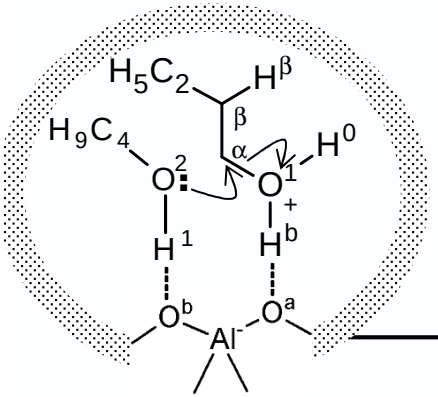


$H_2O_{(g)}$

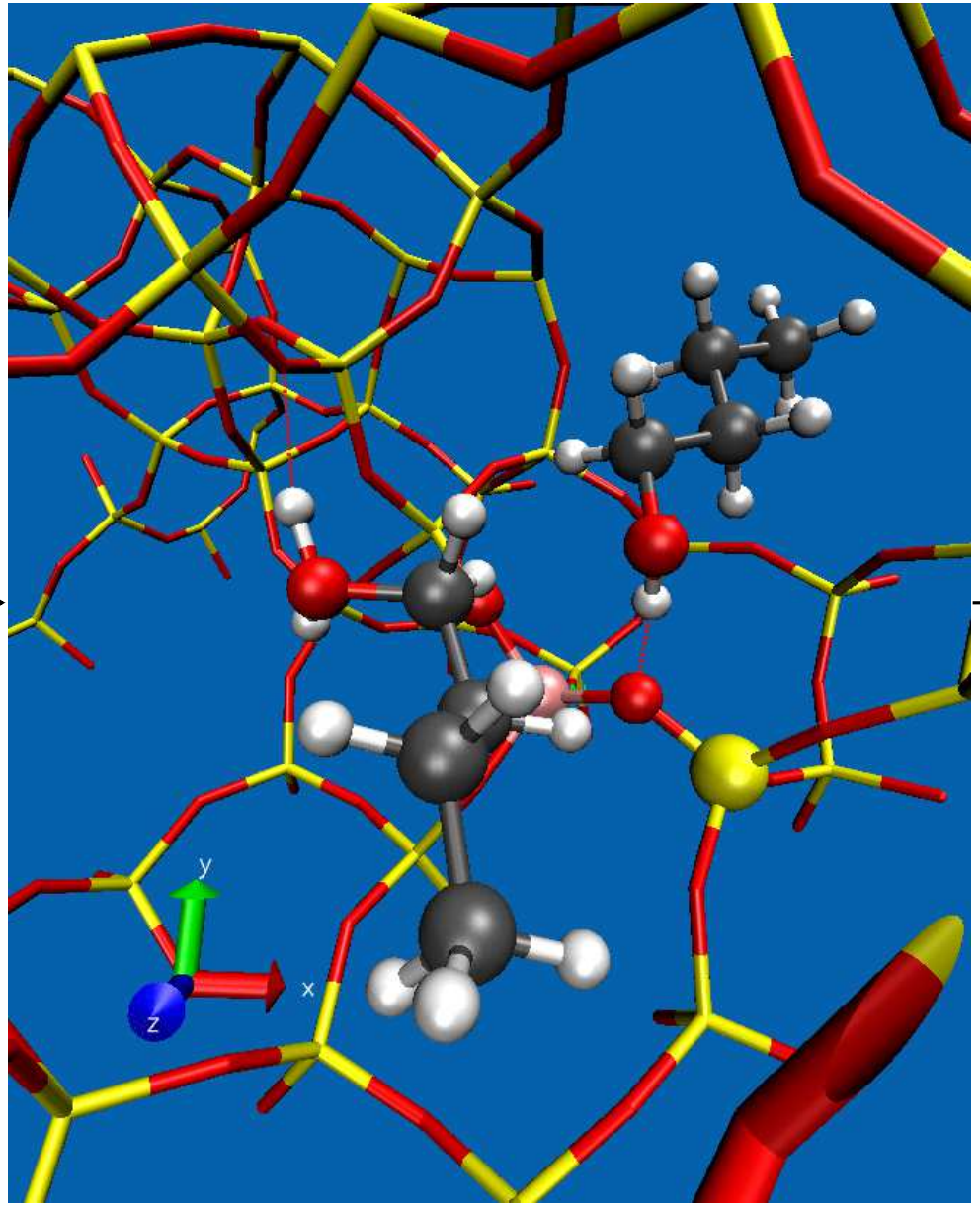
DBE*

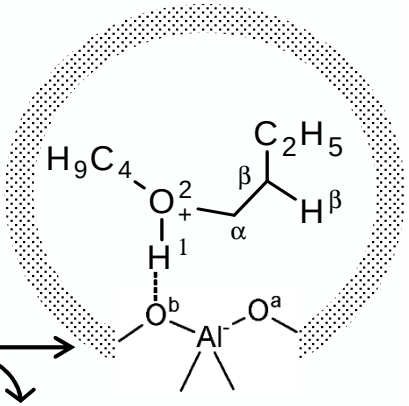
SN2

TS8



D2

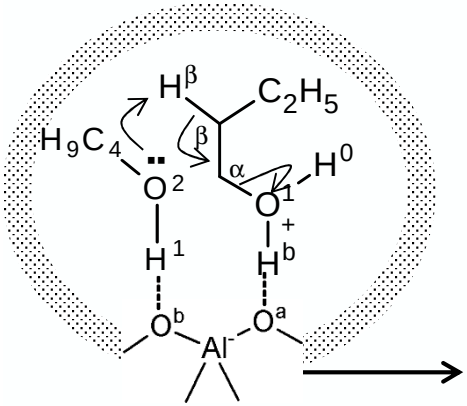




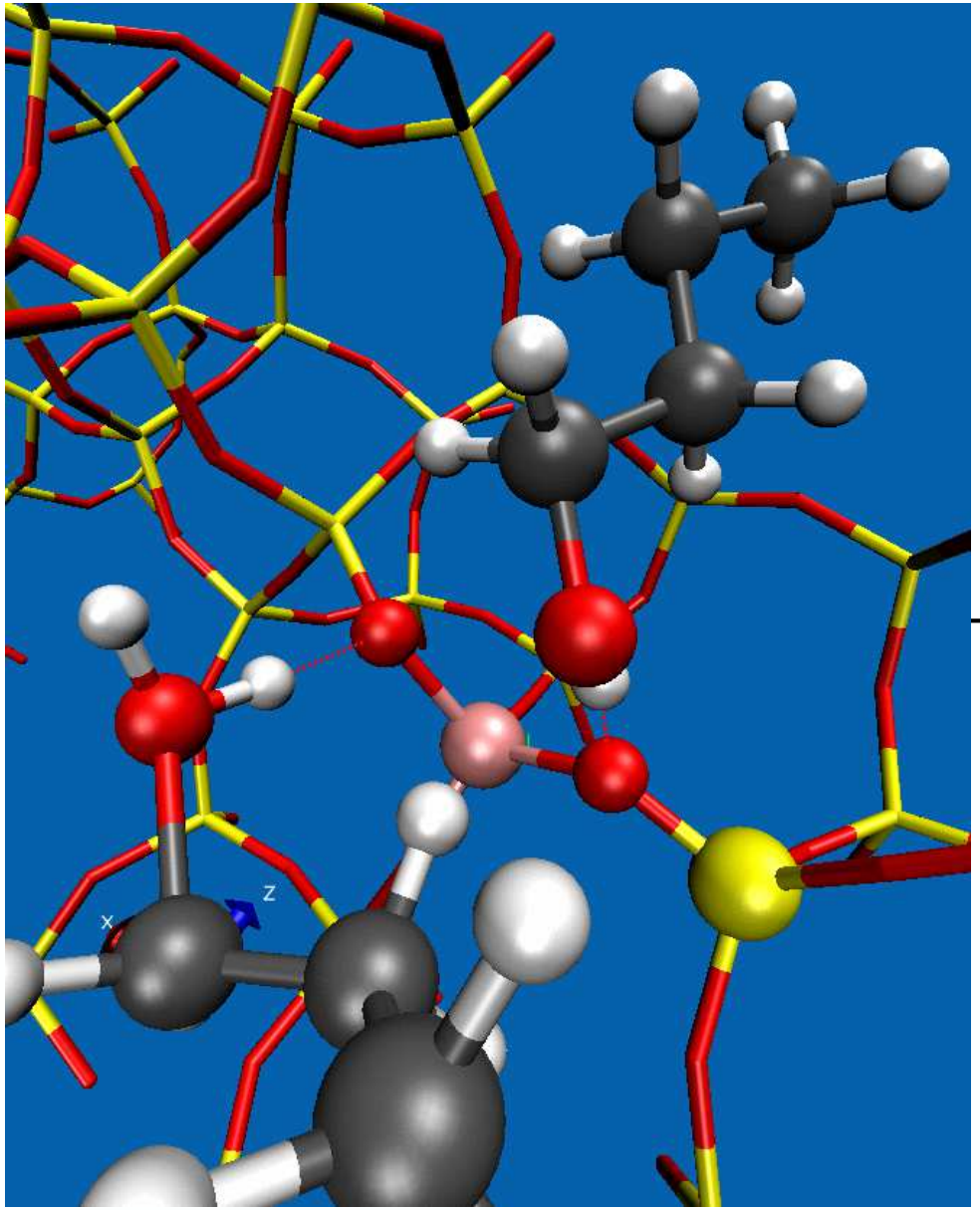
