UNIVERSITEIT GENT
FACULTY OF ENGINEERING AND ARCHITECTURE

Catalysis for renewable resources: bioalcohol conversion

Marie-Françoise Reyniers and Guy B. Marin

Laboratory for Chemical Technology, Ghent University

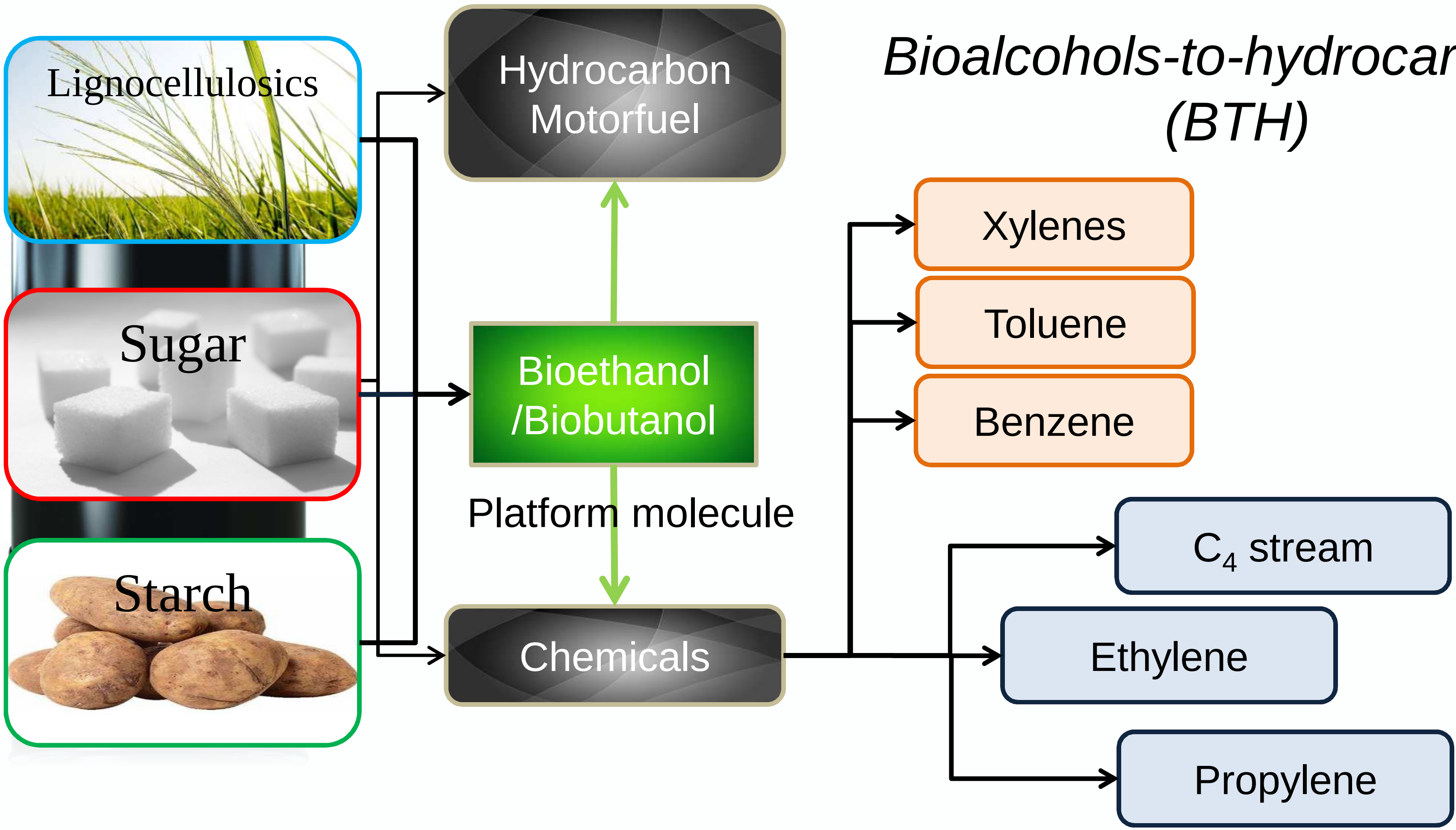
http://www.lct.UGent.be

EUROKIN workshop, EVONIK, Marl, Germany, October 13 2015

Overview

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

Bioalcohols to hydrocarbons as a green route

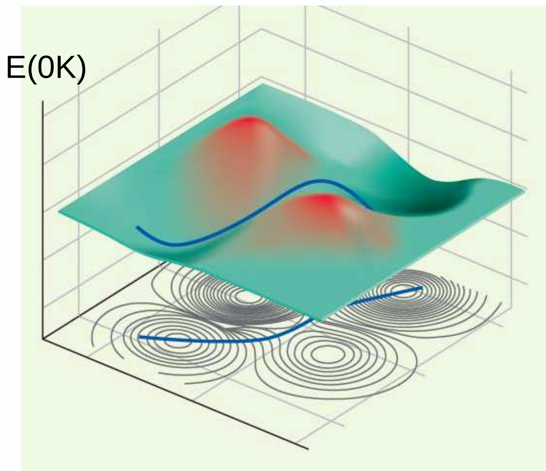


First-principles based multiscale modeling

Electronic structure calculation (0 K)

Vibrational analysis

Statistical thermodynamics



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

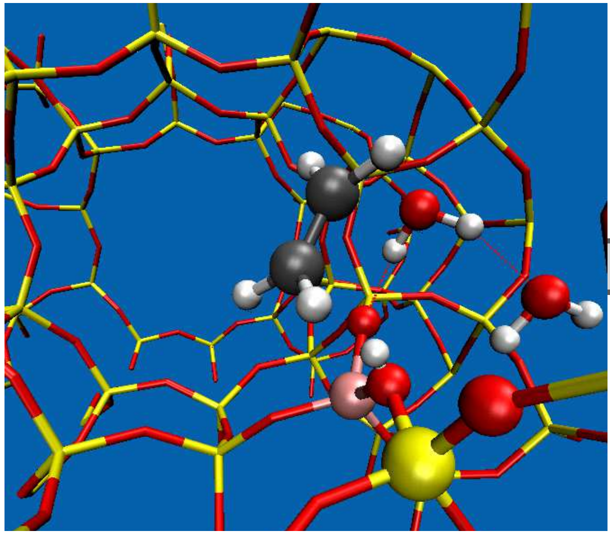
Thermo & Kinetics
K(T), k_+(T), k_-(T)

Reactor hydrodynamics
mass/heat transport

- conversion and product yields
- rate analysis

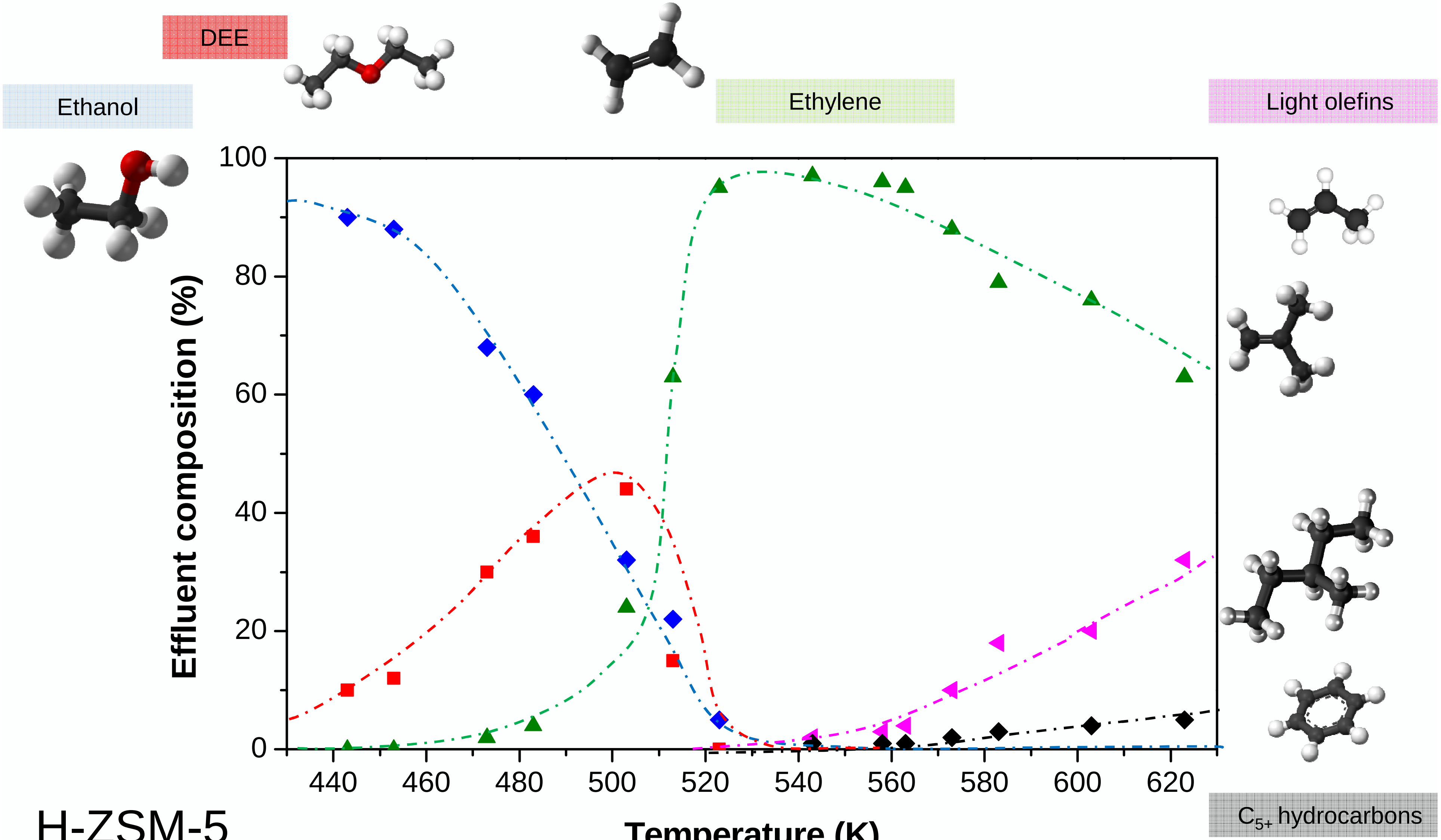
- guidelines process conditions
- guidelines catalyst properties

From molecular to industrial reactor scale



	lab scale	industrial
Catalyst mass (kg)	$1 - 10 \times 10^{-4}$	$1 - 10 \times 10^{3}$
L (m)	0.890	1 – 10
d_r (m)	0.011	0.1 – 2
T^0 (°C)	170 – 250	250 – 500
$p_{EtOH,0}$ (bar)	0.08 – 0.30	5 – 30
$F_{EtOH,0}$	$1 - 10 \times 10^{-4}$ g/s	10 – 1000 kg/s

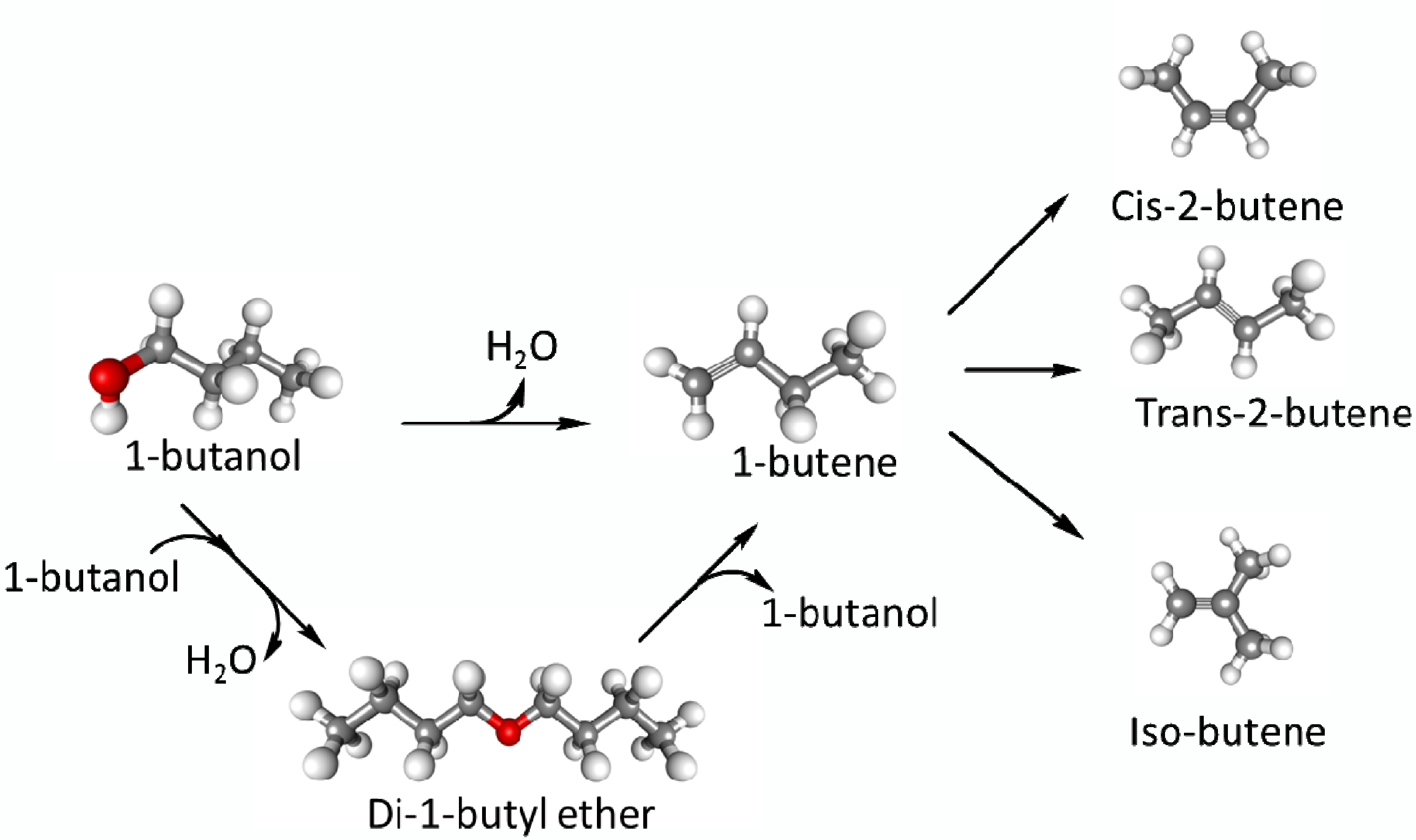
Acid catalyzed ethanol conversion



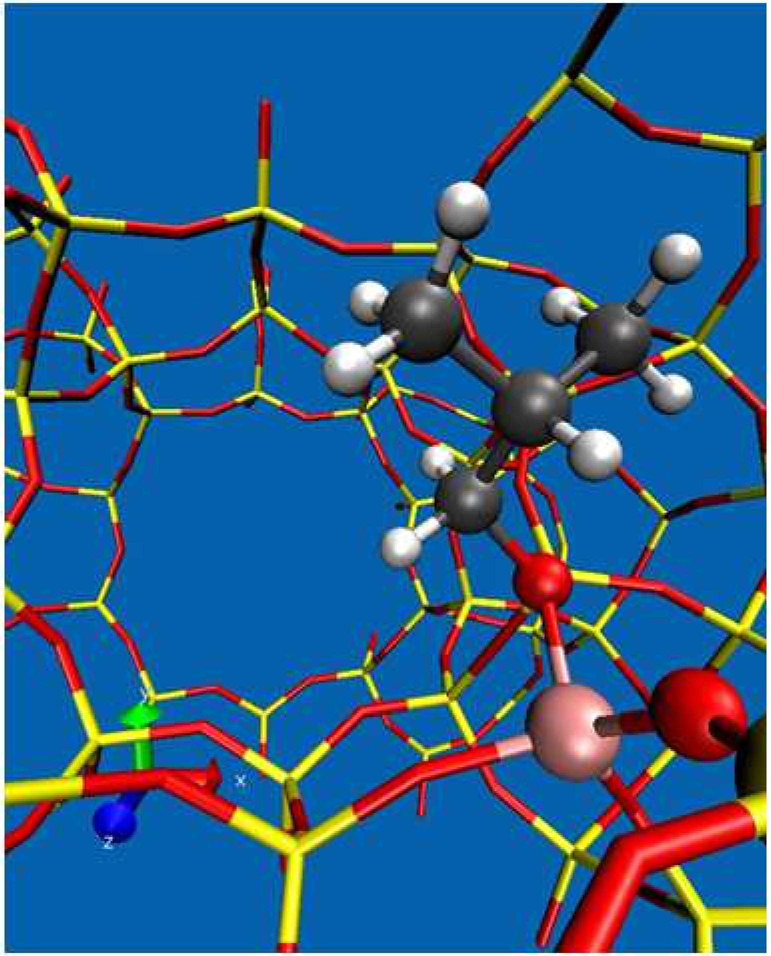
H-ZSM-5

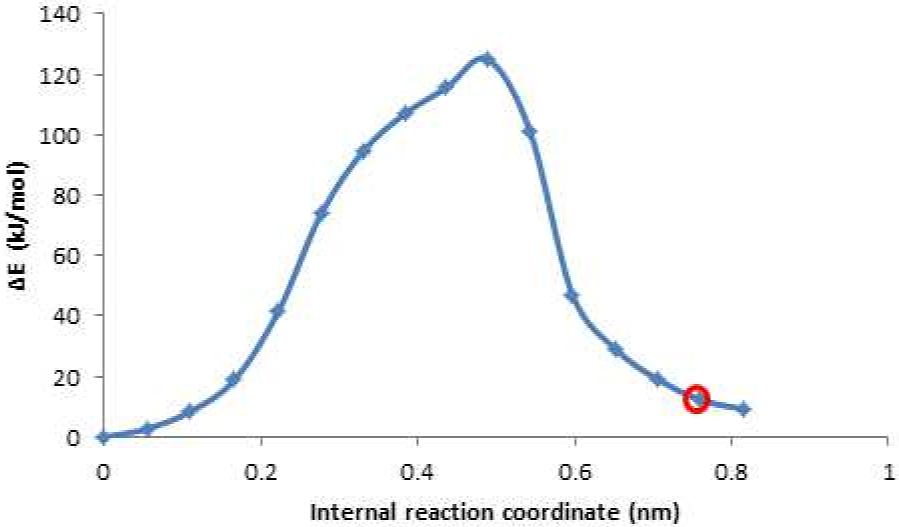
$p_{EtOH,0}$= 20 kPa : $W/F_{EtOH,0}$ = 8 kg s mol^{-1}

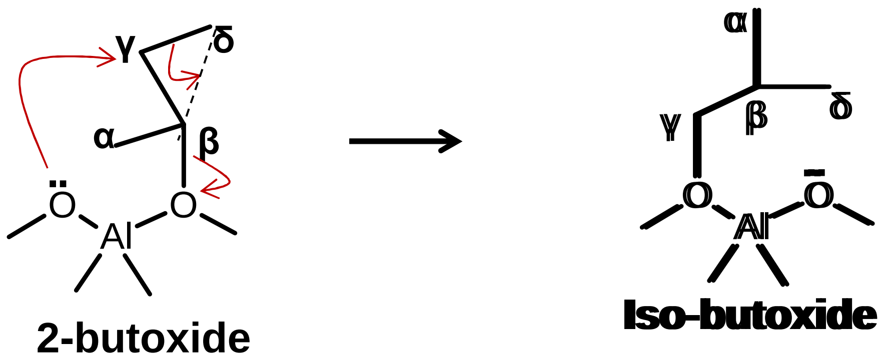
Scope of this presentation: dehydration



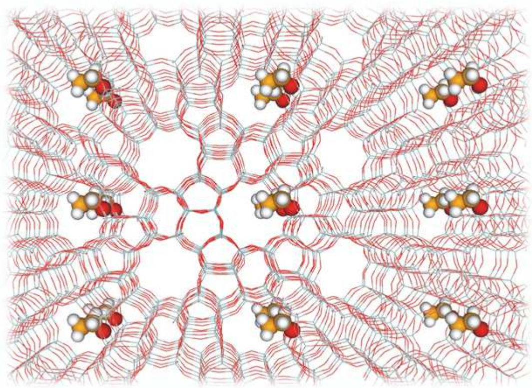
Nudged Elastic Band calculation







Dispersion – corrected pbcDFT-D



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

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

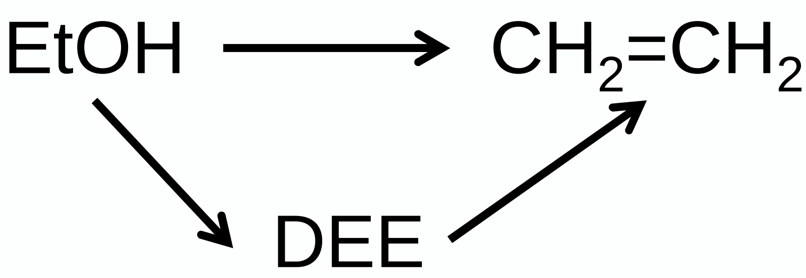
- ***VASP 4.6/5.3***
- **Plane wave basis set** & **Projector Augmented Wave method**
- **GGA PBE-D2** implementation for zeolites [1,2].
- **Brillouin zone sampling** restricted to the *Γ point*.
- **Convergence criteria**: $E_{cutoff} = 600$ eV, $\Delta E_{SCF} = 10^{-6}$ eV, Max force = 0.02 eV/Å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

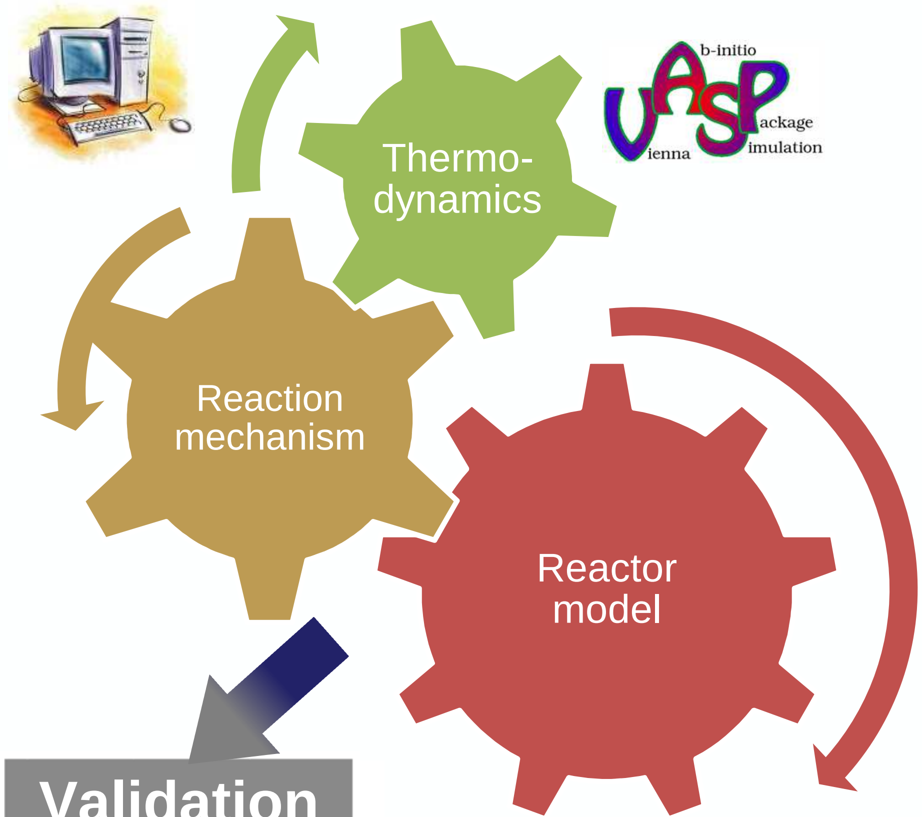
1 **Grimme** *J. Comput. Chem.* **27** (2006) 1787
2 **Kresse** et al. *J. Phys. Rev. B* **48** (1993) 13115
3 **Henkelman** et al. *J. Chem. Phys.* **111** (1999) 7010
4 **De Moor** et al. *J. Chem. Theory Comput.* **7** (2011) 1090

Overview

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

Zeolite-catalyzed alcohol dehydration



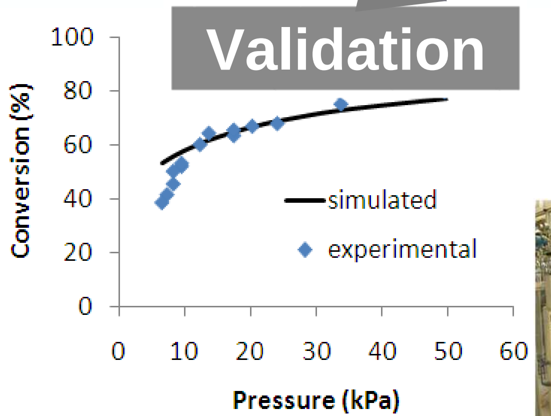


- Influence on yields of
  - reaction conditions?
  - zeolite framework?