$H_2O_{(g)}$

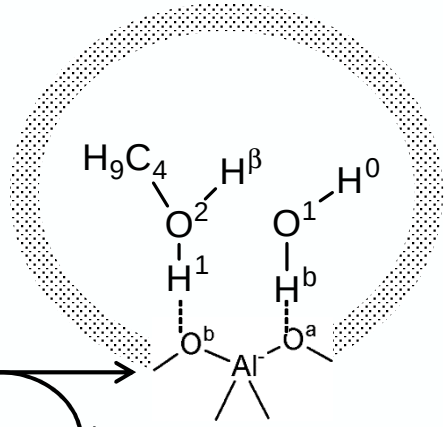
DBE*

butanol-assisted syn-elimination TS9



D2

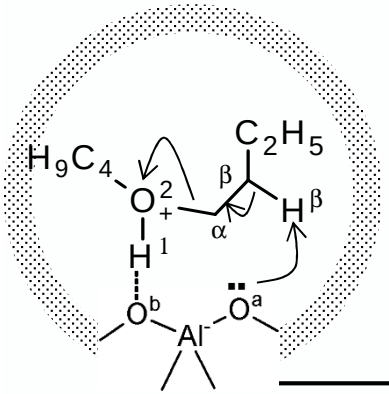




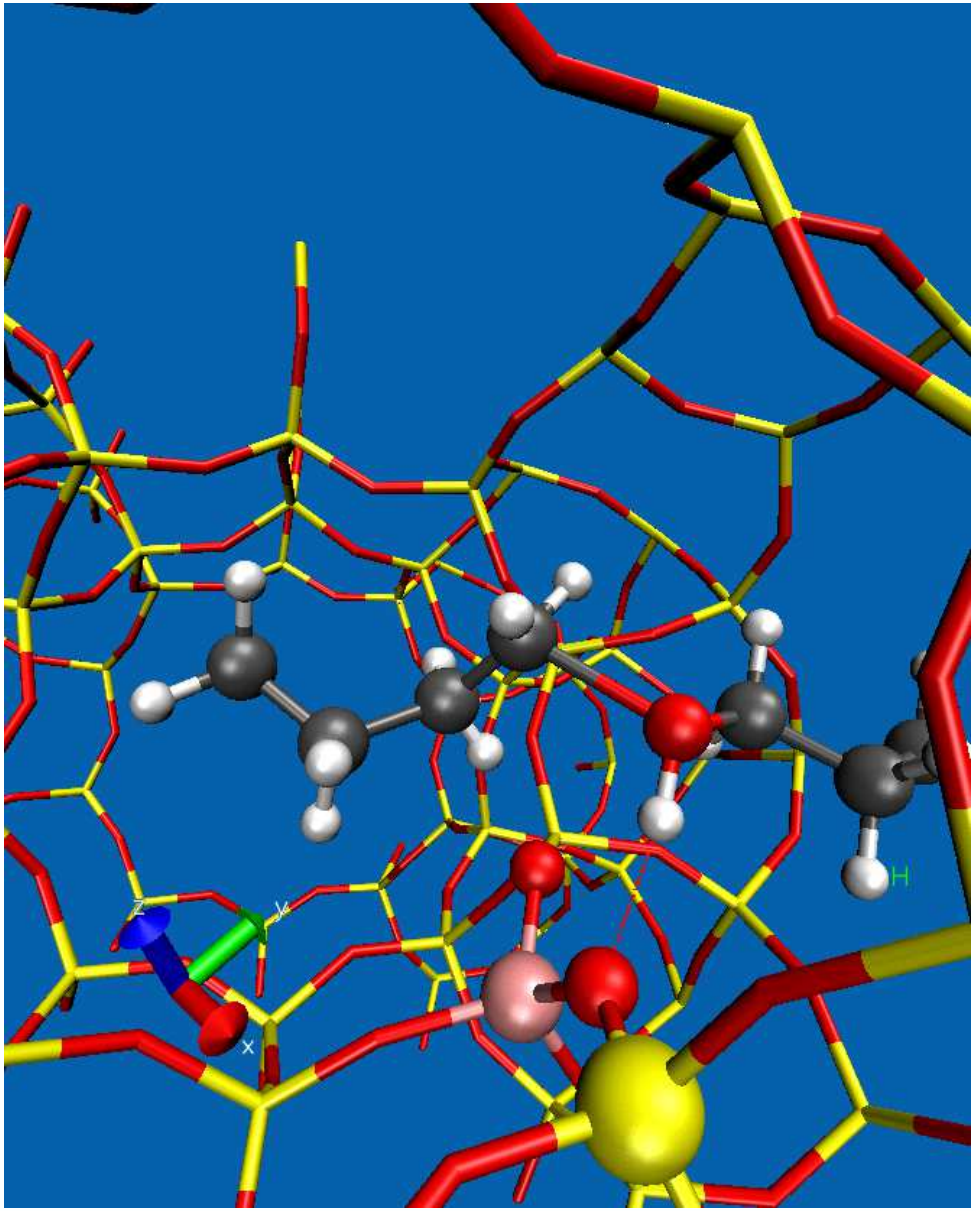
1-butene$_{(g)}$ **C2**

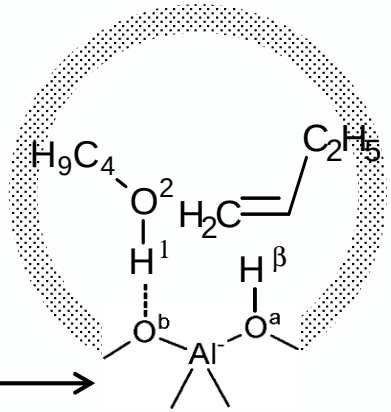
Syn elimination

TS10



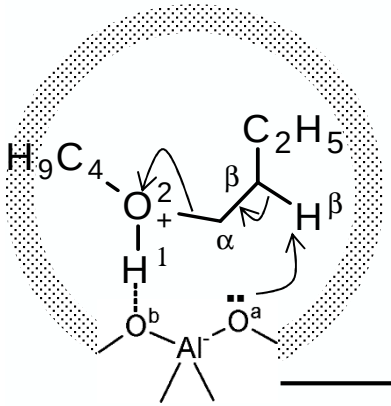
DBE*





C1

TS11



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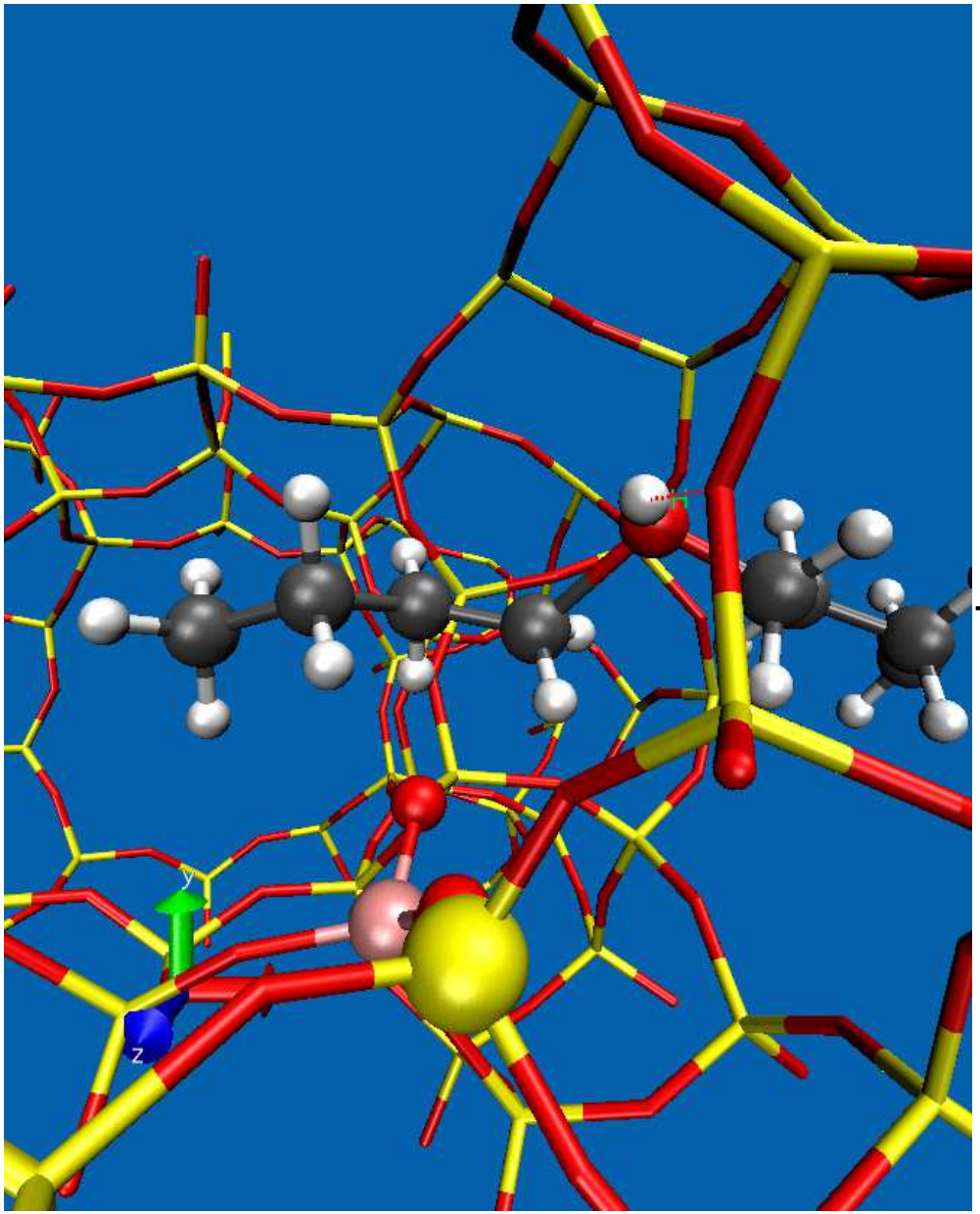
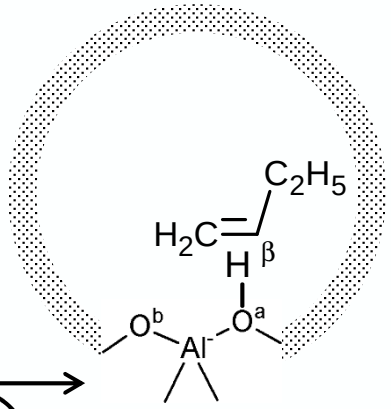