- Need to know
  - reaction mechanism
  - thermo & kinetics

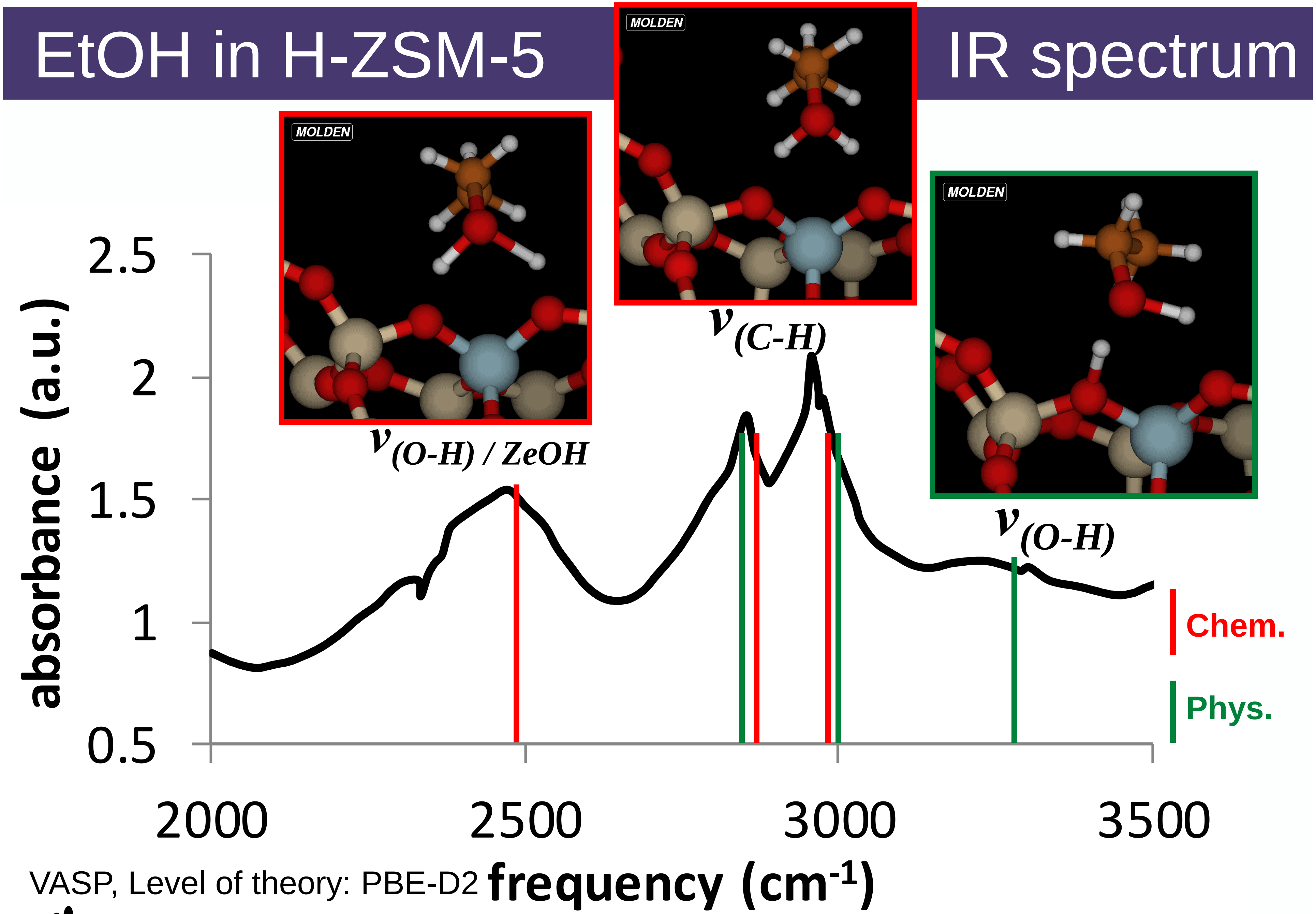
H-FAU H-ZSM-5

H-MOR H-ZSM-22



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

EtOH in H-ZSM-5 IR spectrum



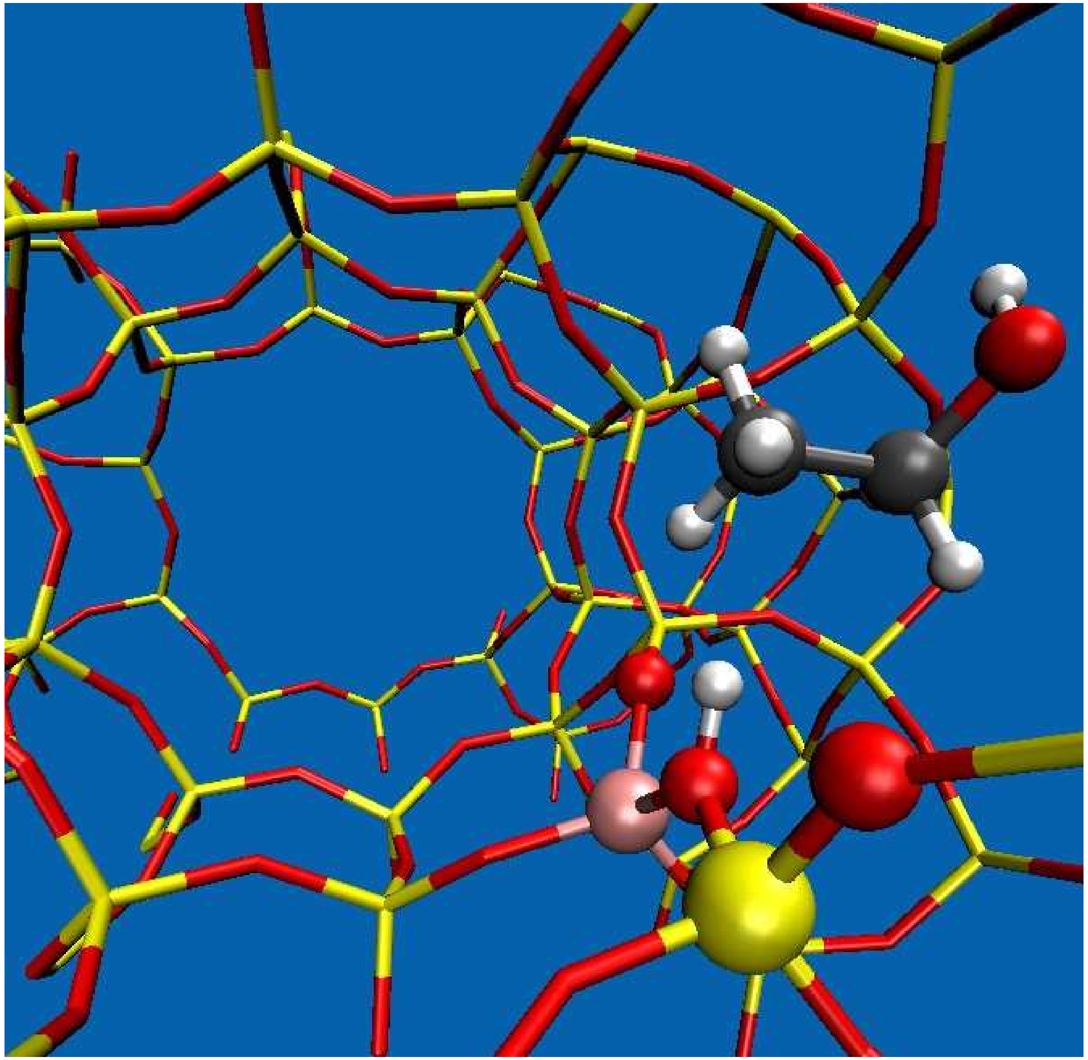
VASP, Level of theory: PBE-D2

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

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

Alcohol adsorption in zeolites

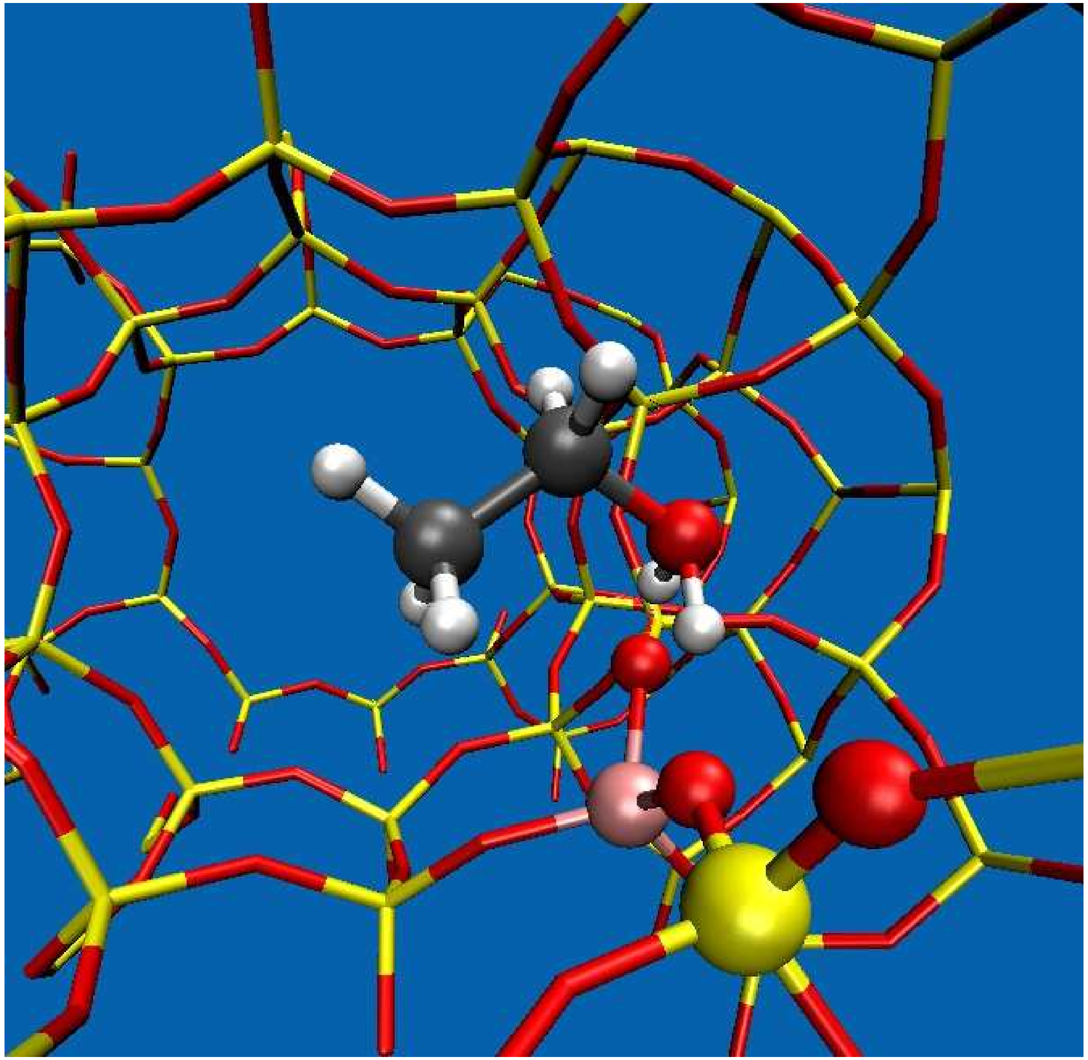
Ethanol adsorption in H-ZSM-5



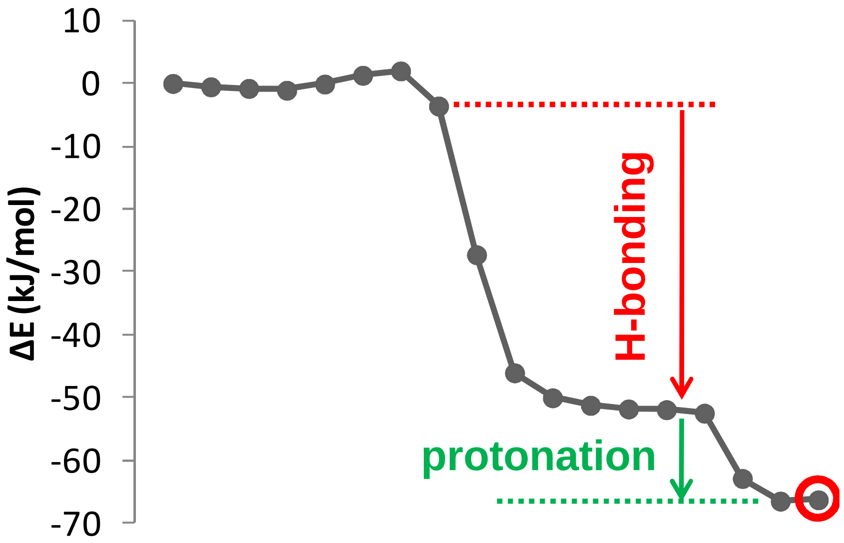
- van der Waals interactions
- H-bonding
- electrostatic interactions
  - depend on:
    - adsorbate structure
    - zeolite structure

H-bonding and protonation

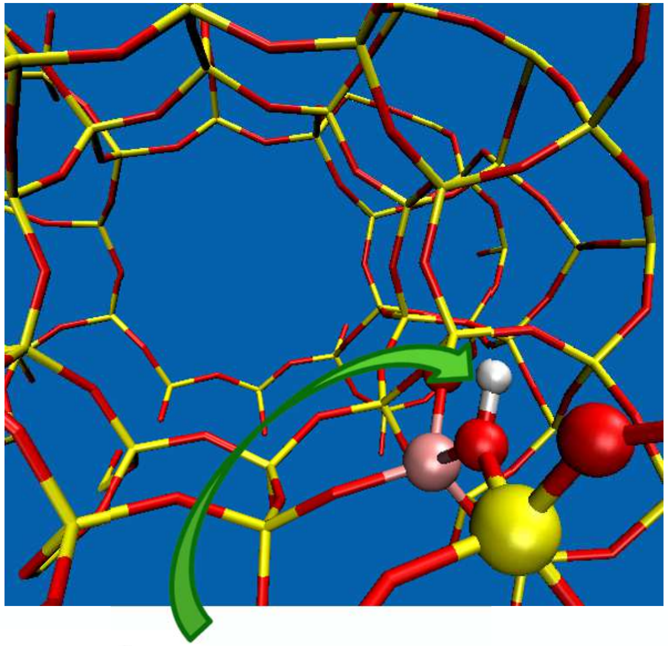
Ethanol adsorption and protonation in H-ZSM-5

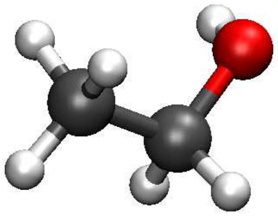


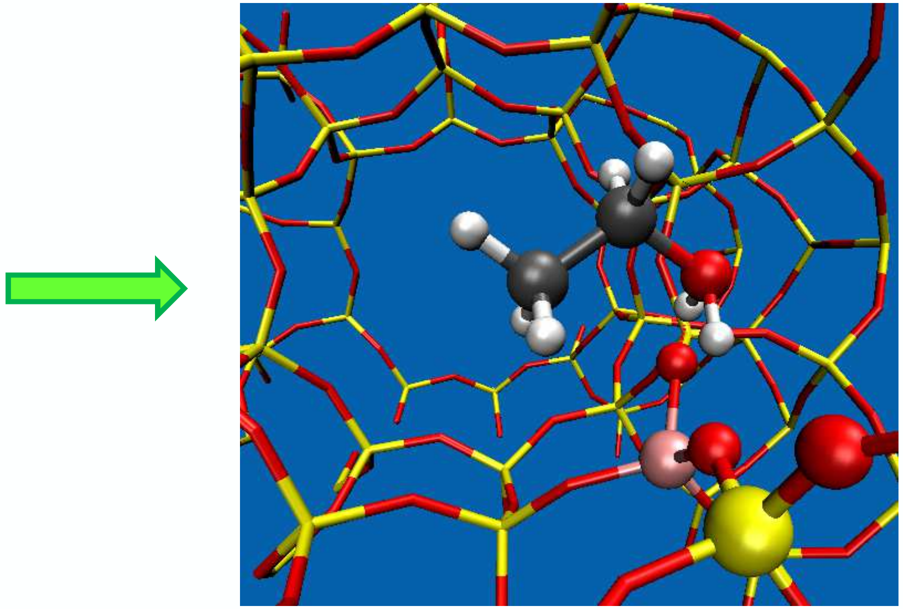
Nudged Elastic Band calculation with PBE-D2 functional