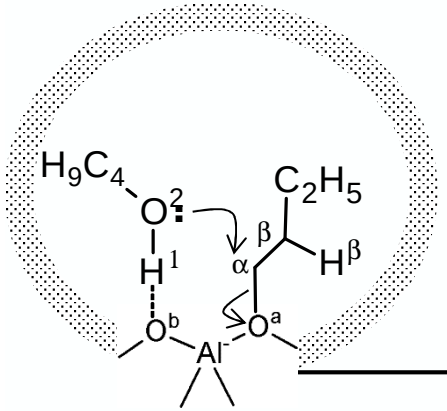


1-butene*

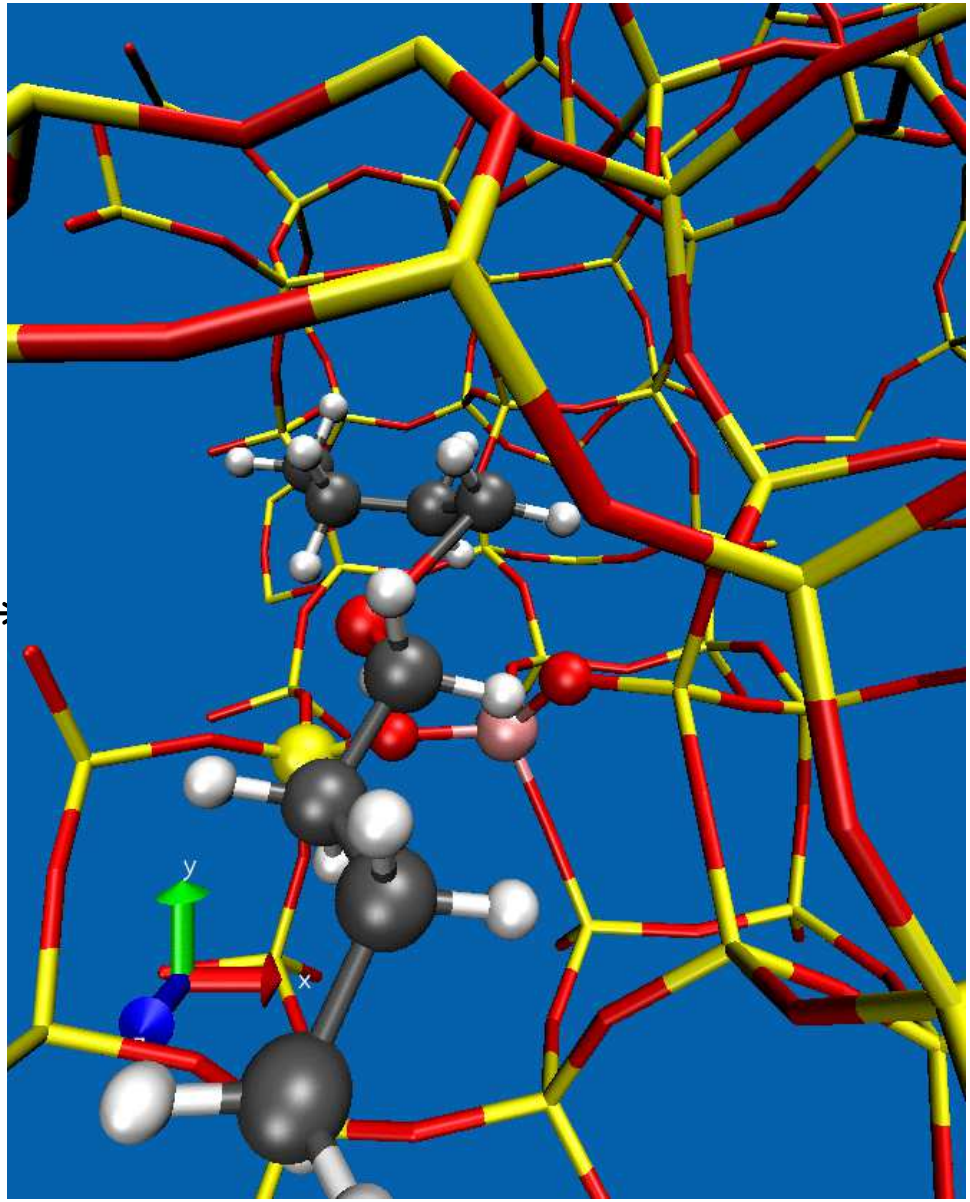
$1\text{-BuOH}_{(g)}$

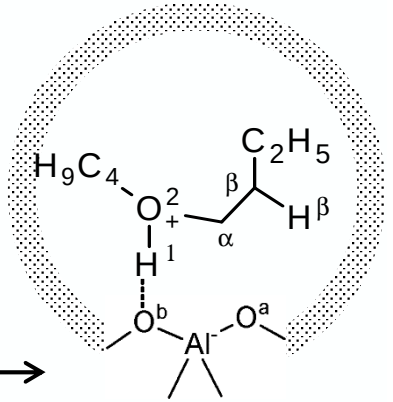
SN1

TS12



1-butoxide +
1-butanol *

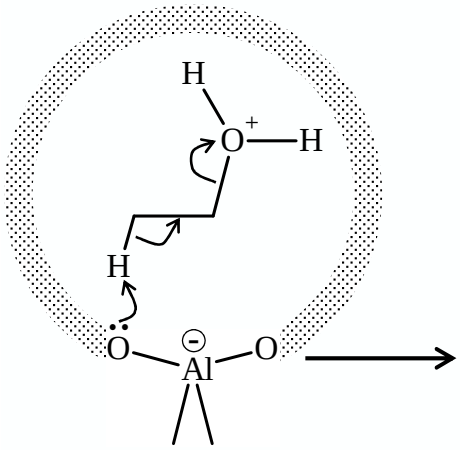




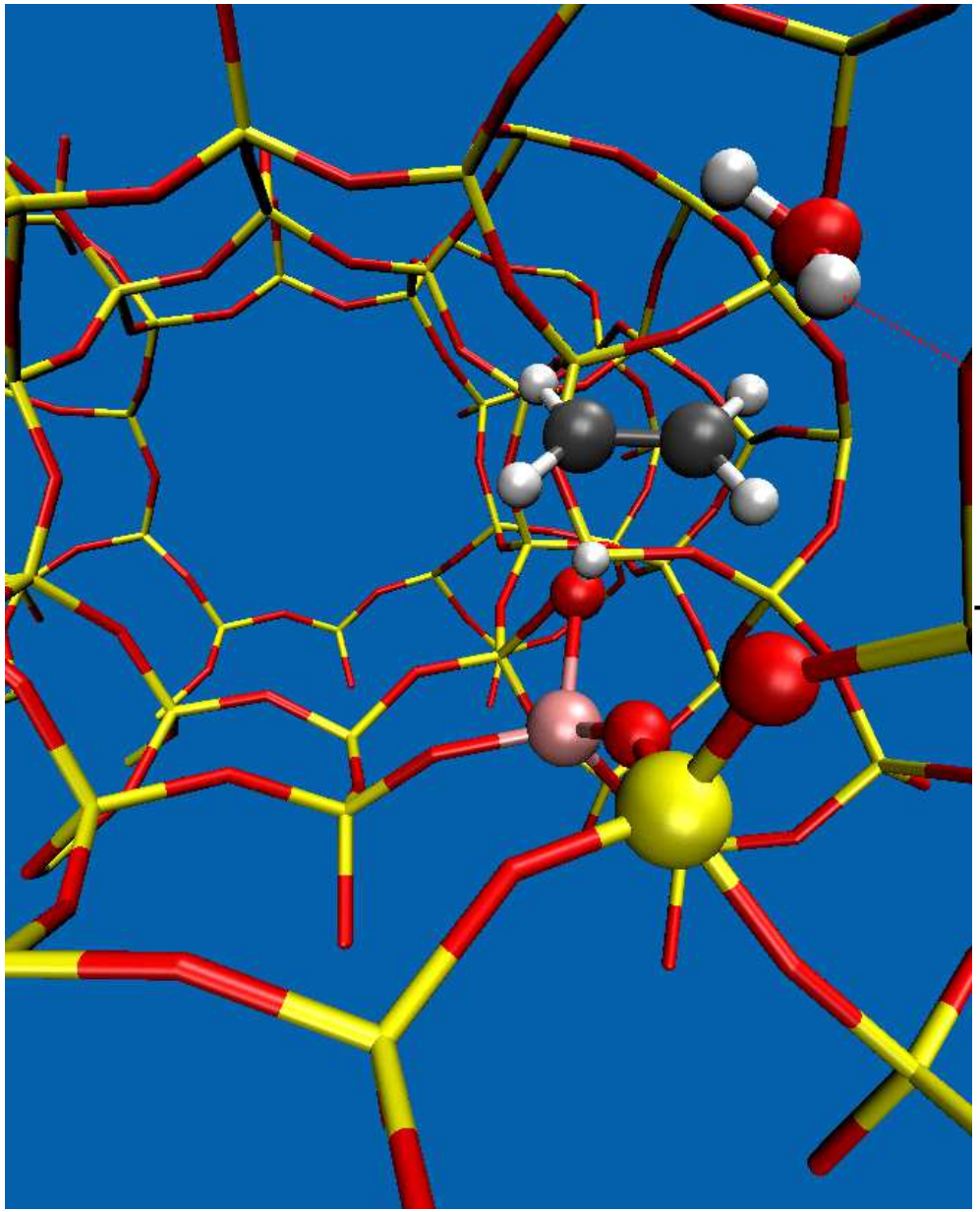
DBE*

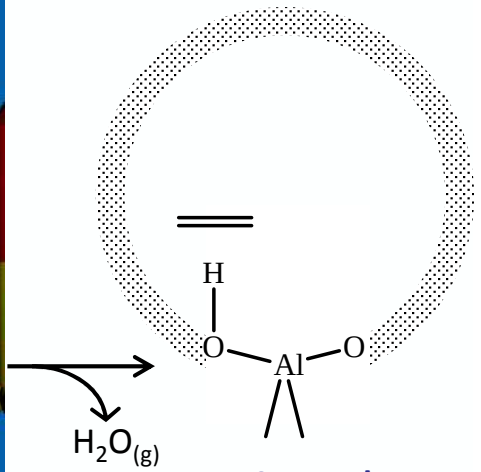
E2 (anti elimination)