Alcohol adsorption & reaction in zeolites





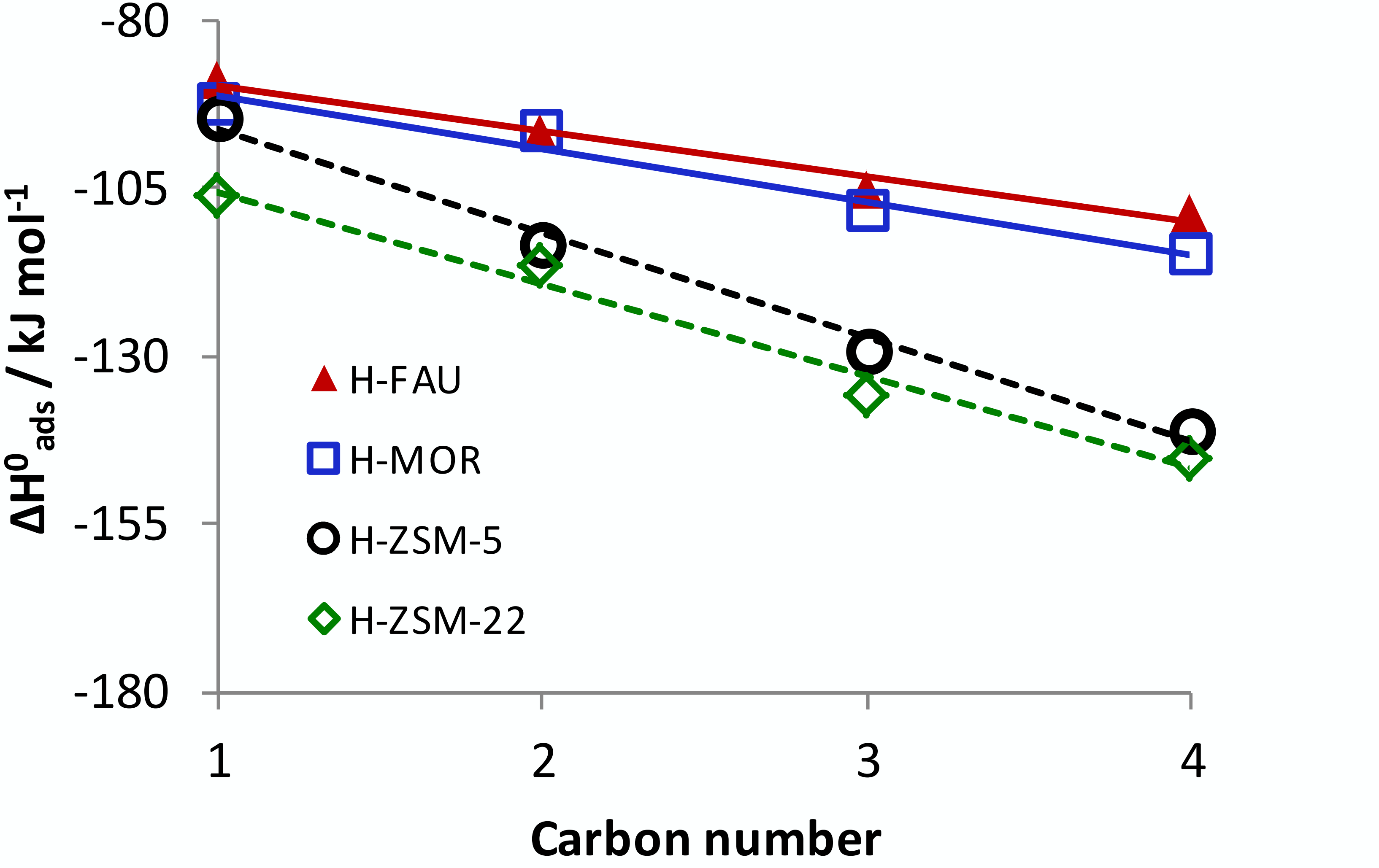


$$r = k\,\theta_{ads,alcohol} = k\,K_{ads}\,p_{alcohol}$$

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

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

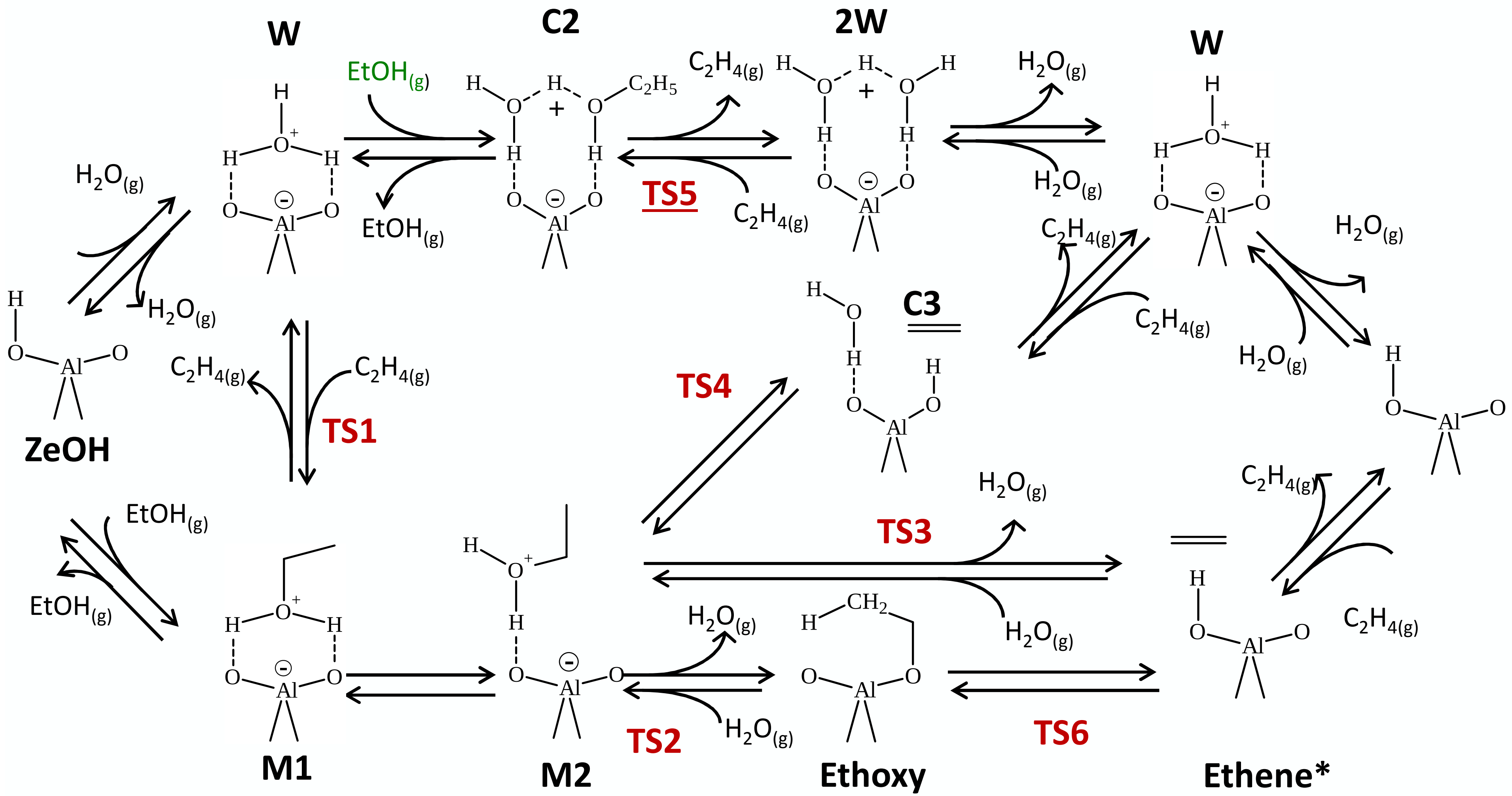
Linear alcohol chemisorption



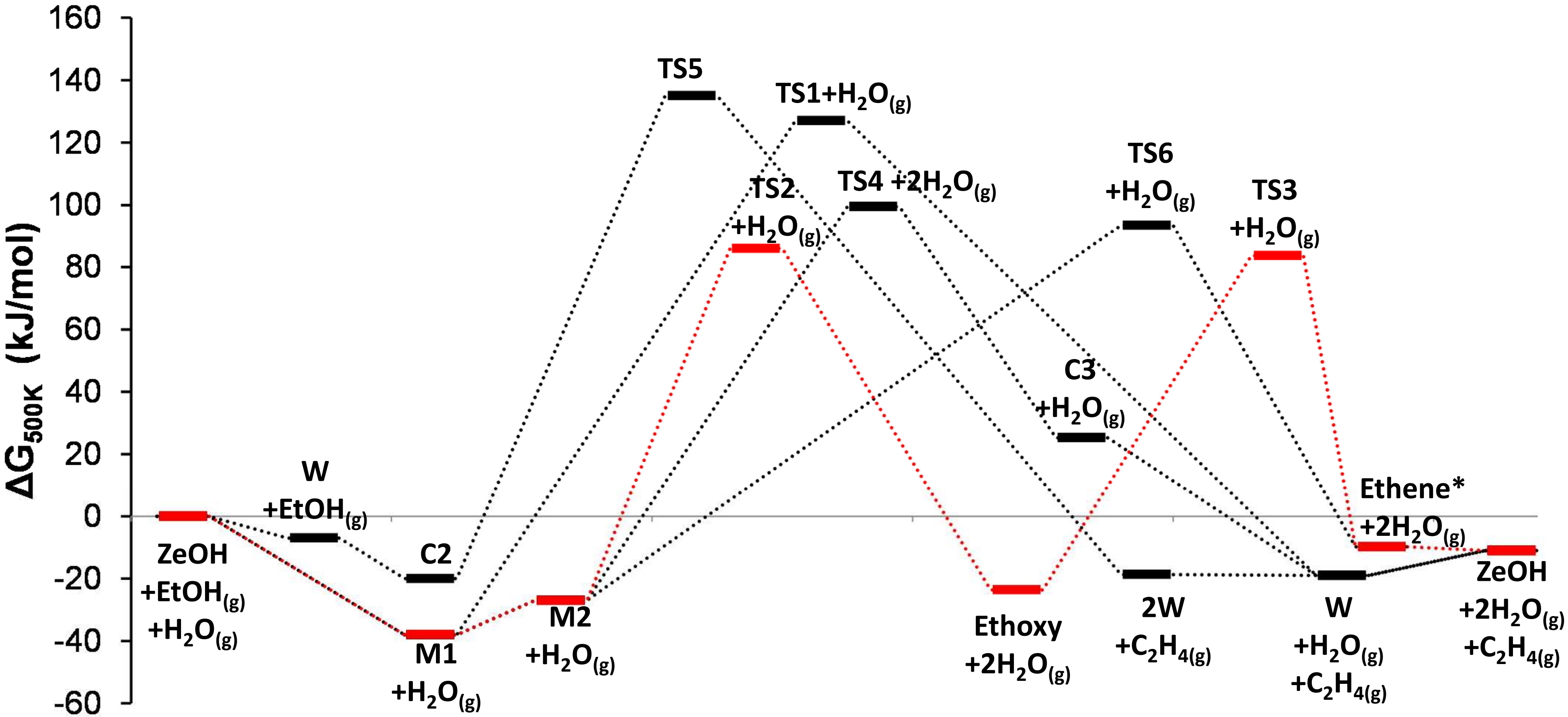
Nguyen et al., J. Catal. (2015) 322,91-103

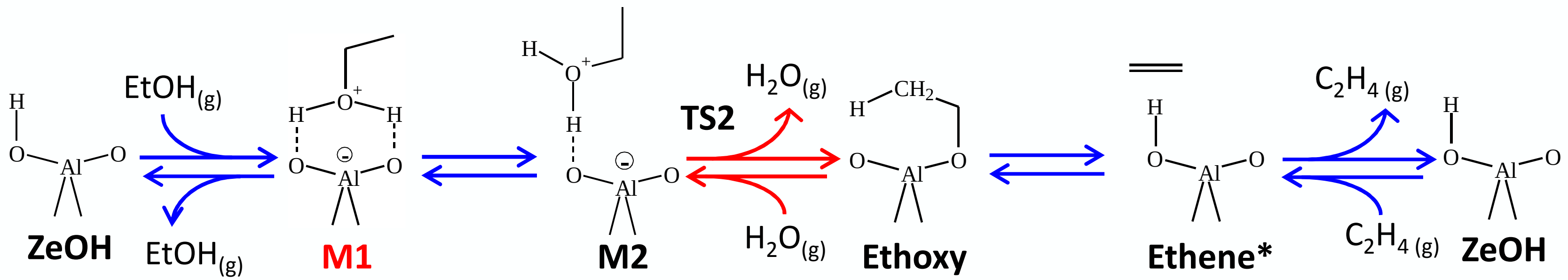
Ethanol to Ethene: H-ZSM-5

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



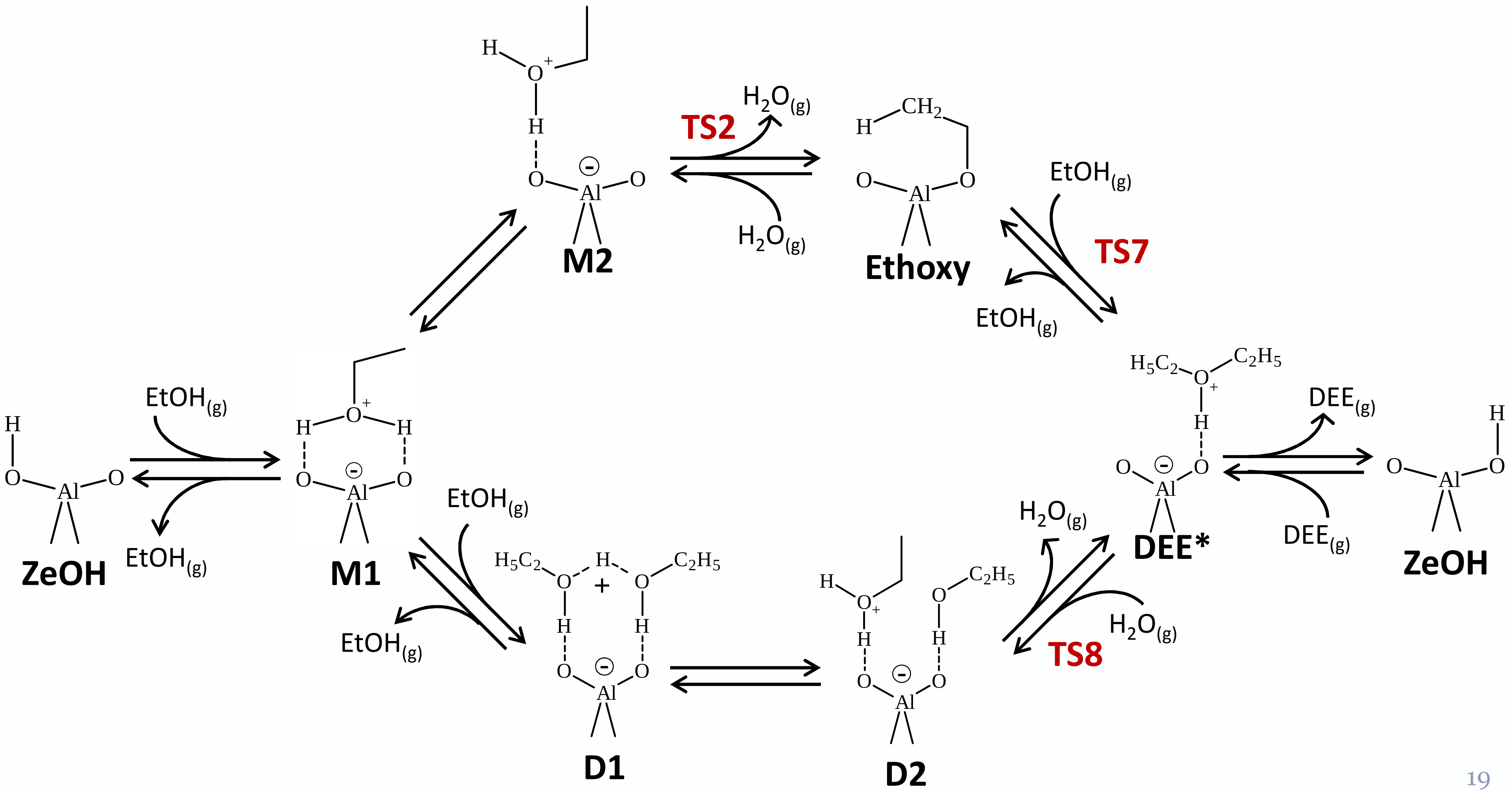
Ethanol to Ethene: H-ZSM-5



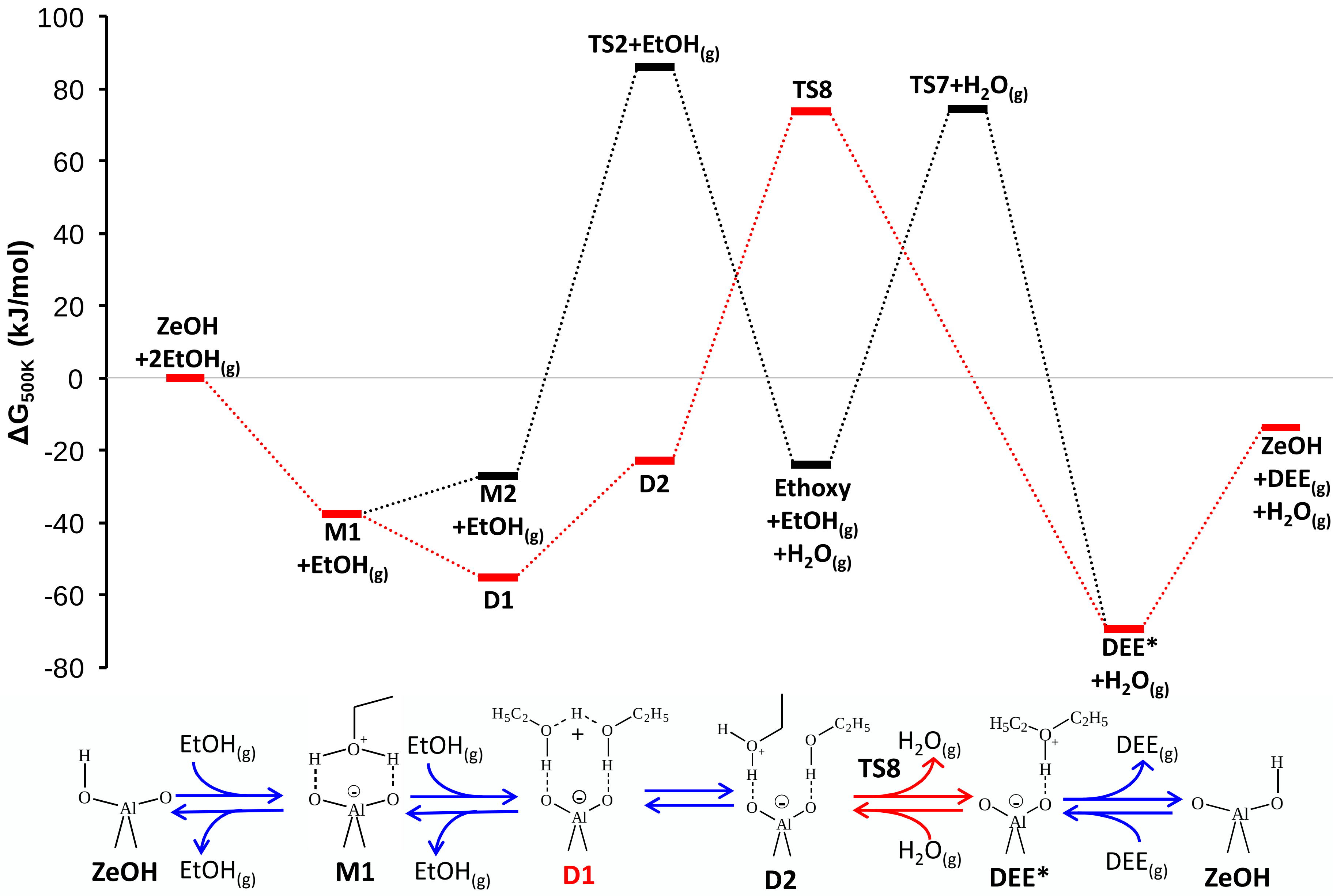


Ethanol to Diethyl ether: H-ZSM-5

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

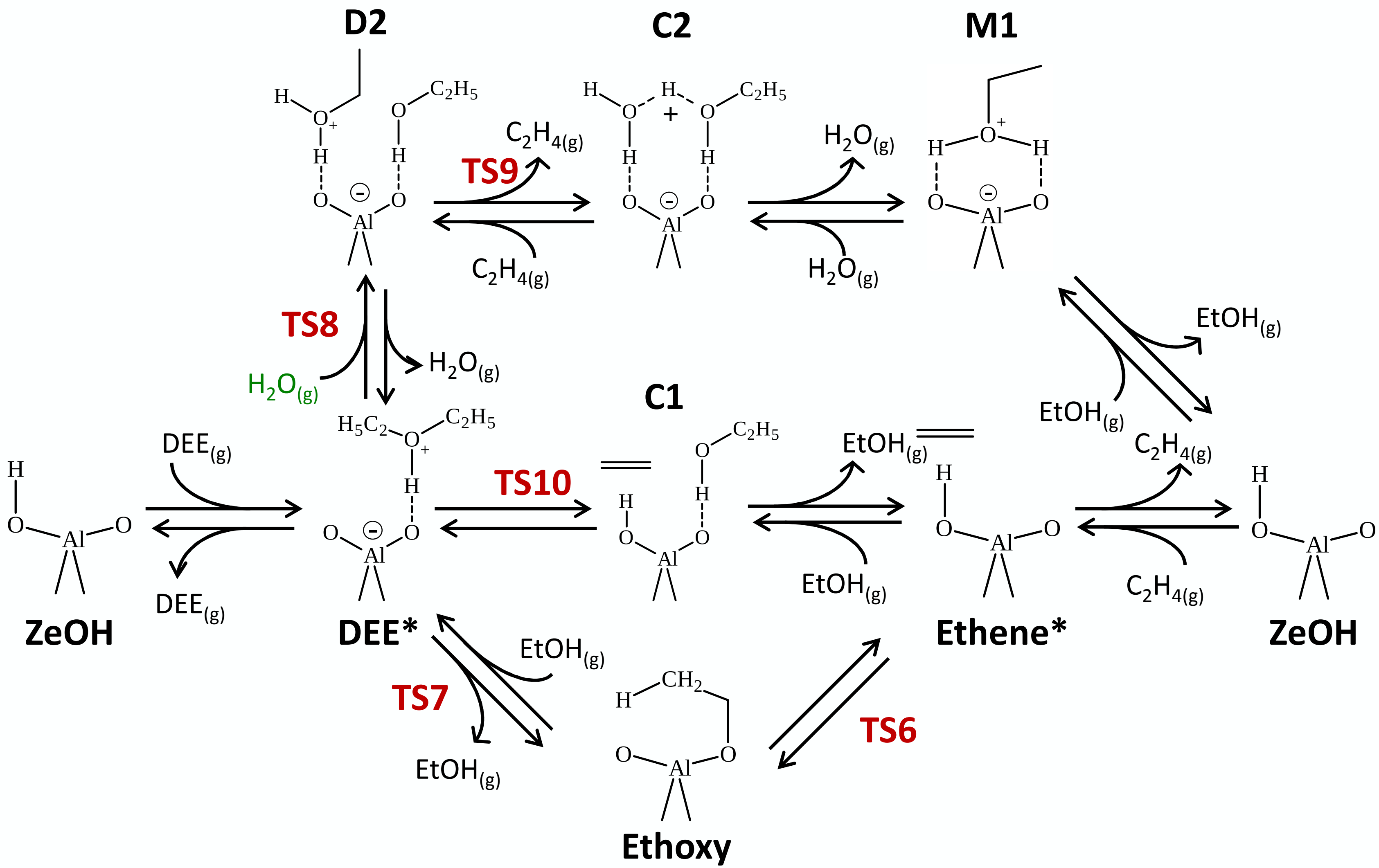


Ethanol to Diethyl ether: H-ZSM-5

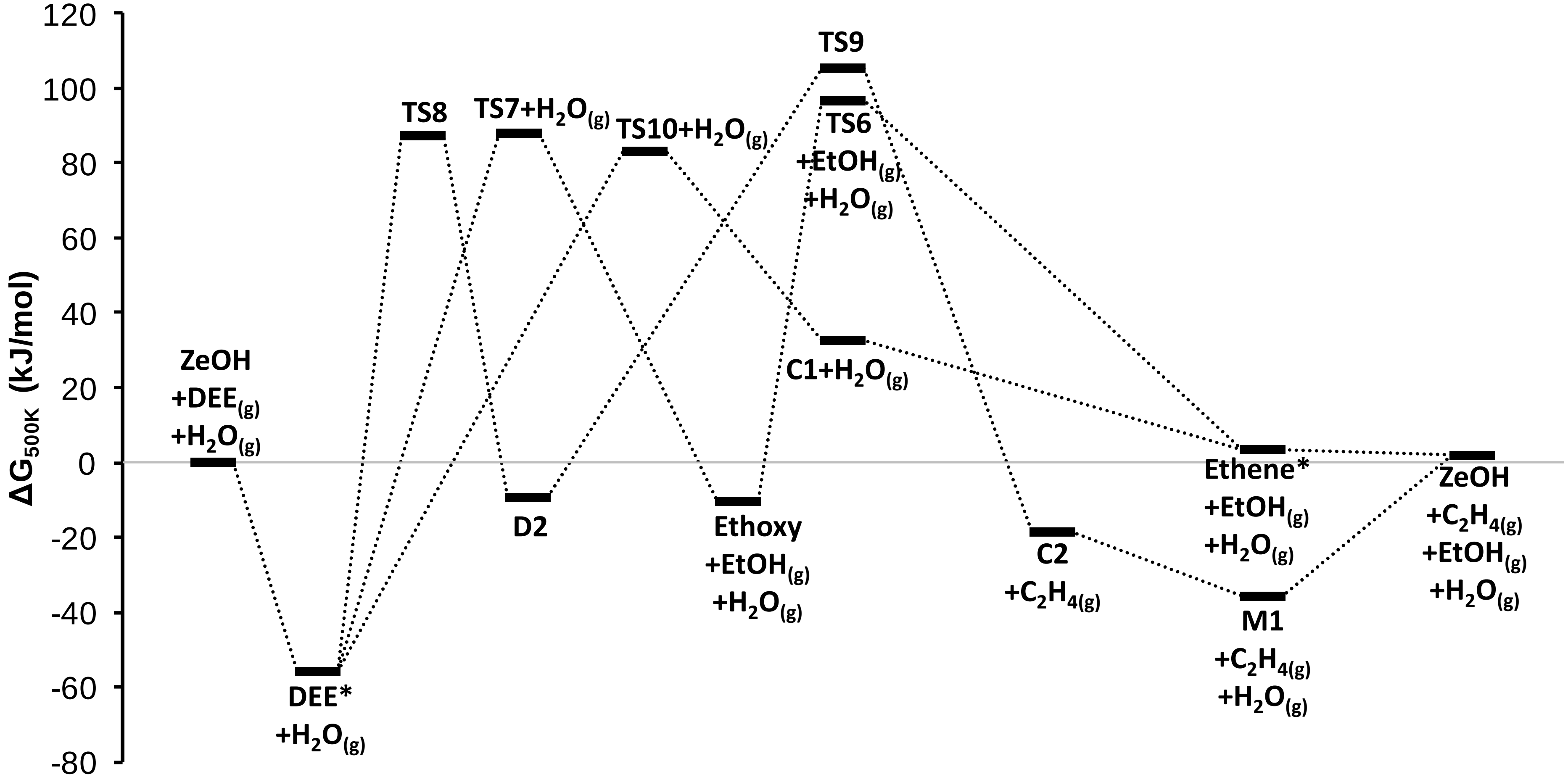


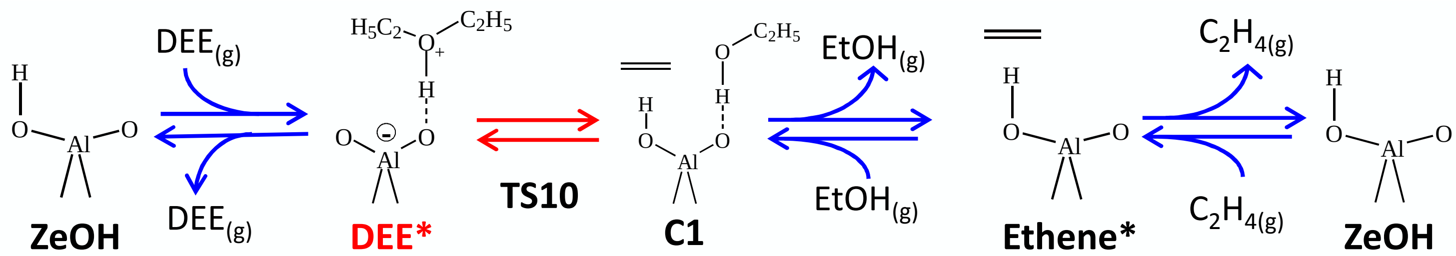
Diethyl ether to Ethene:H-ZSM-5

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

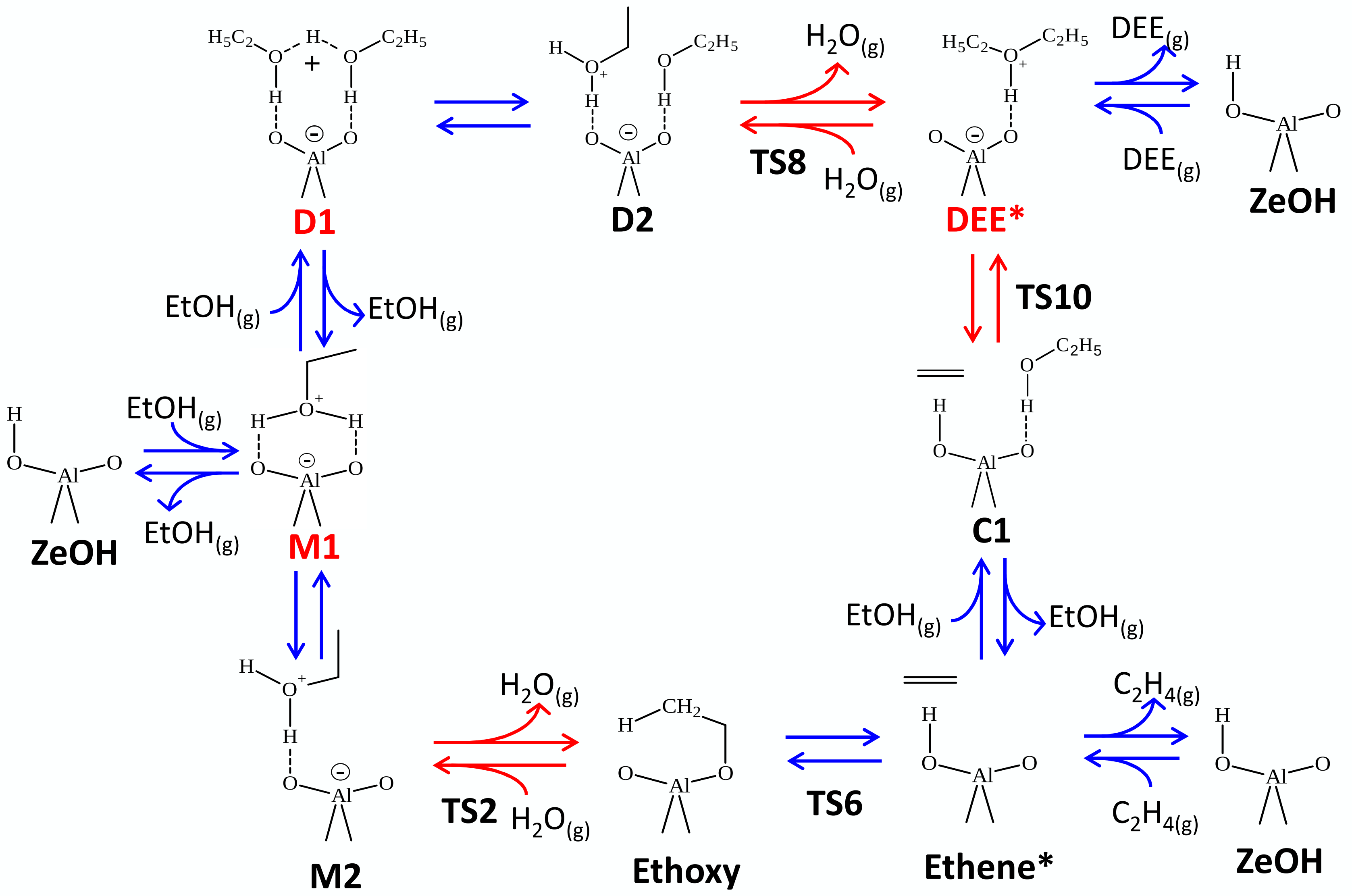


Diethyl ether to Ethene: H-ZSM-5





Reaction mechanism ethanol dehydration



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

MARI's and Rate-Determining Steps

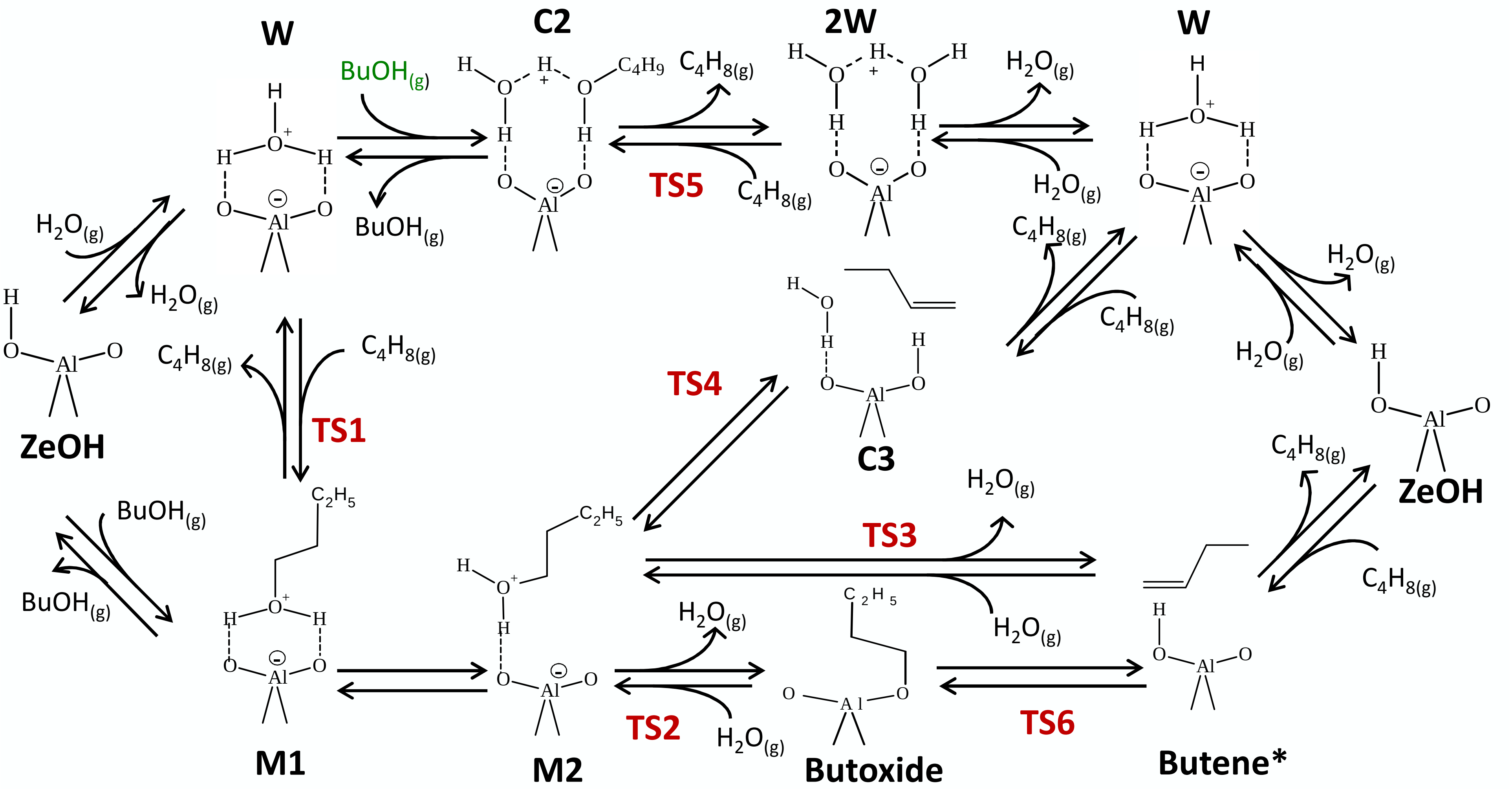
		A	B	C
(1)	EtOH(g) + * ↔ M1	1	1	0
(2)	**M1** ↔ M2	1	0	0
(3)	M2↔ Ethoxy + $H_2O_{(g)}$	**1**	0	0
(4)	Ethoxy ↔ Ethene*	1	0	0
(5)	Ethene* ↔ $Ethene_{(g)}$ + *	1	0	1
(6)	M1 + $EtOH_{(g)}$ ↔ D1	0	1	0
(7)	**D1** ↔ D2	0	1	0
(8)	D2 ↔ DEE* + $H_2O_{(g)}$	0	**1**	0
(9)	DEE* ↔ $DEE_{(g)}$ + *	0	1	-1
(10)	**DEE*** ↔ C1	0	0	**1**
(11)	C1 ↔ Ethene*+ $EtOH_{(g)}$	0	0	1
Path A	$EtOH_{(g)}$ ↔ $Ethene_{(g)}$ +$H_2O_{(g)}$			
Path B	$EtOH_{(g)}$+$EtOH_{(g)}$ ↔ $DEE_{(g)}$ +$H_2O_{(g)}$			
Path C	$DEE_{(g)}$ ↔ $Ethene_{(g)}$ +$EtOH_{(g)}$			