TS3



M2



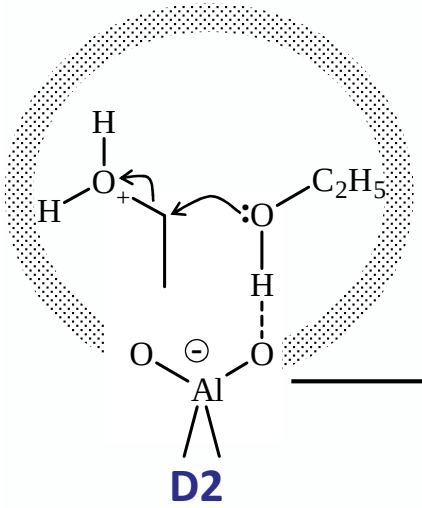


$H_2O_{(g)}$

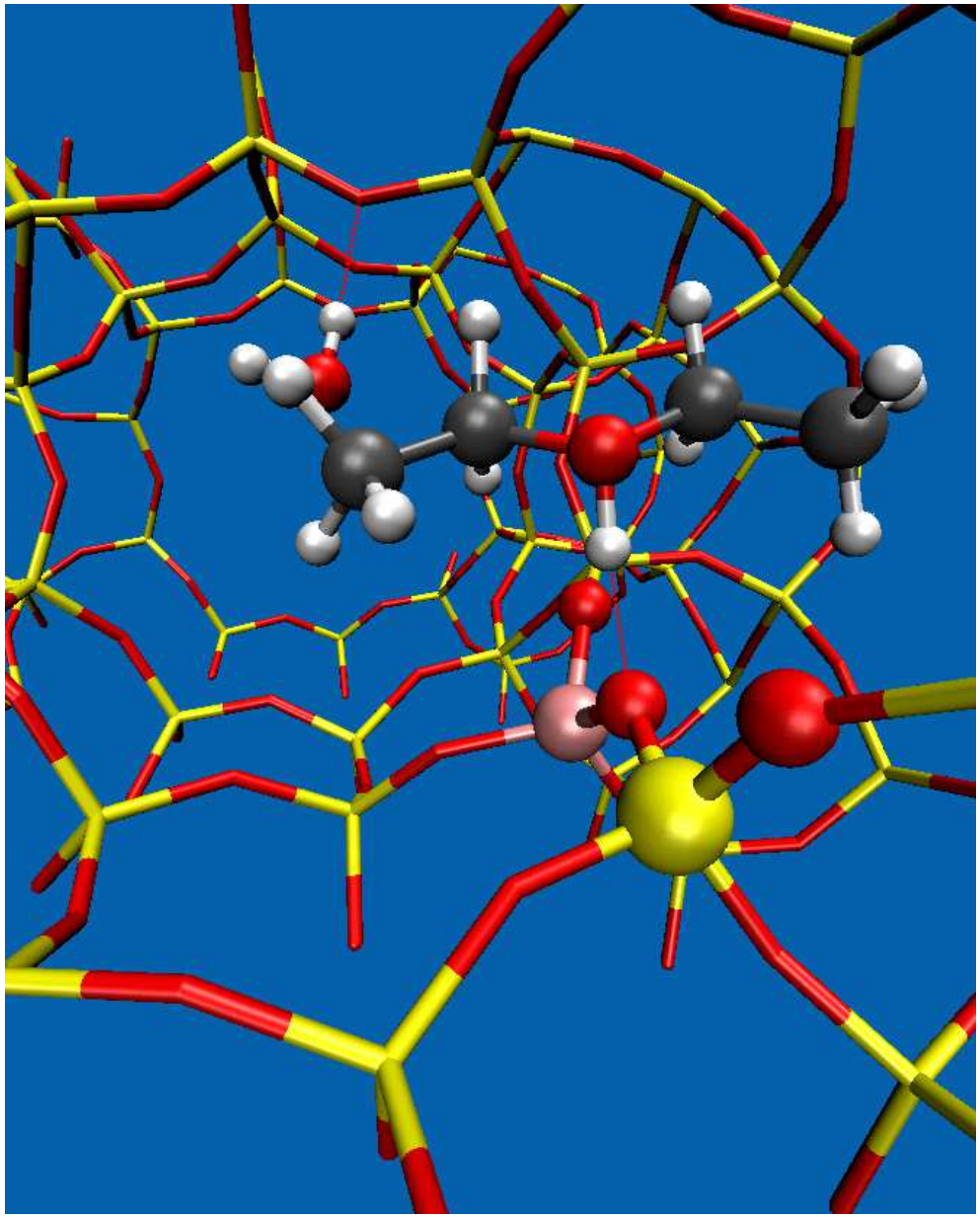
Ethene*

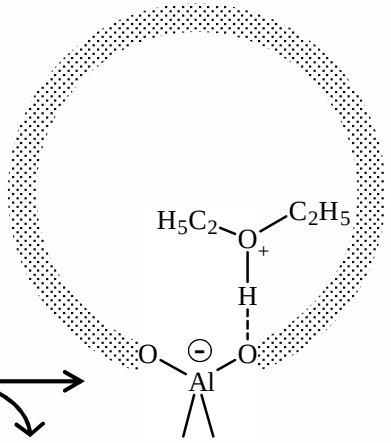
SN2

TS8



D2



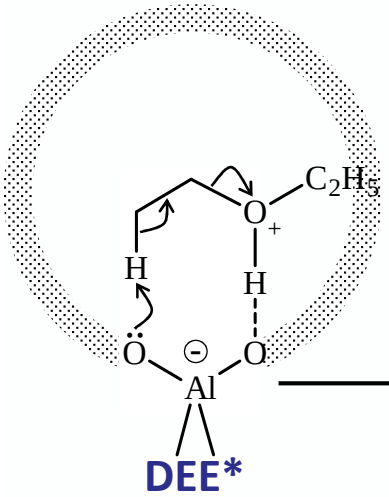


$H_2O_{(g)}$

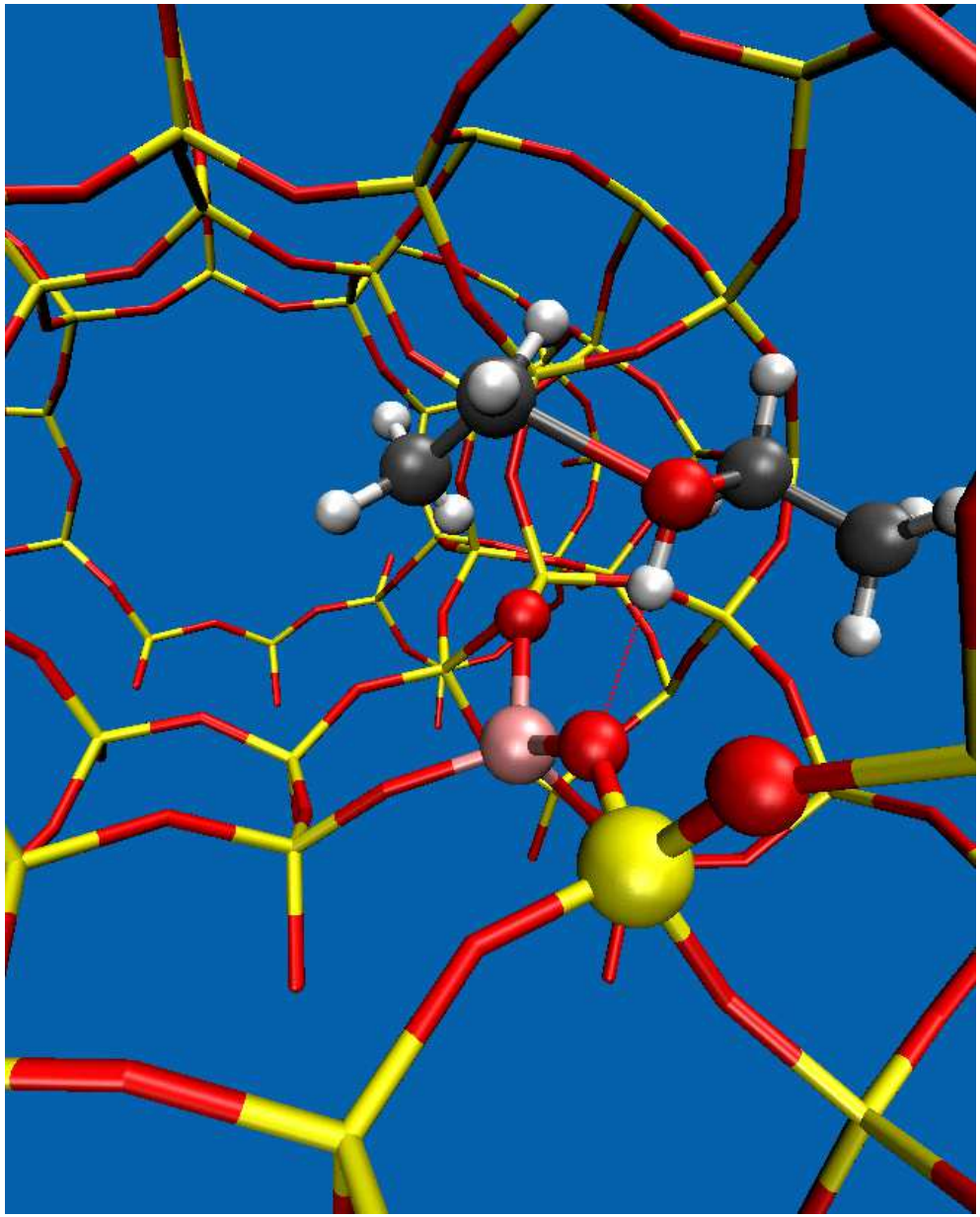
DEE*

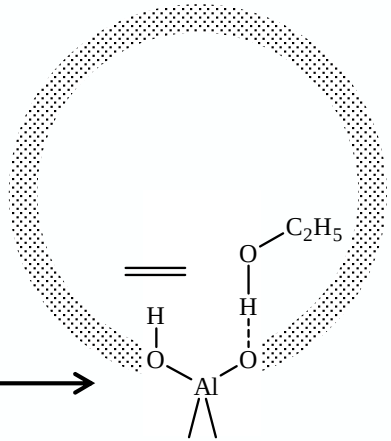
Syn elimination

TS10