Overview

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

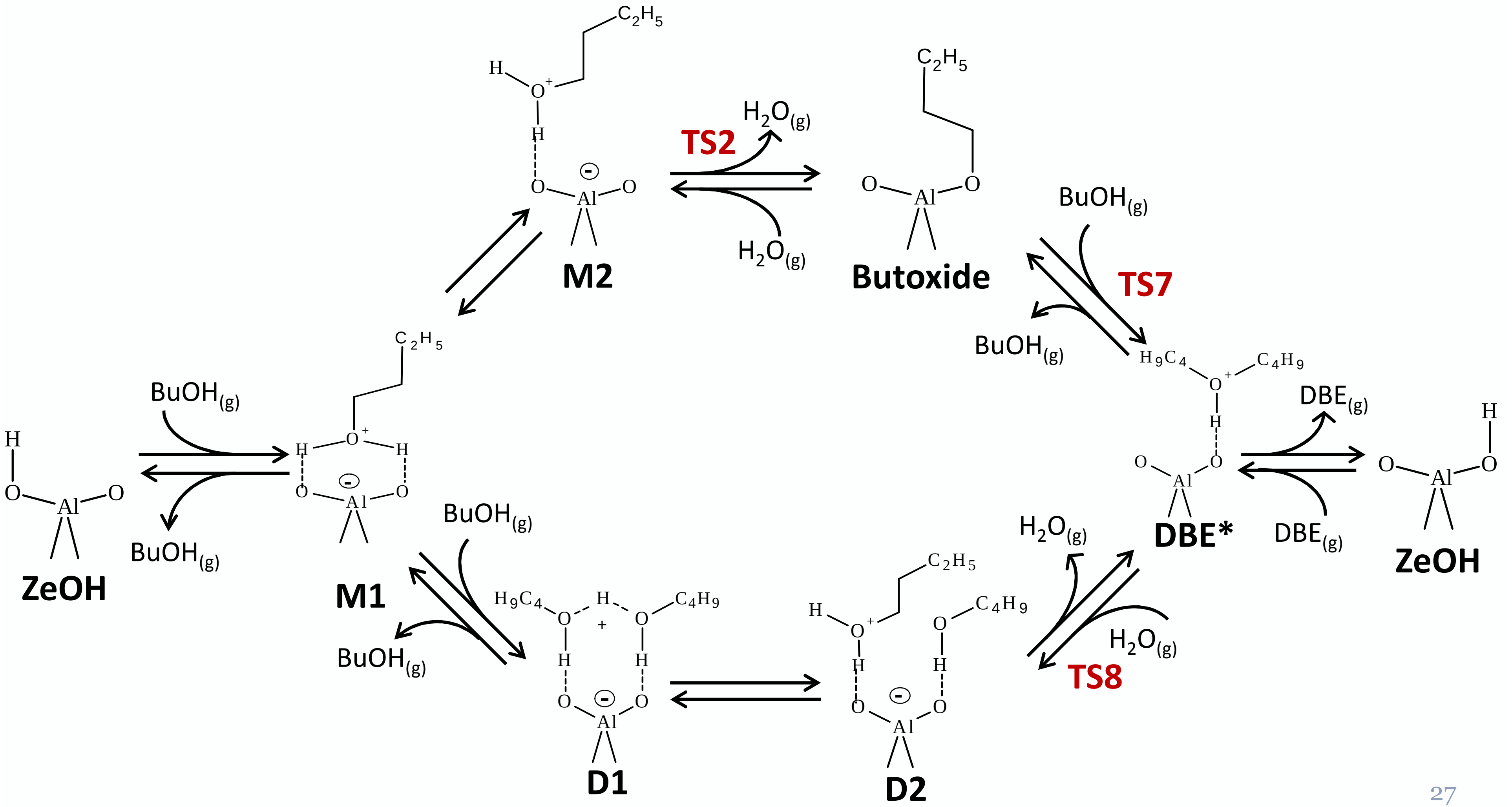
Butanol to Butene: H-ZSM-5

$$BuOH_{(g)} \rightarrow C_4H_{8(g)} + H_2O_{(g)}$$



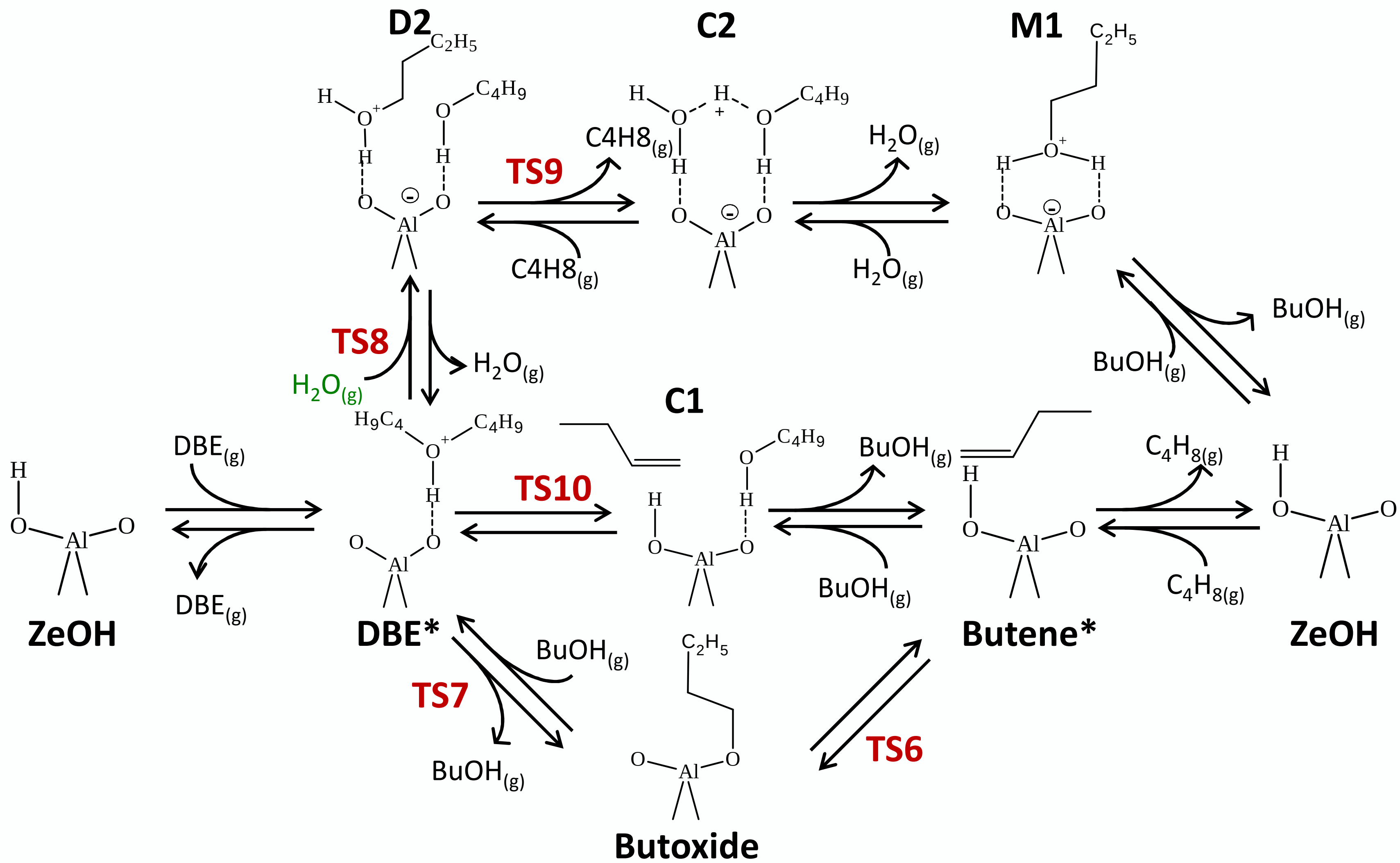
Butanol to Dibutyl ether: H-ZSM-5

$$2BuOH_{(g)} \rightarrow DBE_{(g)} + H_2O_{(g)}$$

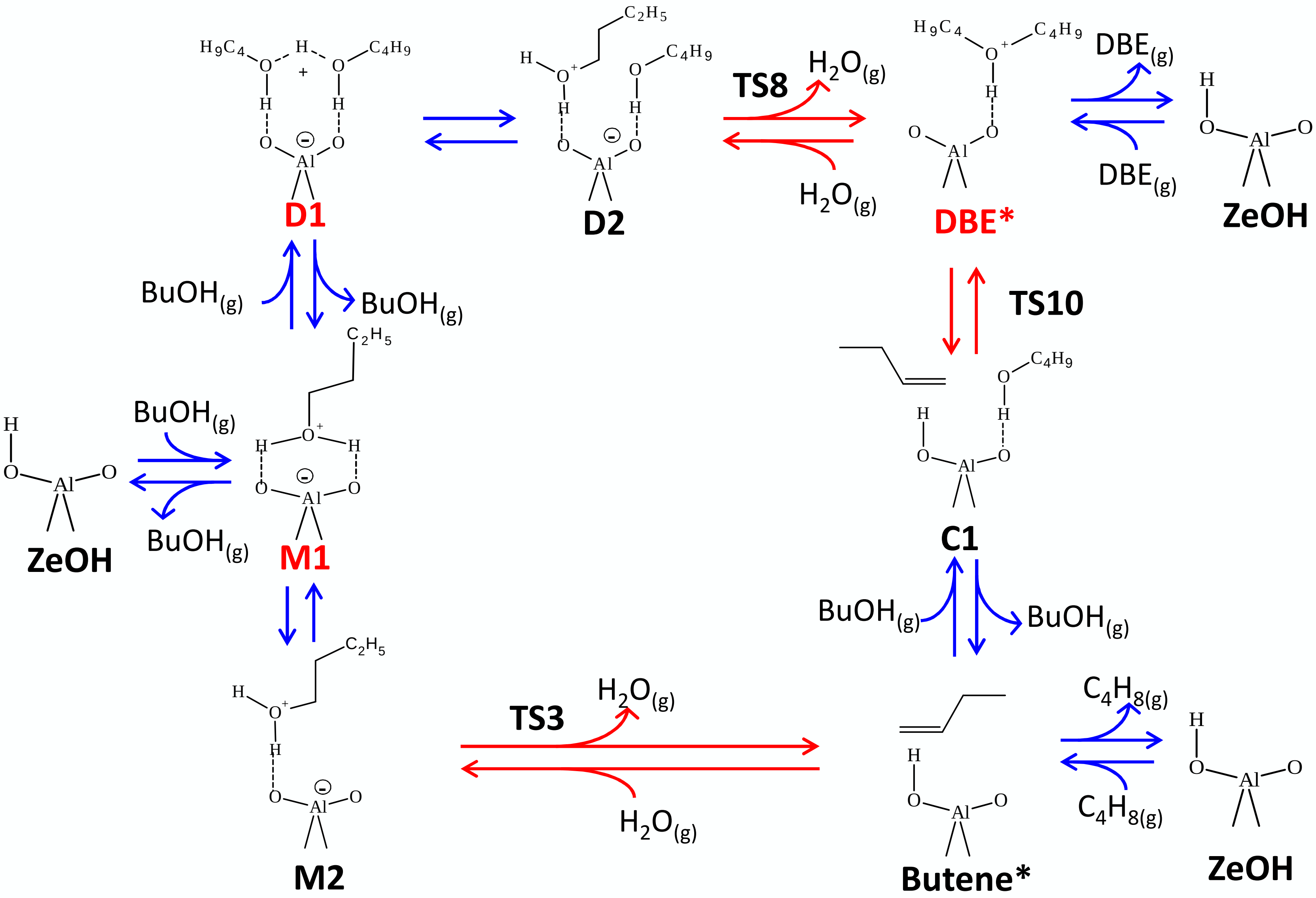


Dibutyl ether to Butene:H-ZSM-5

$$DBE_{(g)} \rightarrow BuOH_{(g)} + C_4H_{8(g)}$$



Reaction mechanism butanol dehydration

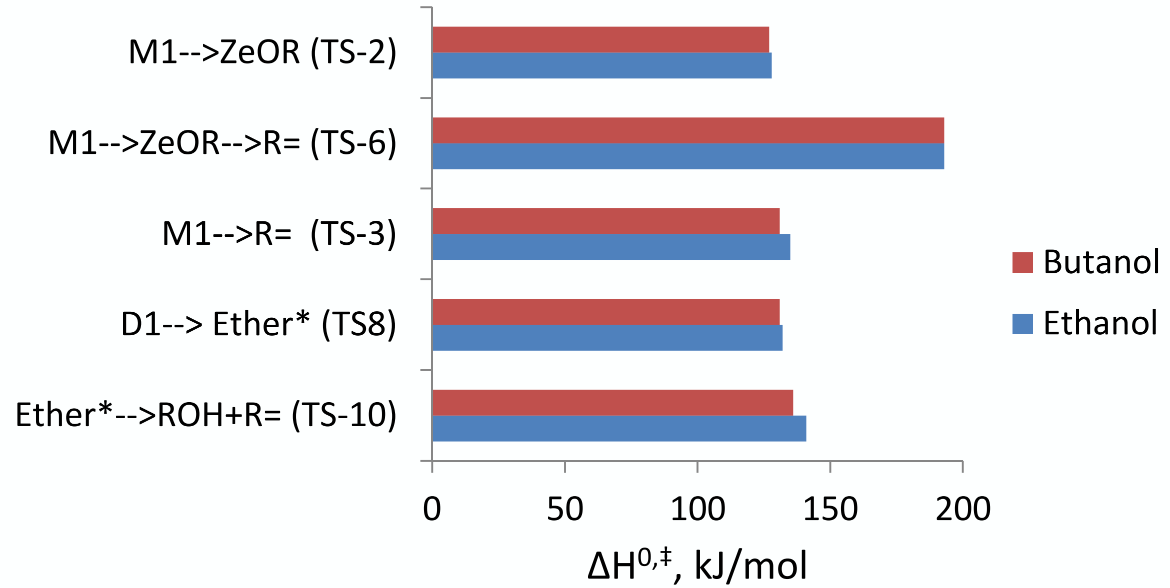


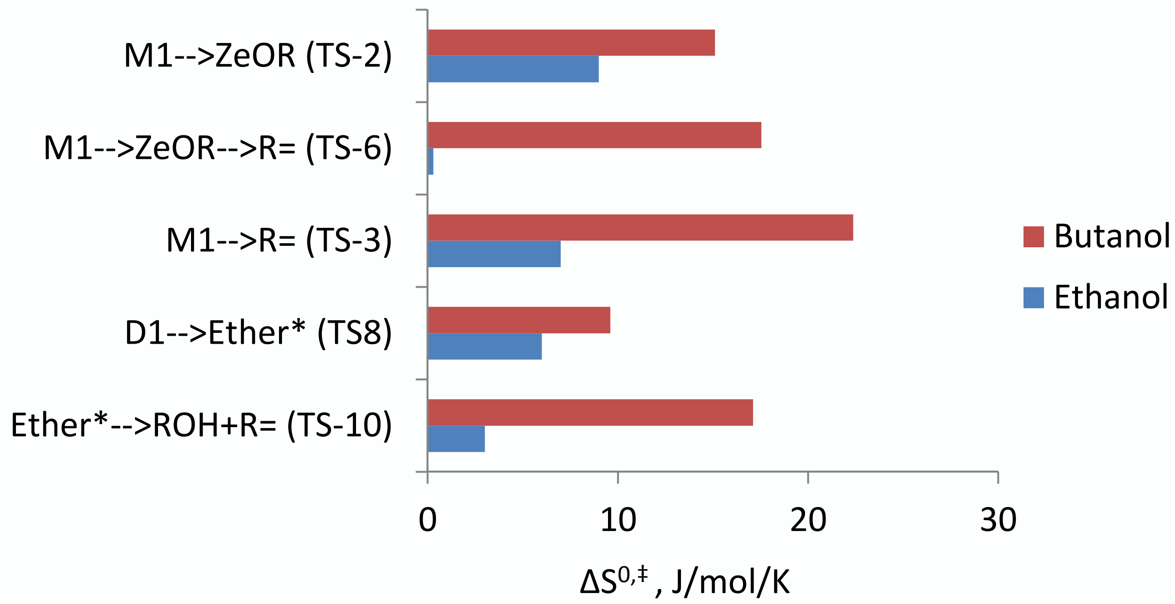
M. John et al., J. Catal. 330 (2015) 28

MARI's and Rate-Determining Steps

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

Effect of chain length on kinetics





	Surface species
M1	Chemisorbed alcohol monomer
ZeOR	Alkoxide (ethoxy, butoxide)
R=	Adsorbed alkene (ethene*/butene*)
D1	Chemisorbed alcohol dimer
Ether*	Adsorbed Ether (DEE/DBE)

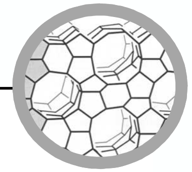
Increase in alcohol chain length has marginal influence on activation enthalpy but leads to significant increase in activation entropy

Overview

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

Experimental procedures

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

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

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

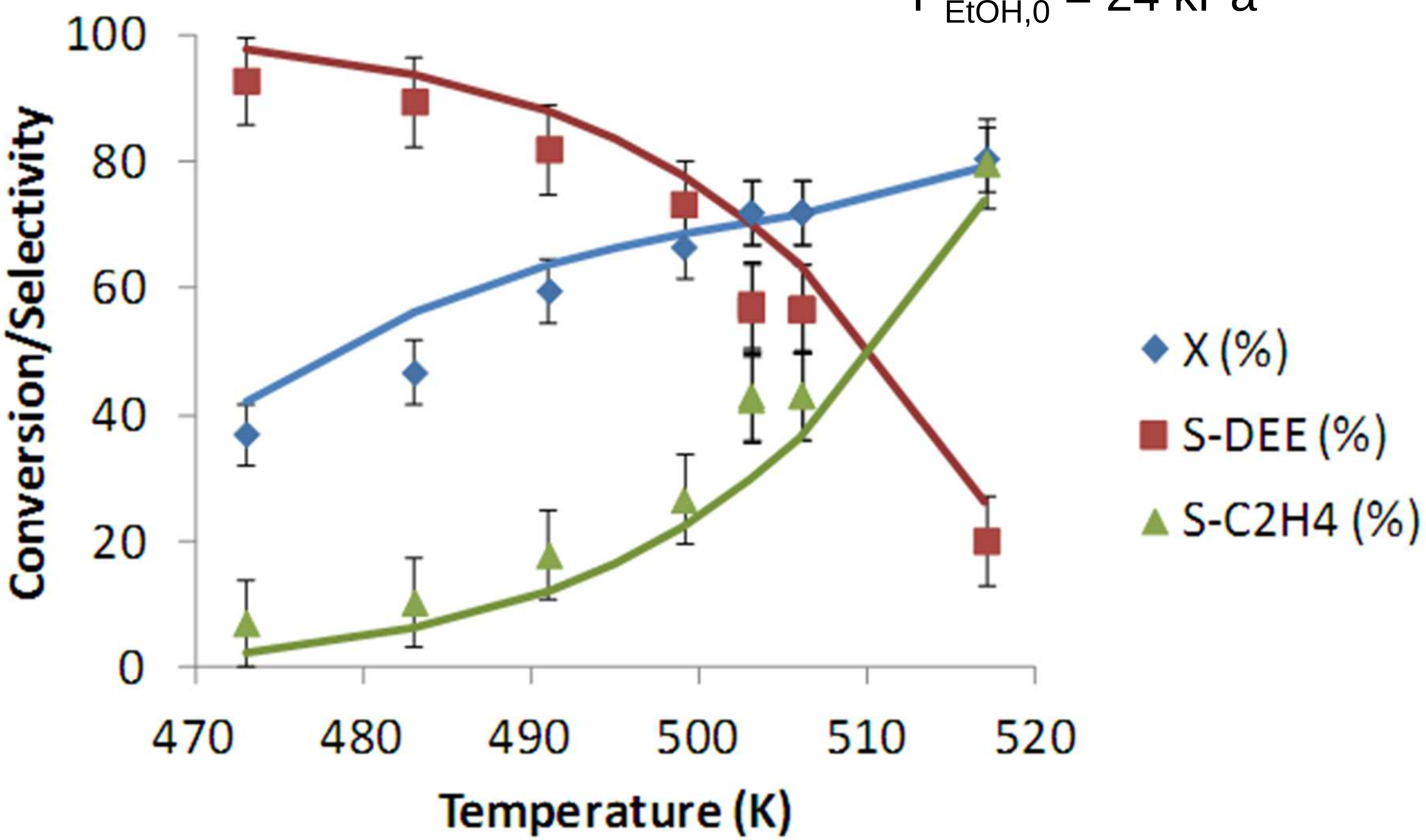
$F_i = F_{i,0}$ at $W=0$

- 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*

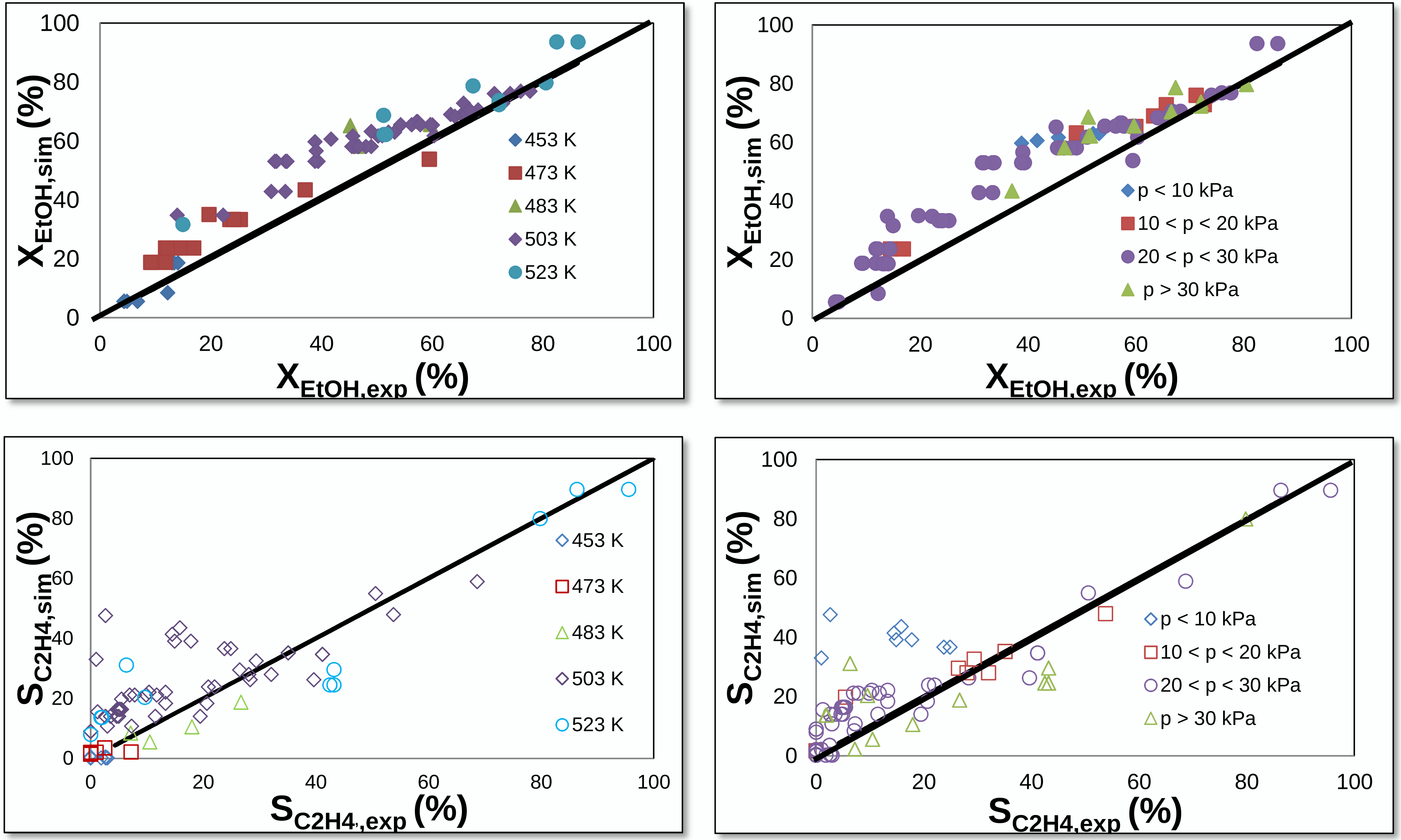
Experimental validation

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

$P_{EtOH,0}$ = 24 kPa



Parity diagrams



Overview

- Introduction
- Dehydration of bioalcohols on zeolites
  - First principles kinetic model development
  - Experimental validation
    - ➢ Butanol dehydration

Comparison with literature data

H-ZSM-5
T : 400 K
$P_{BuOH,0}$: 0.7 kPa
P_{total} : 101 kPa
Site time: 37 mol_{H+} s mol^{-1}

#			This work	Experimental #
1	TOF for production of Butene	(mol /mol H+ /s)	$3.5\ 10^{-5}$	$4.1\ 10^{-5}$
2	TOF for production of DBE	(mol /mol H+ /s)	$2.3\ 10^{-4}$	$5.1\ 10^{-4}$
3	Conversion	(mol %)	2.1	~ 2

Experimental result of Makarova et al., J. Catal. 149 (1994) 36

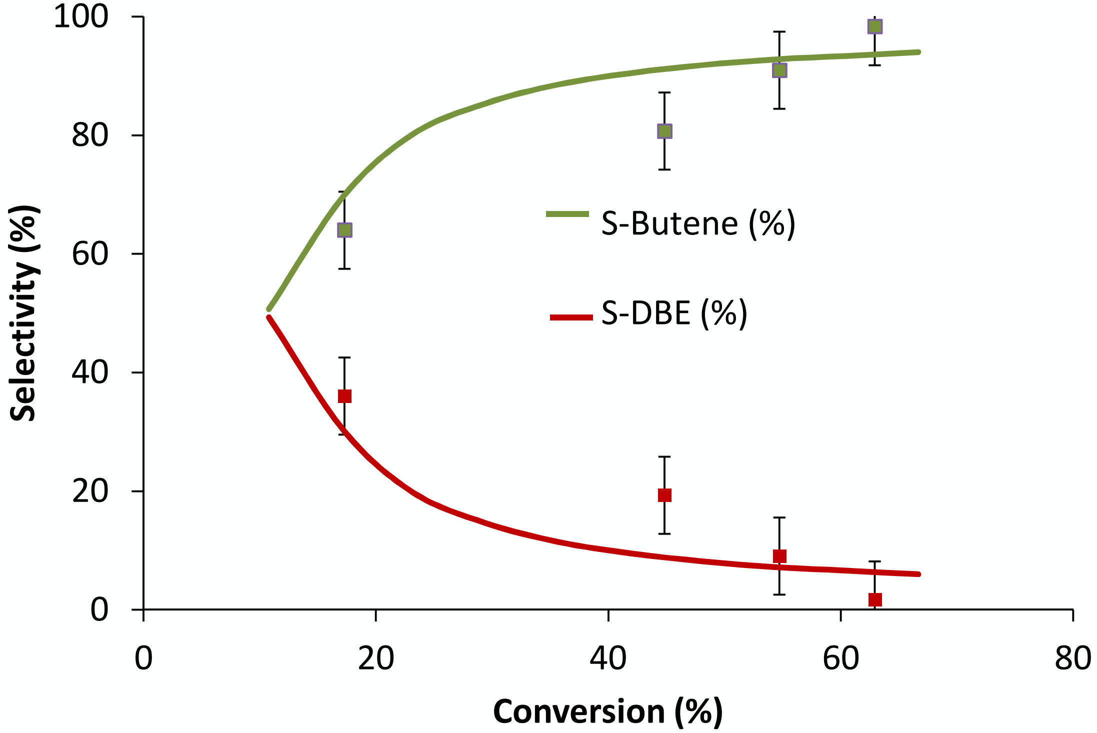
Experimental validation

H-ZSM-5 Si/Al : 15.5

$W_{cat}/F_{EtOH,0}$: 3-16 kg.s/mol

$P_{BuOH,0}$: 30 kPa

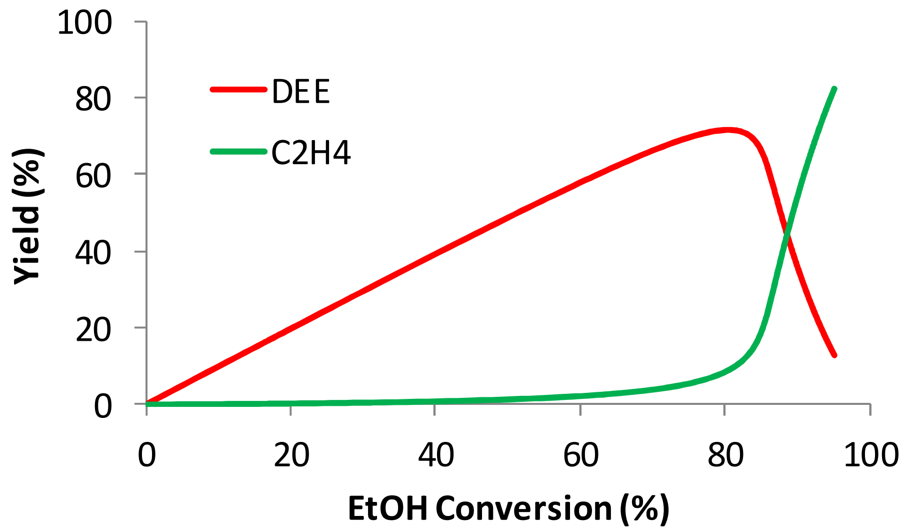
T : 503 K



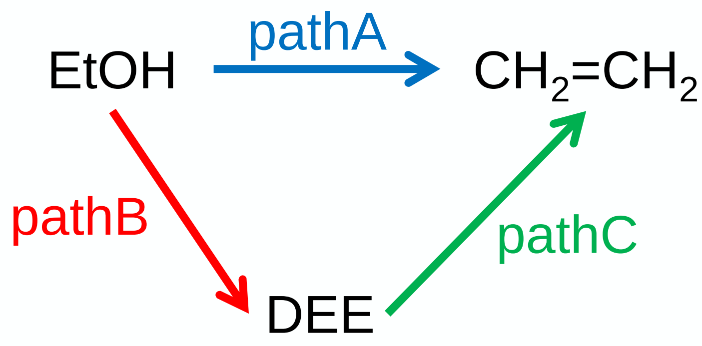
Overview

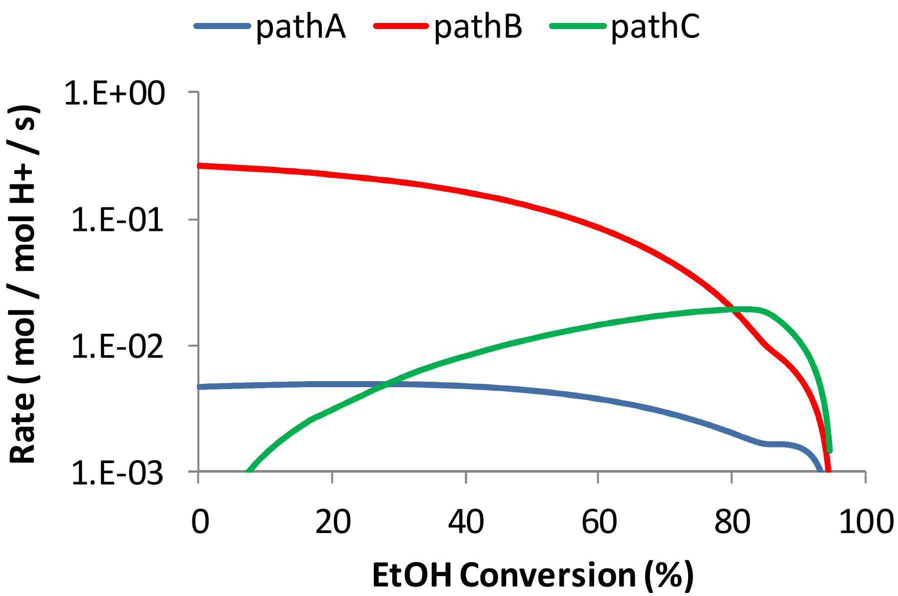
- Introduction
- Dehydration of bioalcohols on zeolites
  - First principles kinetic model development
  - Experimental validation
  - Reaction path analysis: Ethanol dehydration

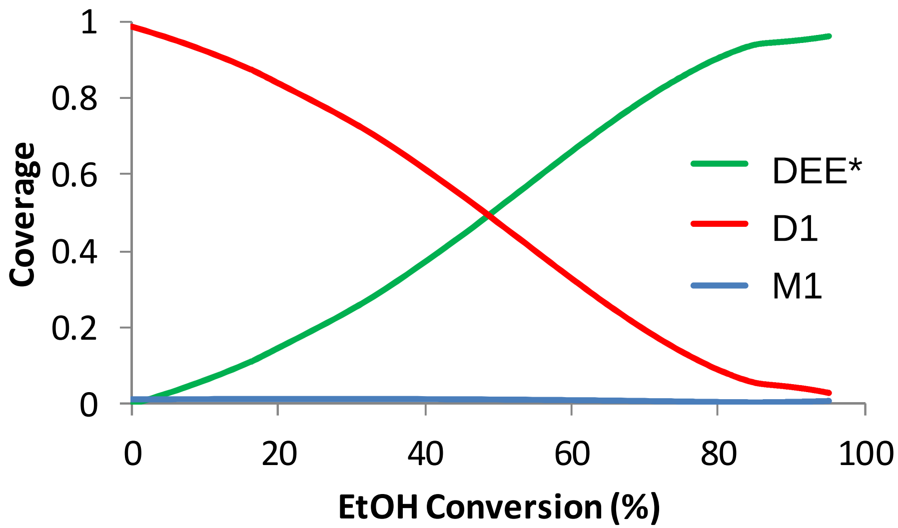
Reaction path analysis



T : 500 K, $P_{EtOH,0}$: 100 kPa







Overview

- Introduction
- Dehydration of bioalcohols on zeolites
  - First principles kinetic model development
  - Experimental validation
  - Reaction path analysis: butanol dehydration

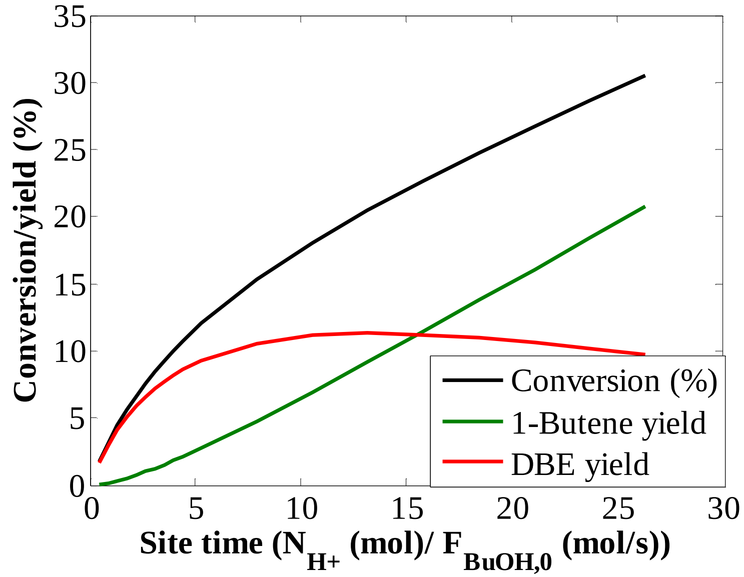
Reaction path analysis

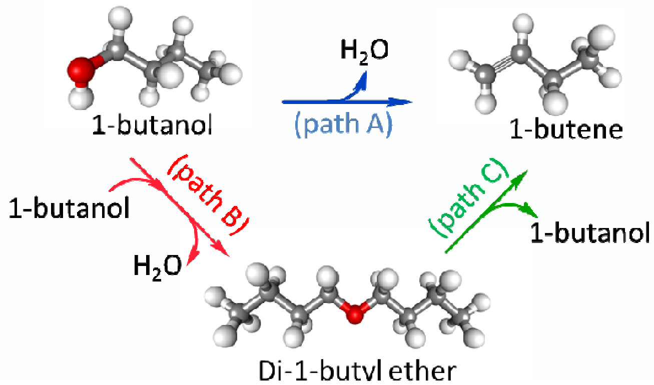
H-ZSM-5

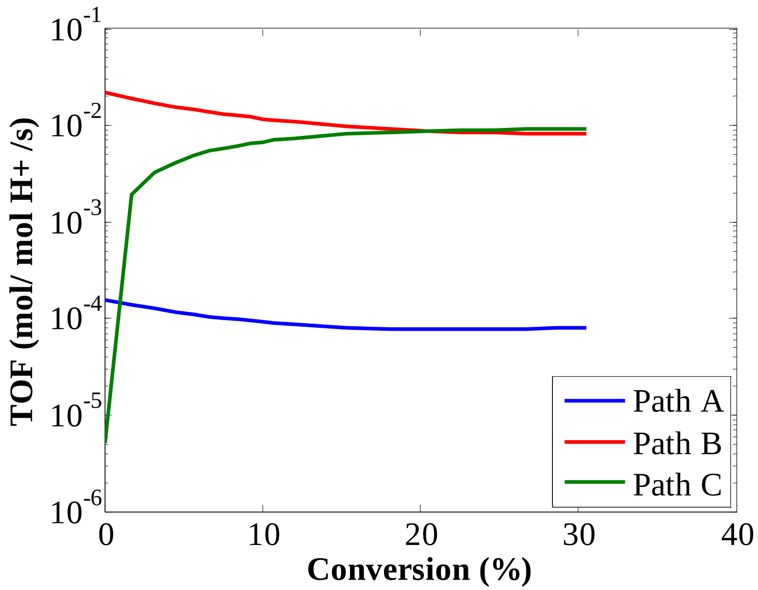
T : 450 K

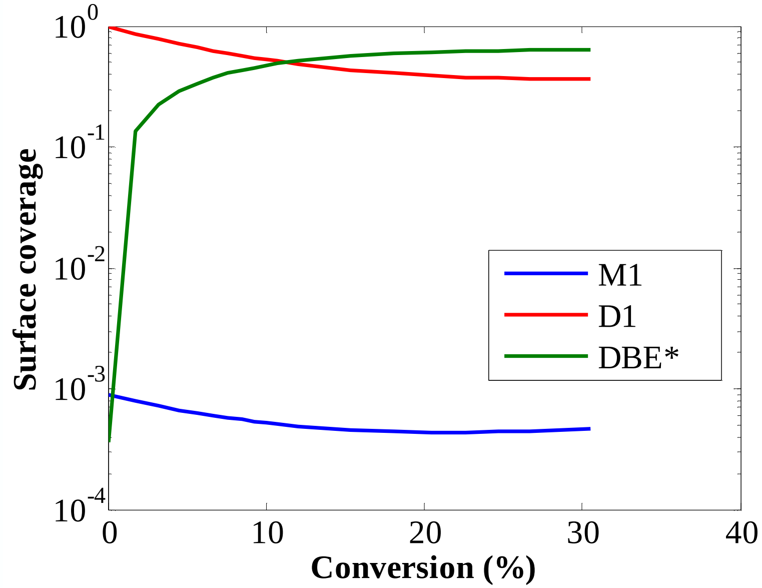
$P_{BuOH,0}$:1 kPa

X < 30% (to avoid other products)

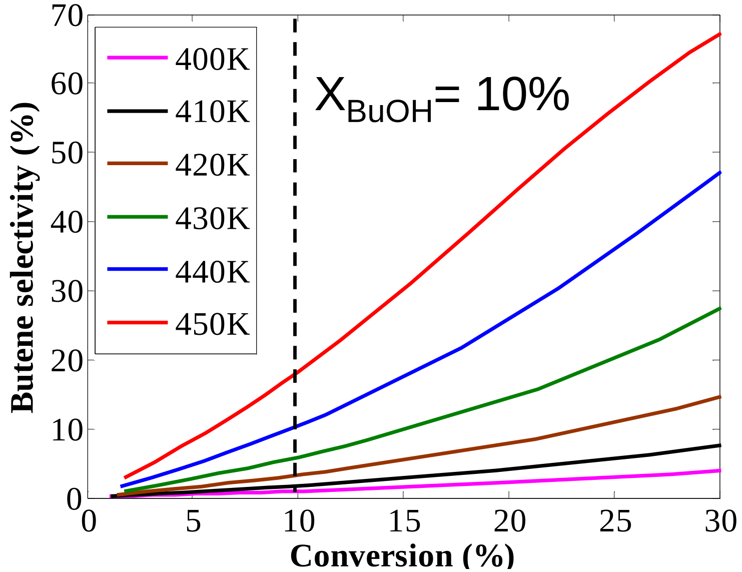








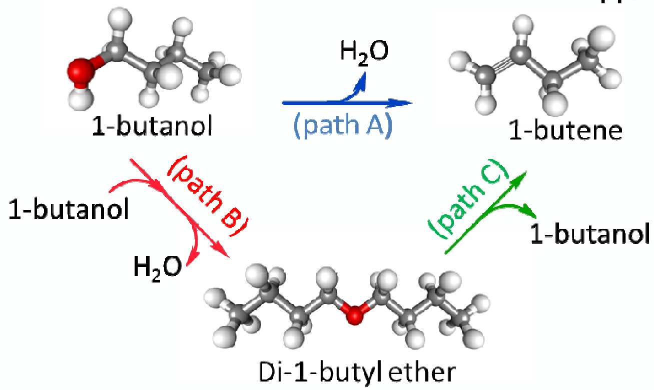
Effect of temperature

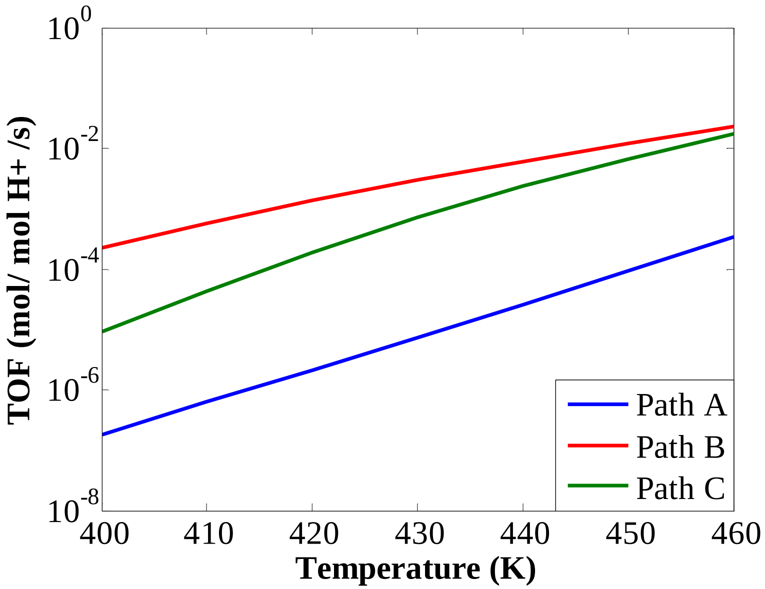


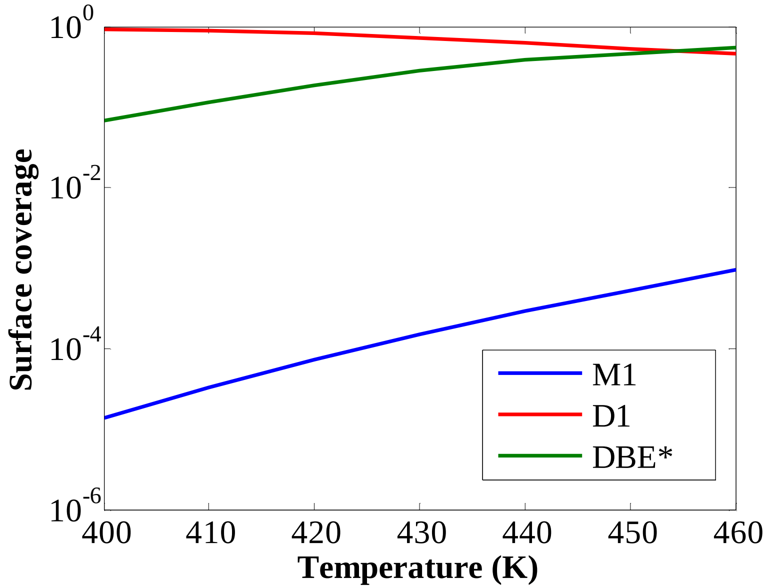
H-ZSM-5

$P_{BuOH,0}$: 1 kPa,

Site time : 0- 200 mol_{H+} s/mol







Effect of partial pressure of water

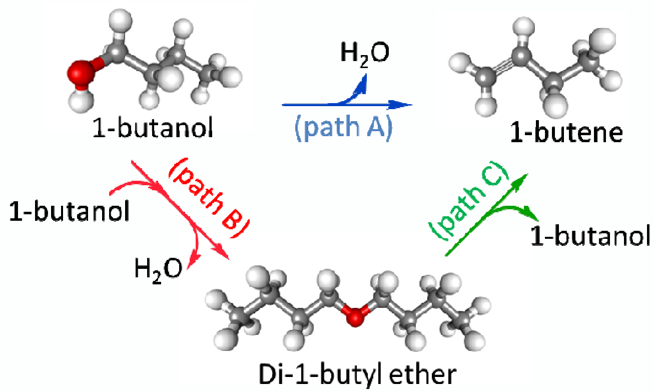
Zeolite: H-ZSM-5

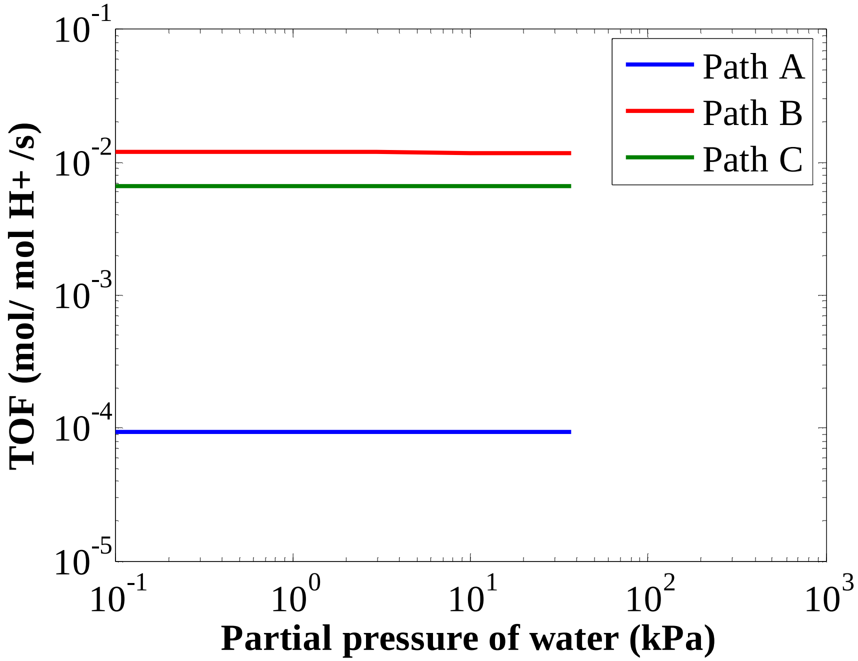
T: 450 K

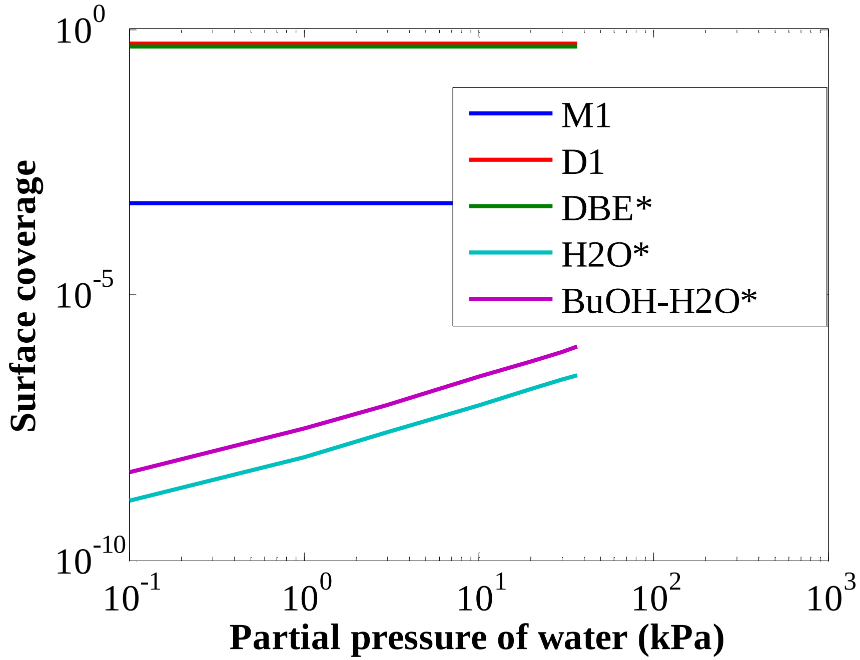
$P_{BuOH,0}$: 1 kPa,

$P_{H2O,0}$: 1 - 40 kPa,

X_{BuOH} : 10%





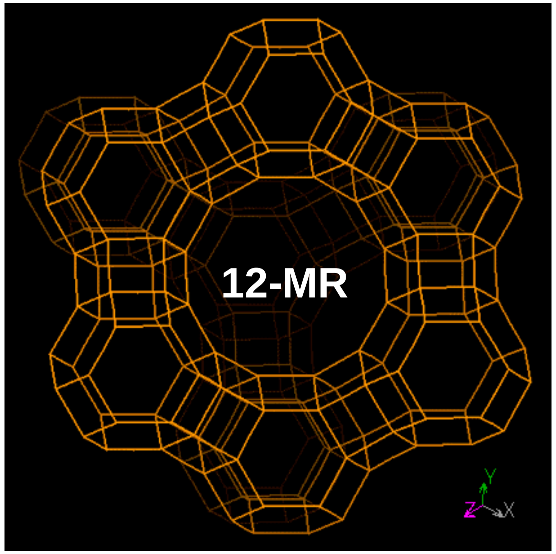


Overview

- Introduction
- Dehydration of bioalcohols on zeolites
  - First principles kinetic model development
  - Experimental validation
  - Reaction path analysis
  - Effect of zeolite
    - ➢ Ethanol dehydration