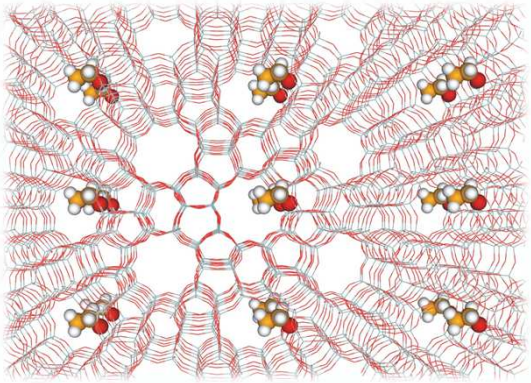
DEE*



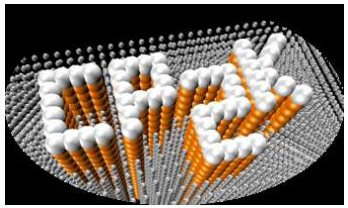


C1

Dispersion – corrected pbcDFT-D



$$E_{DFT-D} = E_{DFT} + E_D$$



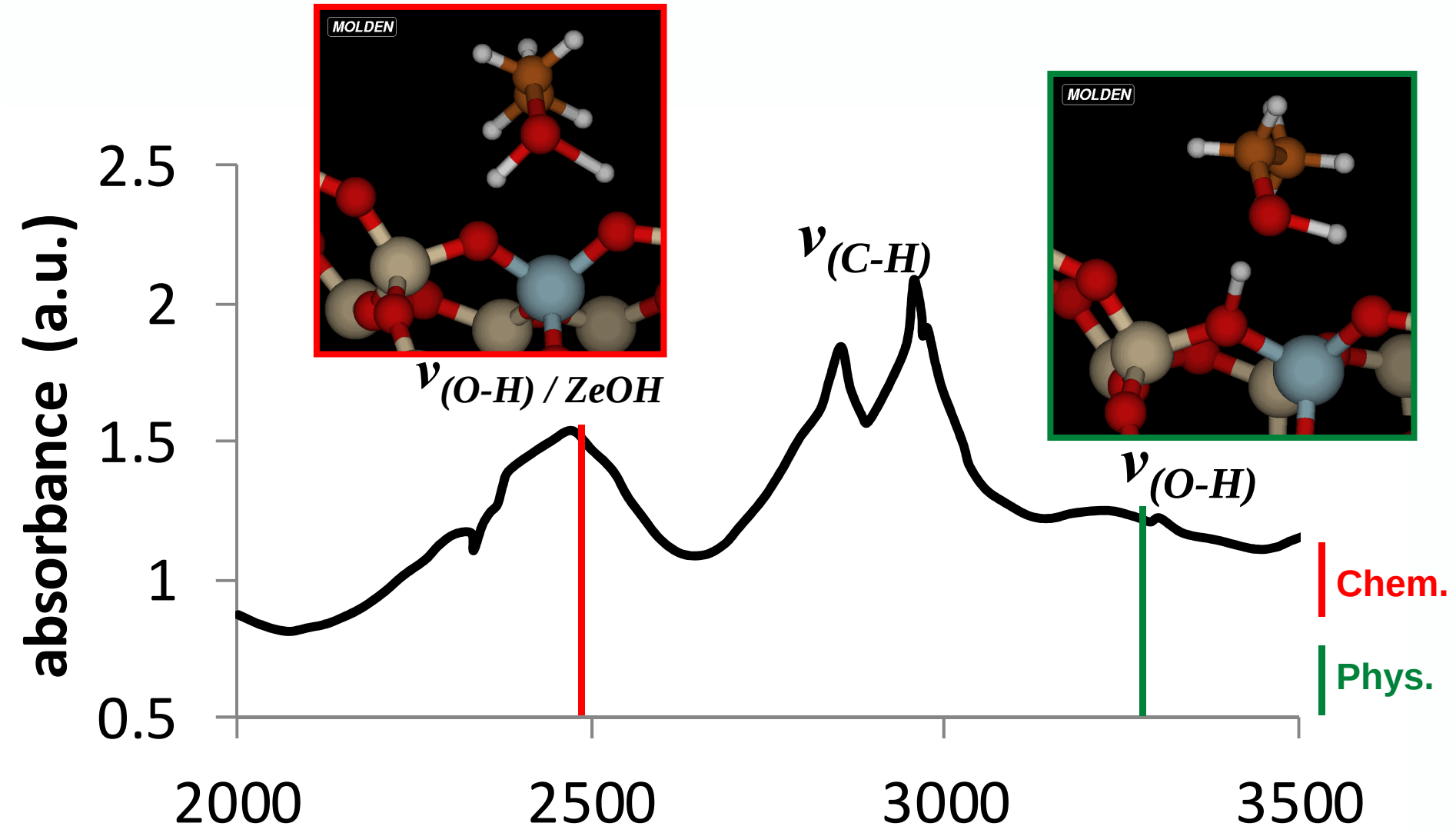
$$E_D = -\frac{s_6}{2}\sum_{L}\sum_{i,j\in L=0}\frac{\sqrt{c_6^i c_6^j}}{\left|r_{ij}-L\right|^6} f_D\left(\left|r_{ij}-L\right|\right)$$