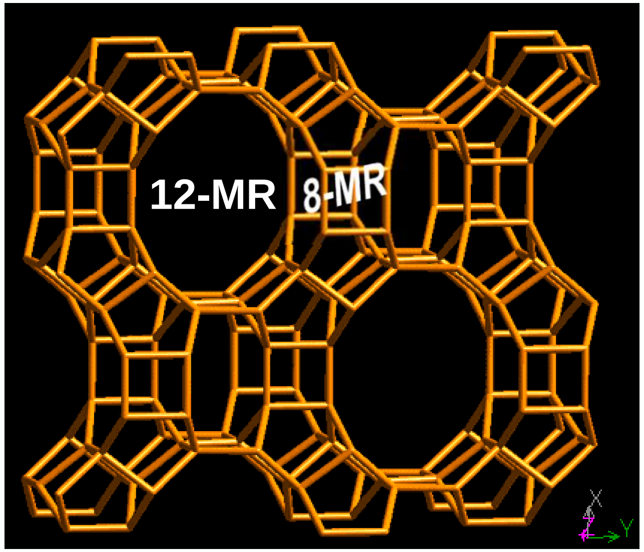
Zeolite Frameworks

H-FAU



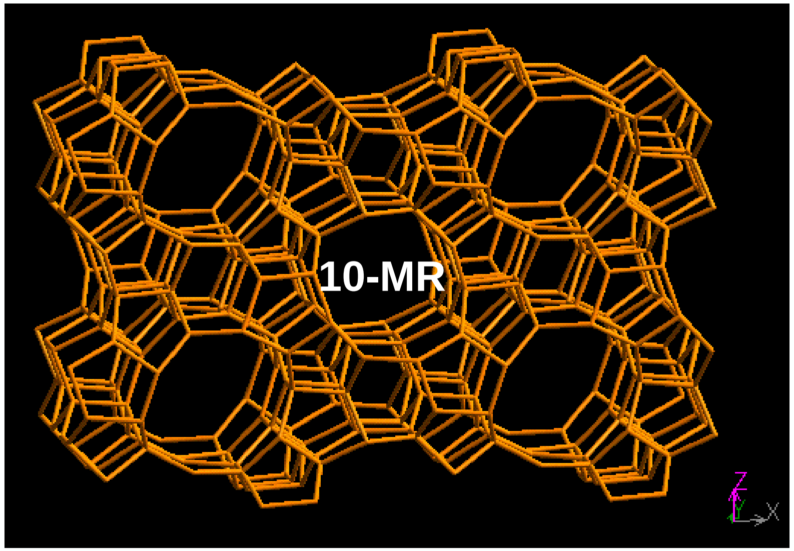
Si/Al = 47

H-MOR



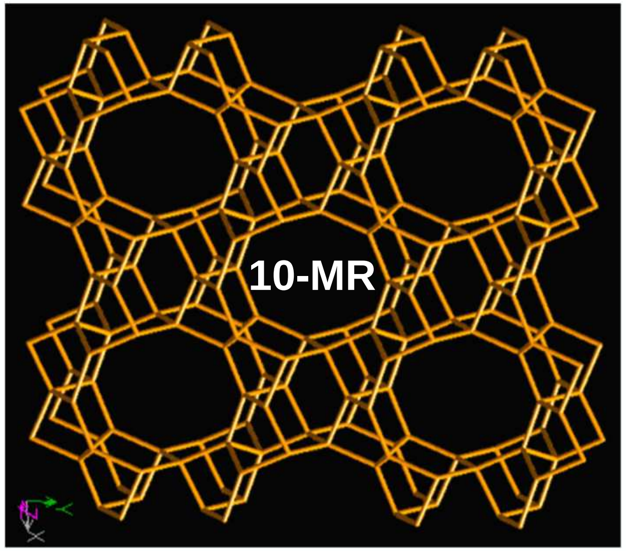
Si/Al = 95

H-ZSM-5



Si/Al = 95

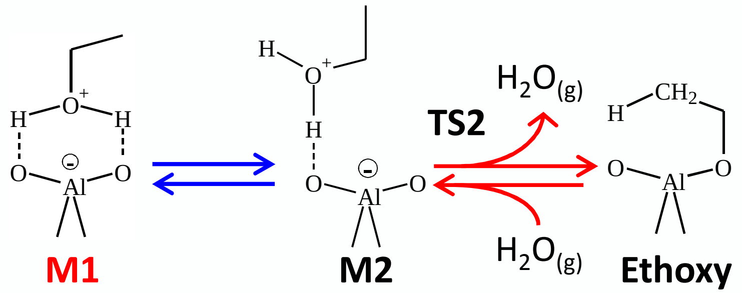
H-ZSM-22



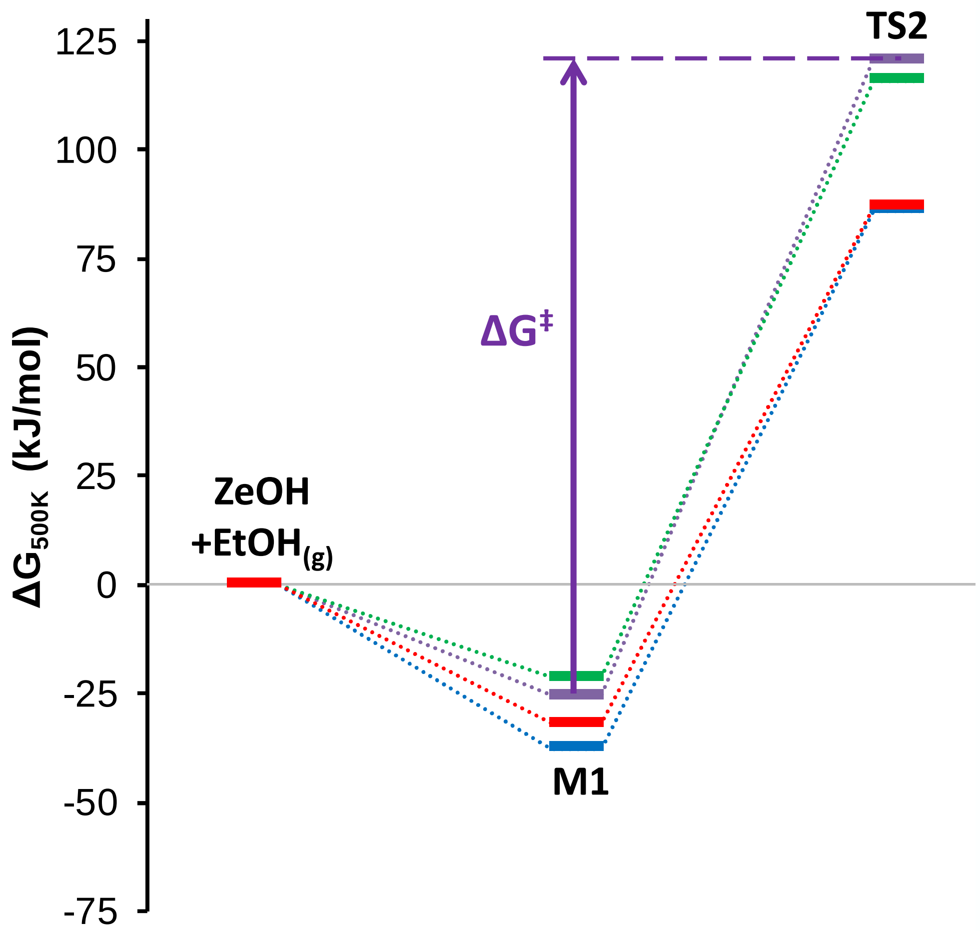
Si/Al = 35

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

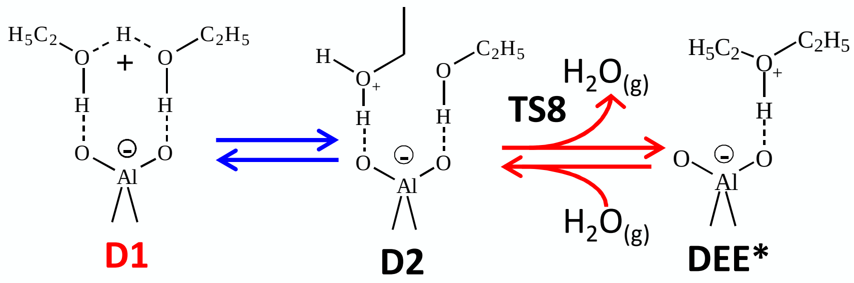


10-MR zeolites more reactive than 12-MR zeolites

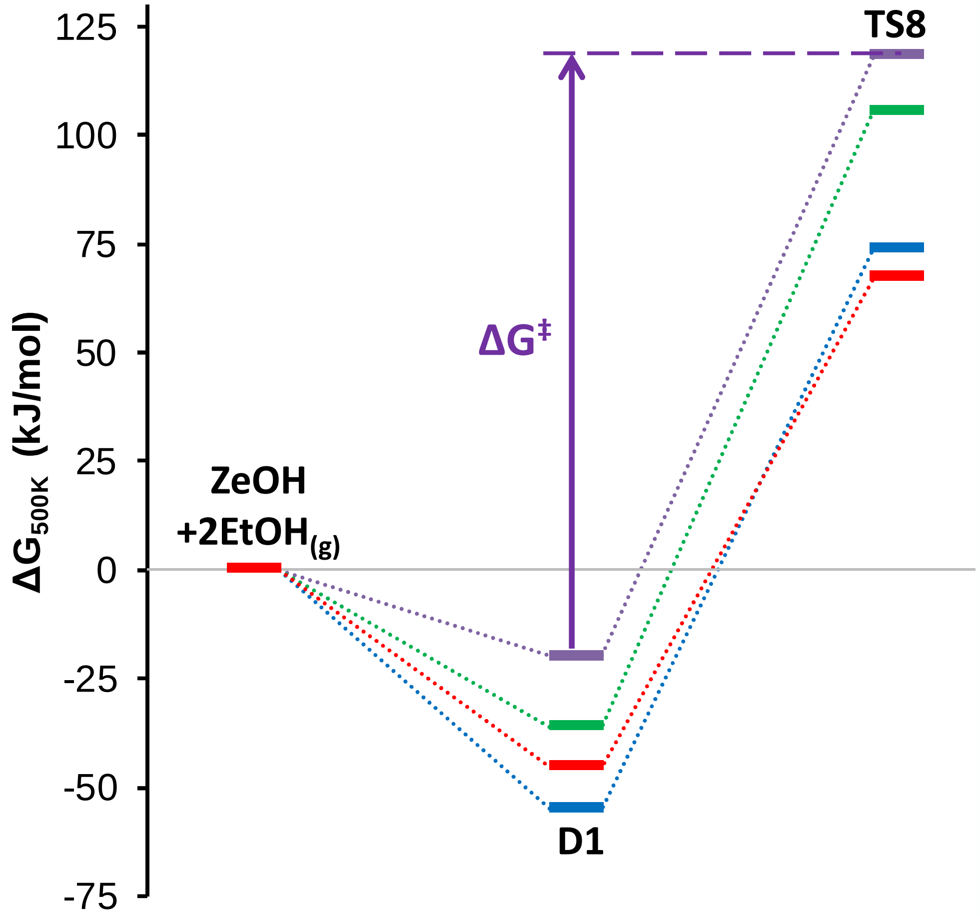


Effect of zeolite: B Ethanol to Diethyl ether:

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

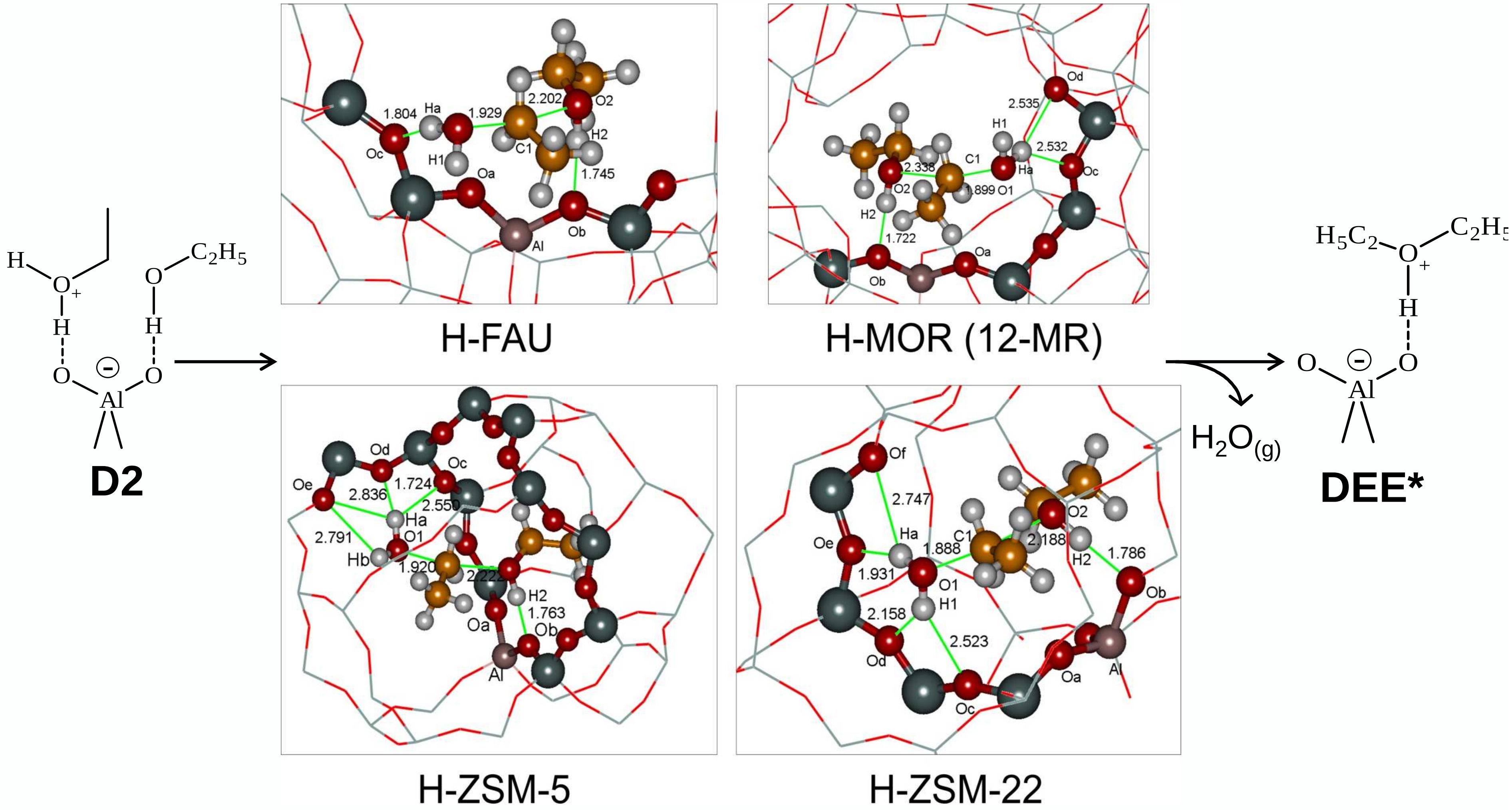


10-MR zeolites more reactive than 12-MR zeolites



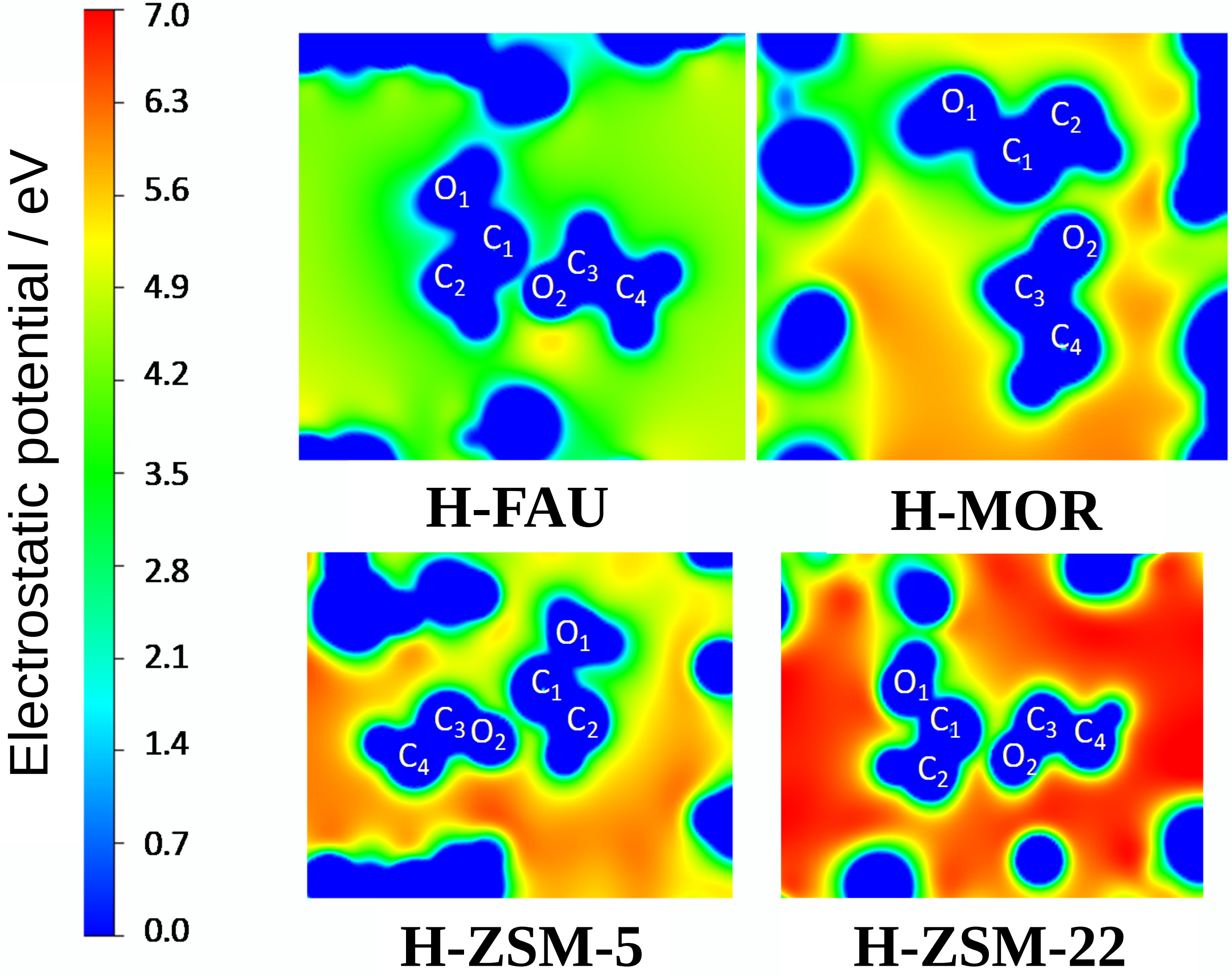
TS stabilization: vdW & hydrogen bonds

TS-8



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

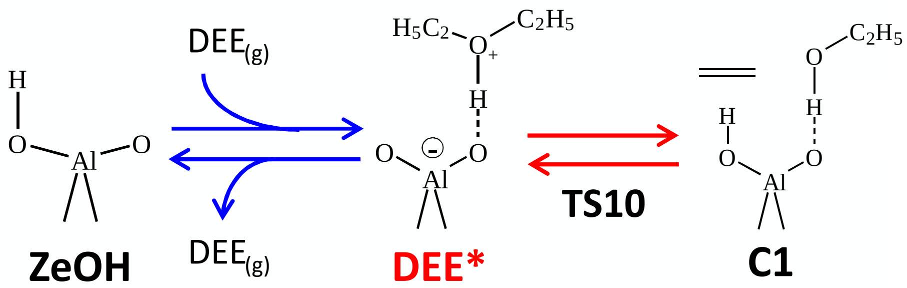
TS 8 stabilization: electrostatic interactions

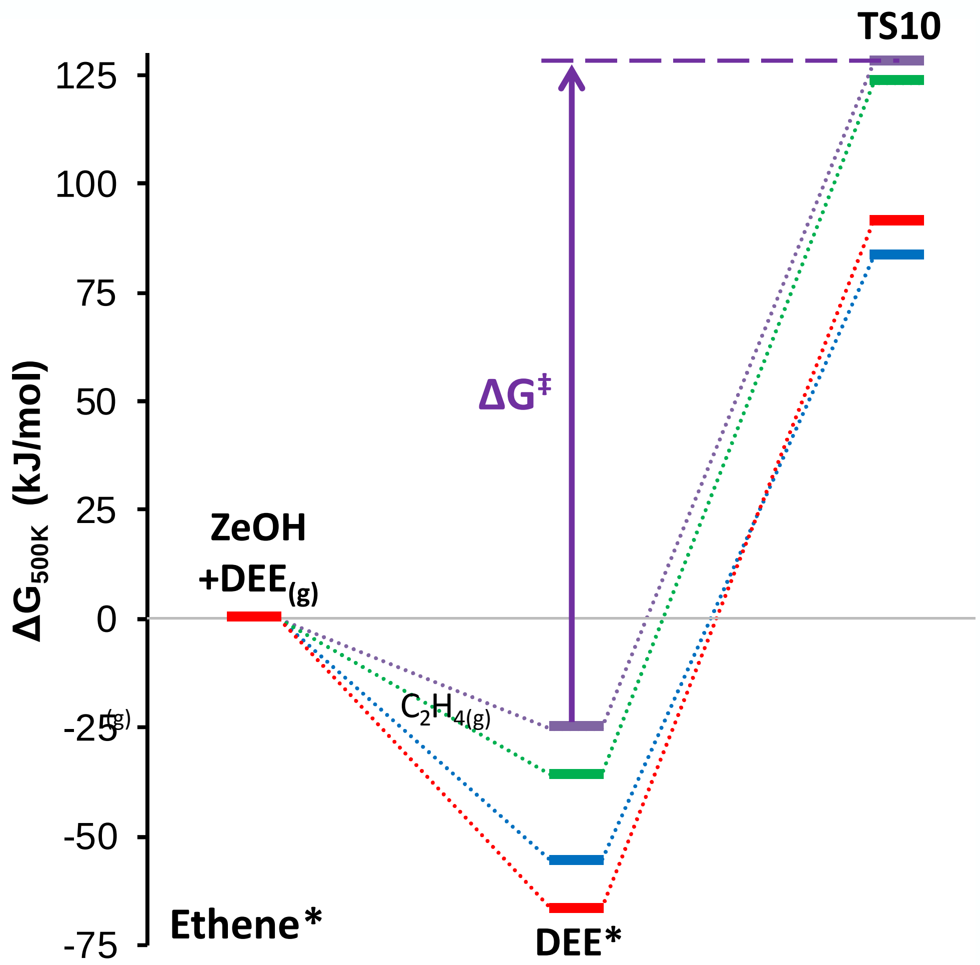


FAU < MOR < ZSM-5 < ZSM-22

Effect of zeolite: C Diethyl ether to Ethene

ZeOH	$\Delta G^{\ddagger} = G_{TS10} - G_{DEE*}$ (kJ/mol)
H-FAU	153
H-MOR	159
H-ZSM-5	139
H-ZSM-22	158



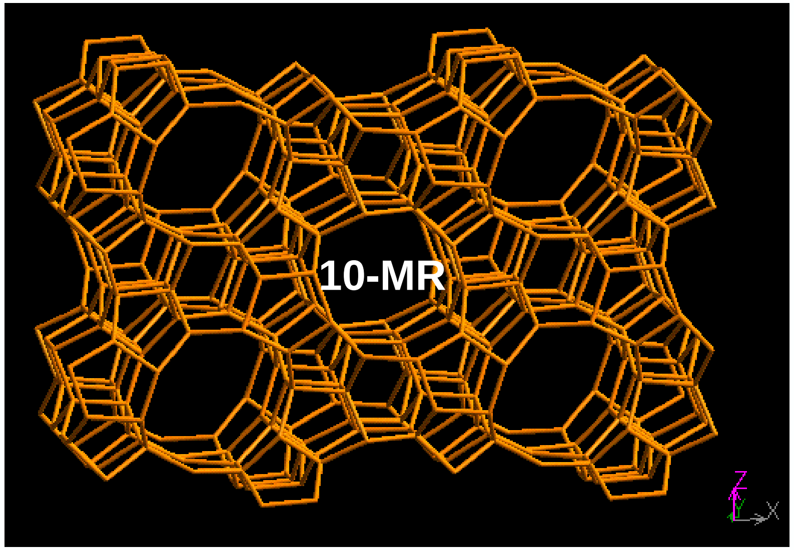


Overview

- Introduction
- Dehydration of bioalcohols on zeolites
  - First principles kinetic model development
  - Experimental validation
  - Reaction path analysis
  - Effect of zeolite
    - ➢ Butanol dehydration

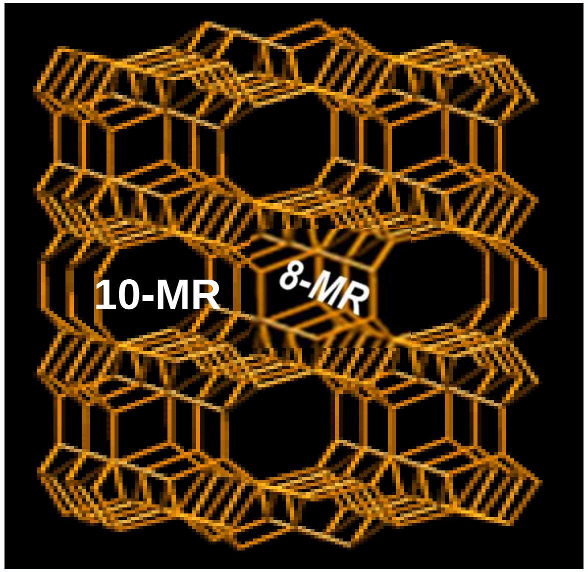
Zeolite Frameworks

H-ZSM-5



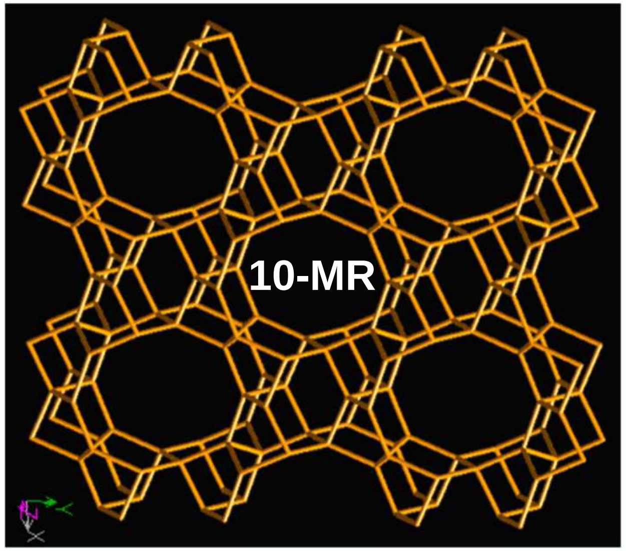
Si/Al = 95

H-FER



Si/Al = 71

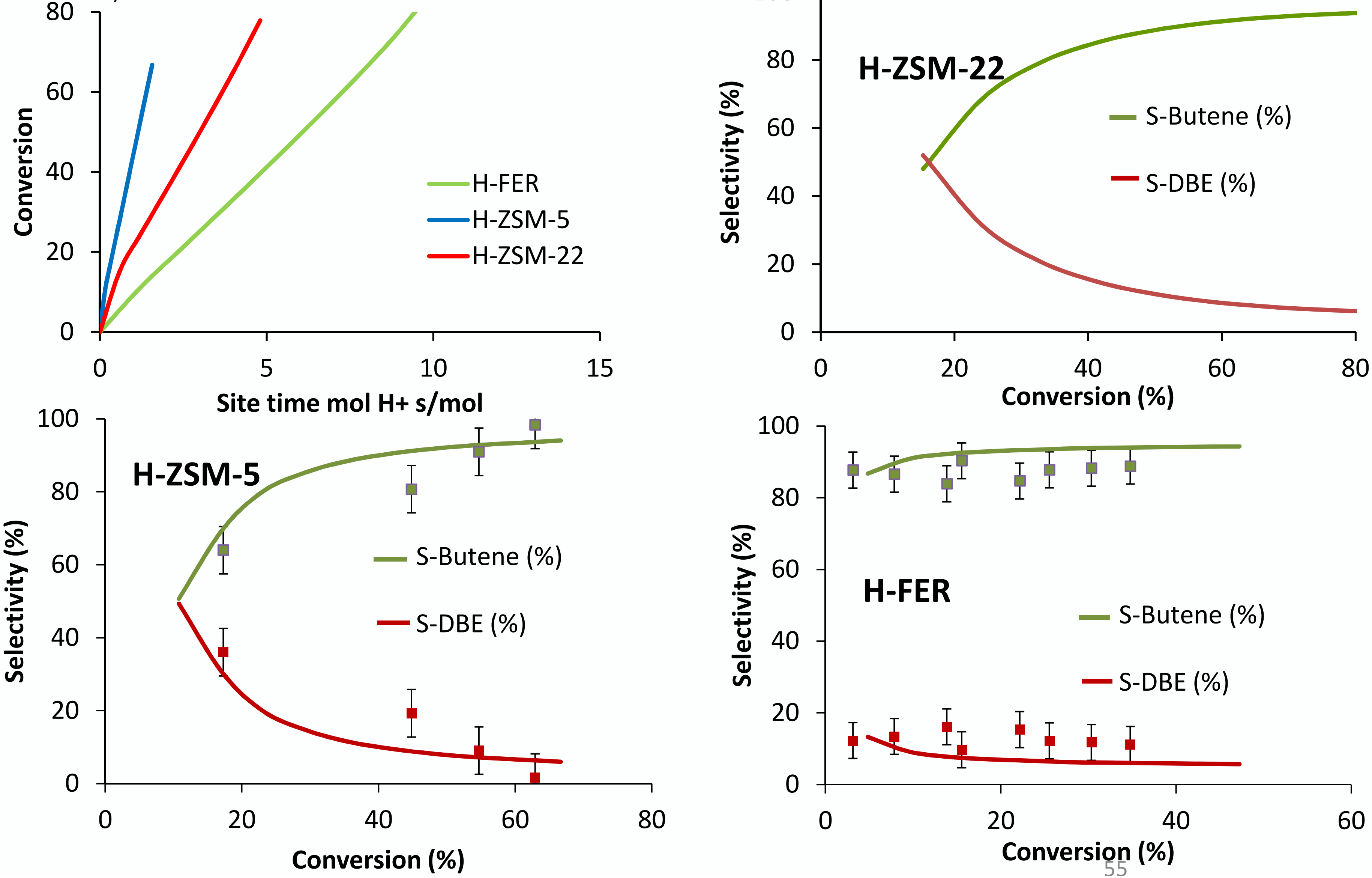
H-ZSM-22



Si/Al = 35

Butanol dehydration: Effect of Zeolite

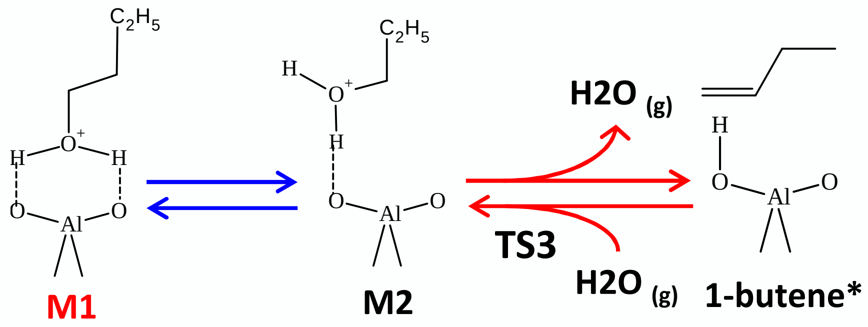
$P_{BuOH,0}$ = 30 kPa Temperature = 503 K