- ***VASP 4.6/5.3***
- **Plane wave basis set** & **Projector Augmented Wave method**
- **GGA PBE-D2** implementation for zeolites [1,2].
- **Brillouin zone sampling** restricted to the *Γ point*.
- **Convergence criteria**: E_{cutoff} = *600 eV*, ΔE_{SCF} = 10^{-6} *eV*, *Max force = 0.02 eV/Å*
- **Dimer method** for transition state location [3]
- **Statistical thermodynamics** & ***PHVA – MBH*** [4]

TAMkin

1 **Grimme** *J. Comput. Chem.* **27** (2006) 1787
2 **Kresse** et al. *J. Phys. Rev. B* **48** (1993) 13115
3 **Henkelman** et al. *J. Chem. Phys.* **111** (1999) 7010
4 **De Moor** et al. *J. Chem. Theory Comput.* **7** (2011) 1090

ROH in H-ZSM-5 IR spectrum



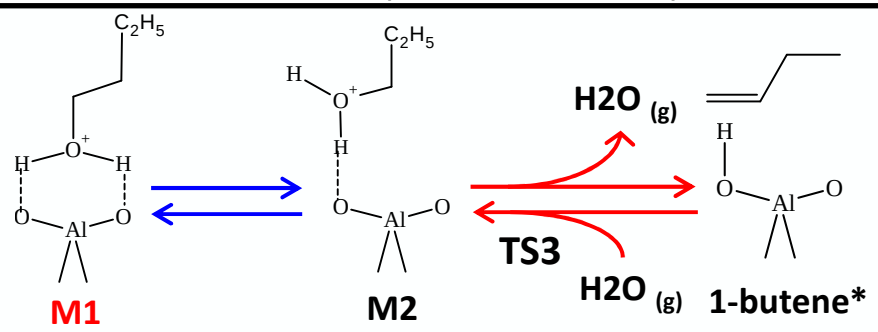
VASP, Level of theory: PBE-D2

Bonn et al. *Chem. Phys. Letts. 278* (1997) 213

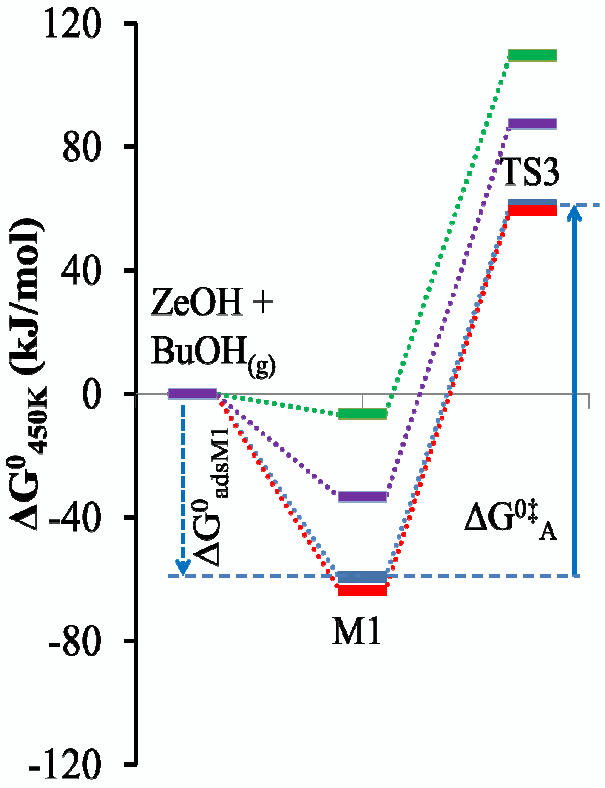
Nguyen et al. Phys. Chem. Chem. Phys. 12 (2010) 9481

Effect of zeolite : path A

Zeolite	Frame work structure	Pore dimension (pm)	$\Delta G^{\circ\ddagger} = G_{TS3} - G_{M1}$ (kJ/mol)
H-FAU	3D (12 MR)	740 x 740 [1 1 1]	134
H-ZSM-5	3D (10 MR)	510 x 550 [100], 530 x 560 [010]	127
H-ZSM-22	1D (10 MR)	460 x 570 [001]	131
H-FER	2D (10 and 8 MR)	420 x 540 [001], 350 x 480[010]	137



M1	ΔH°_{ads} (kJ/mol)	ΔS°_{ads} (J/mol/K)
H-FAU	–121	–195
H-ZSM-5	–146	–192
H-ZSM-22	–150	–192
H-FER	–106	–222



Entropy considerations on monomolecular catalytic cracking

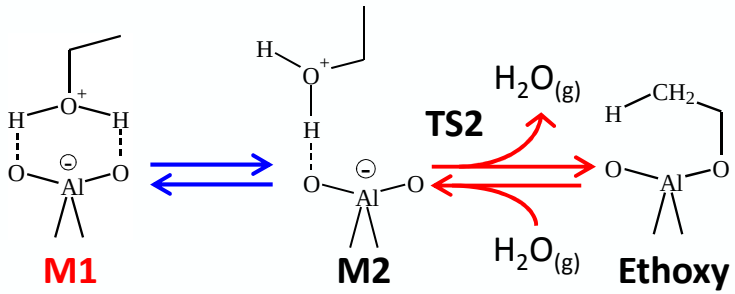
Bhan and Iglesia J Catal 2008

"The size-independent barrier for this transition suggests that the extent of charge separation and the C-H-C bond configuration in transition states, relative to those in adsorbed alkanes, is essentially independent of chain size. The larger entropy loss upon adsorption of larger alkanes ultimately leads to a larger entropy gain as they form higher energy complexes along the reaction coordinate towards the transition states required for C-C bond activation, as shown by the linear trend of ΔS_{act} with carbon number in Fig 1

"Monomolecular cracking reactions lead to substantial entropy gains as six internal modes are incipiently converted into three translational and rotational degrees of freedom in the transition state [18]. A part of this entropy gain arises from rocking vibrations of the two fragments, which become hindered rotations as C–C bonds are elongated in the transition state, a process inferred from ab initio and density functional calculations [19,20]. This process decreases the directionality and restoring forces for the movement of one fragment relative to the other. We surmise that the entropy gains that favor reactions of larger alkanes arise from an increase in the number of accessible configurations from the adsorbed state to the transition state and from the mass of the two fragments involved in these hindered rotations [18]."

Effect of zeolite:Path A Ethanol to Ethene

ZeOH	$\Delta G^{\ddagger} = G_{TS2} - G_{M1}$ (kJ/mol)
H-FAU	146
H-MOR	137
H-ZSM-5	124
H-ZSM-22	119



10-MR zeolites more active than 12-MR zeolites