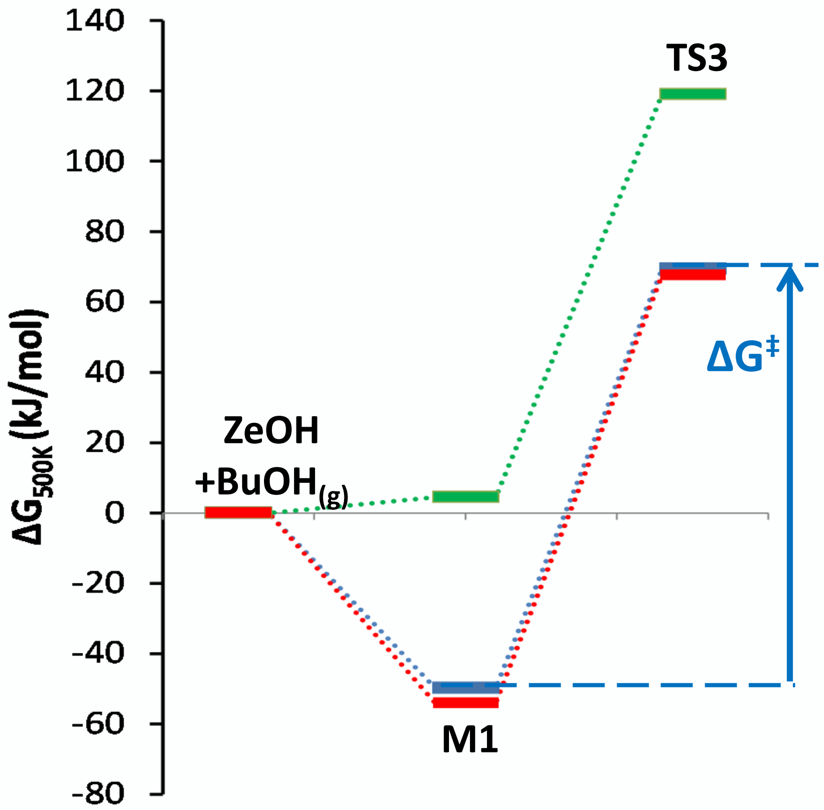
55

Effect of zeolite on conversion: paths A and B

Zeolite	Frame work structure	Pore dimension	$\Delta G^{\ddagger} = G_{TS3} - G_{M1}$ (kJ/mol)
H-FER	2D (10 and 8 MR)	4.2 x 5.4 [001], 3.5 x 4.8[010]	115
H-ZSM-5	3D (10 MR)	5.1 x 5.5 [100], 5.3 x 5.6 [010]	119
H-ZSM-22	1D (10 MR)	4.6 x 5.7 [001]	122

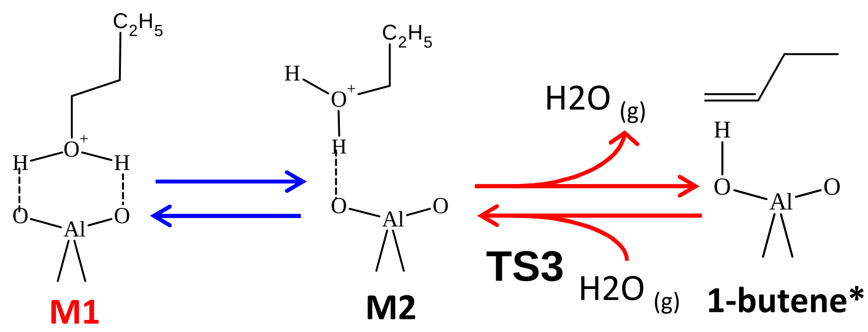


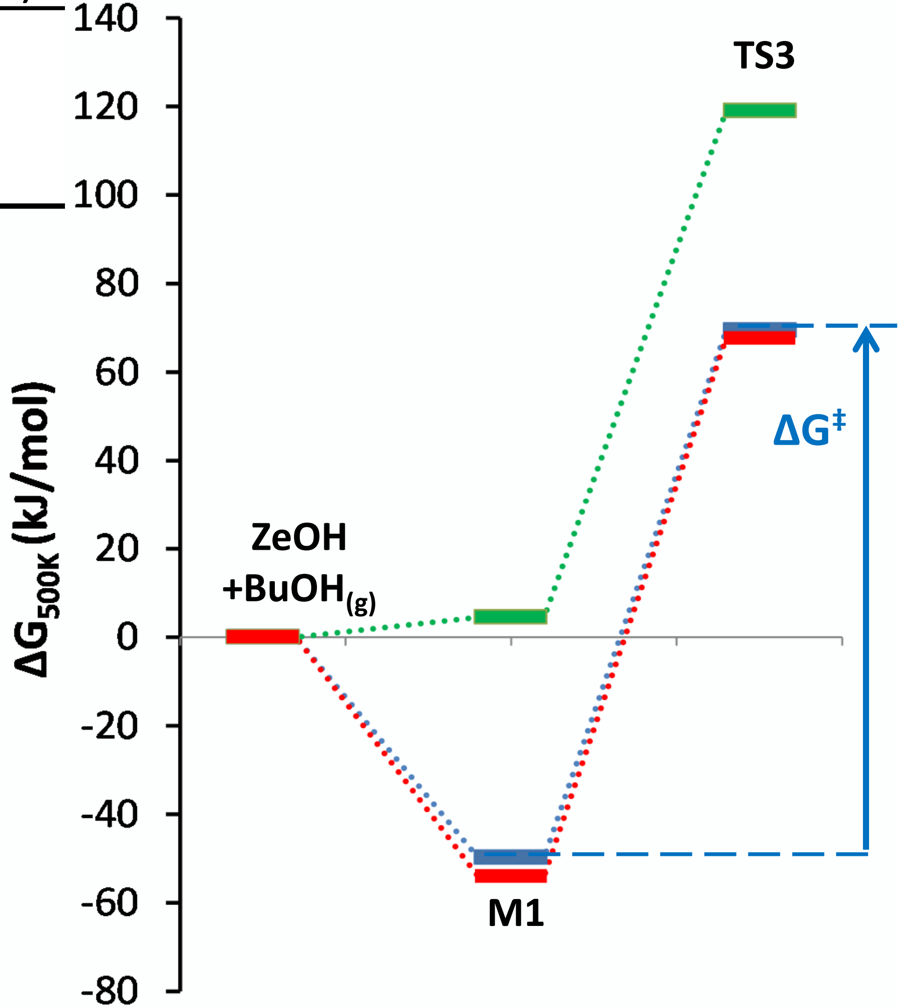
M1	ΔH°ads (kJ/mol)	ΔS°ads (J/mol/K)
H-ZSM-5	–146	–192
H-FER	–106	–222
H-ZSM-22	–150	–192



Effect of zeolite: Path A Butanol to Butene

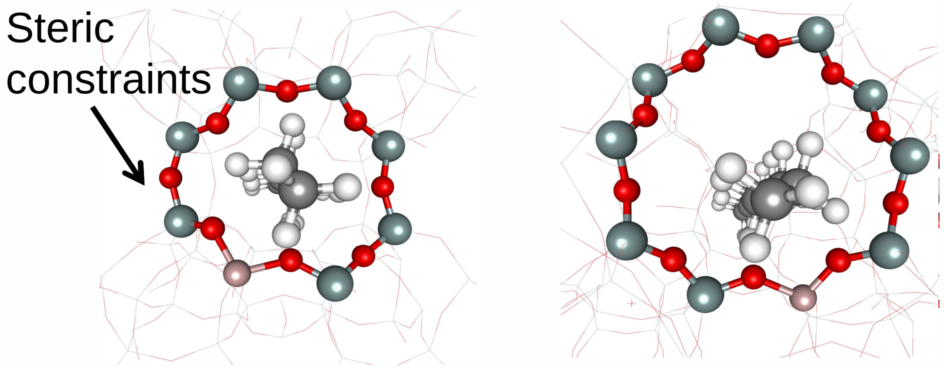
ZeOH	$\Delta G^{\ddagger} = G_{TS3} - G_{M1}$ (kJ/mol)	$\Delta H^{\ddagger}$ (kJ/mol)	$T\Delta S^{\ddagger}$ (kJ/mol)
H-FER	115	130	15
H-ZSM-5	119	132	13
H-ZSM-22	122	136	14



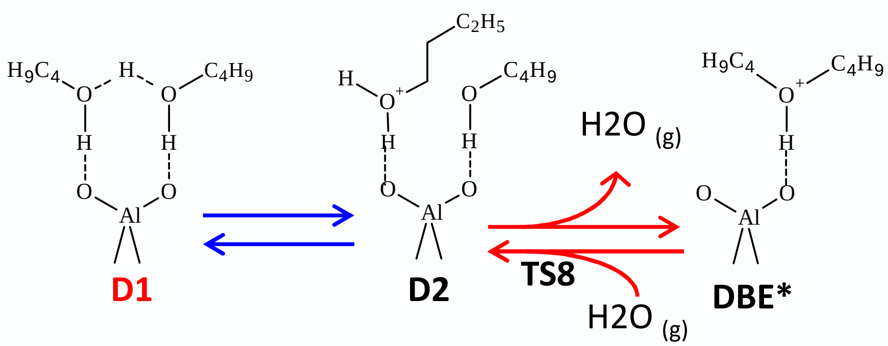


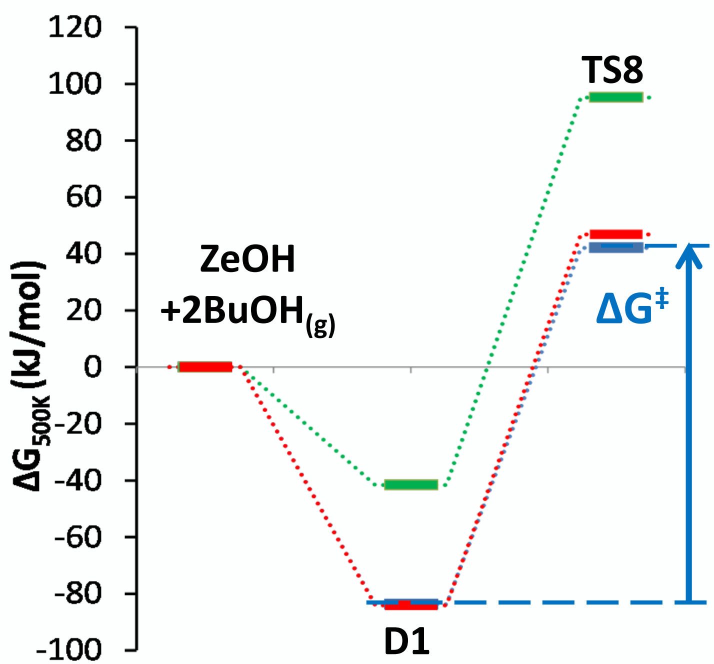
Effect of zeolite: Path B Butanol to Ether

Zeolite	Frame work structure	Pore dimension	$\Delta G^{\ddagger} = G_{TS8} - G_{D1}$ (kJ/mol)
H-FER	2D (10 and 8 MR)	4.2 x 5.4 [001], 3.5 x 4.8[010]	137
H-ZSM-5	3D (10 MR)	5.1 x 5.5 [100], 5.3 x 5.6 [010]	126
H-ZSM-22	1D (10 MR)	4.6 x 5.7 [001]	131



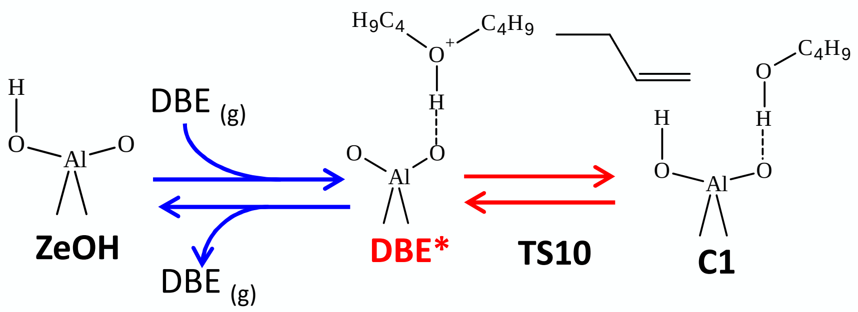
DBE* (FER) DBE* (MFI)

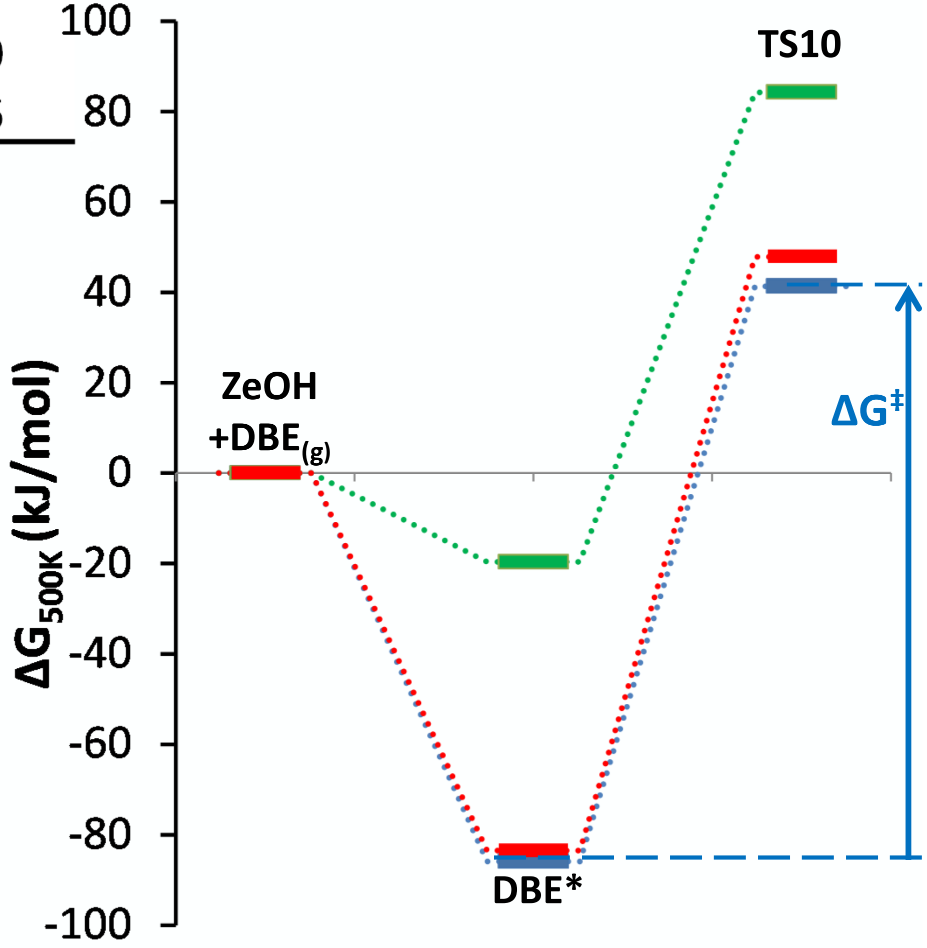




Effect of zeolite: Path C Dibutyl ether to Butene

ZeOH	$\Delta G^{\ddagger} = G_{TS10} - G_{DBE*}$ (kJ/mol)	$\Delta H^{\ddagger}$ (kJ/mol)	$T\Delta S^{\ddagger}$ (kJ/mol)
H-FER	104	113	9
H-ZSM-5	127	137	10
H-ZSM-22	131	147	16





Overview

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

From lab to industrial reactor

Total Petrochemicals

United States Patent
Coupard et al.
Patent No.: US 7,994,377 B2
Date of Patent: Aug. 9, 2011

United States Patent
Le Van Mao

Minoux et al.
US 2011/0105815 A1
Pub. Date: May 5, 2011

Patents ethanol conversion

United States Patent
Tsao et al.
4,134,926
Jan. 16, 1979

United States Patent
Uytterhoeven et al.
Patent Number: 4,727,214
Date of Patent: Feb. 23, 1988

IFPEN

JOURNAL OF CATALYSIS 53, 40–55 (1978)

Elucidation of the Mechanism of Conversion of Methanol and Ethanol to Hydrocarbons on a New Type of Synthetic Zeolite

ERIC G. DEROUANE,*,[1] JANOS B. NAGY,* PIERRE DEJAIFVE,* JAN H. C. VAN HOOFF,† BEN P. SPEKMAN,† JACQUES C. VÉDRINE, AND CLAUDE NACCACHE‡

* Laboratoire de Catalyse, Facultés Universitaires de Namur, 61 Rue de Bruxelles, 5000 Namur, Belgium; † Laboratory of Inorganic Chemistry, Eindhoven University of Technology, P.O. Box 513, Eindhoven, The Netherlands; and ‡ Institut de Recherches sur la Catalyse (CNRS), 79 Boulevard du 11 Novembre 1918, 69626 Villeurbanne Cedex, France

Received November 11, 1977

Alcohol conversion on ZSM-5

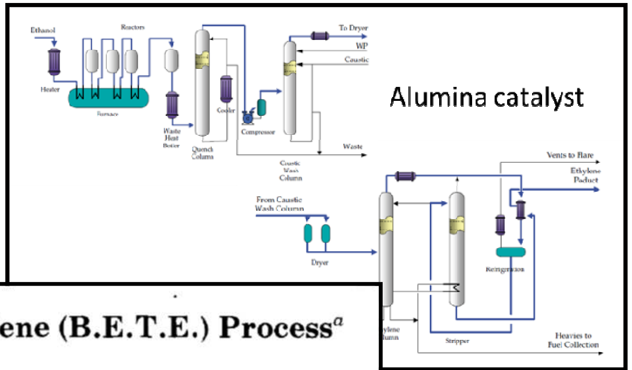
1965 · 1967 · 1977 · 1978 · 1989 · 2010 · 2014

Invention ZSM-5

Industrial zeolite based ethanol dehydration reactor

Typical process conditions	
Temperature (K)	523 - 773
P_t *(kPa)*	101 - 3010

Start-up ethanol dehydration plant



The Bioethanol-to-Ethylene (B.E.T.E.) Process[a]

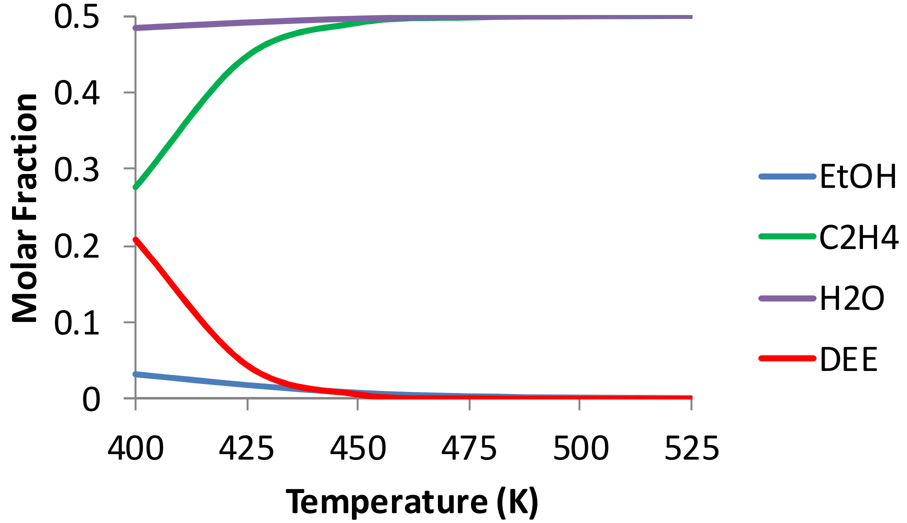
RAYMOND LE VAN MAO*, THANH MY NGUYEN and GERALD P. MCLAUGHLIN

Catalysis Research Laboratory, Department of Chemistry and Laboratories for Inorganic Materials, Concordia University, 1455 De Maisonneuve Blvd. West, Montreal, Quebec H3G 1M8 (Canada)

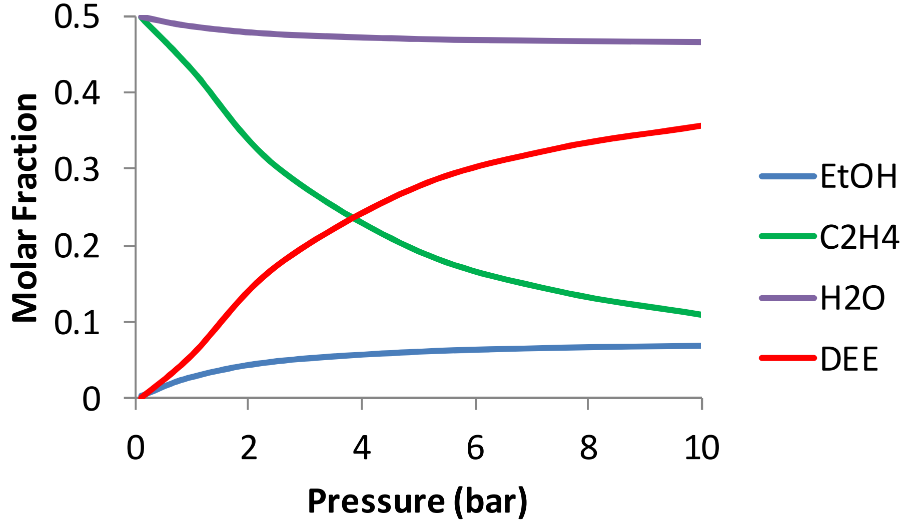
(Received 6 June 1988, revised manuscript received 11 October 1988)

Equilibrium composition

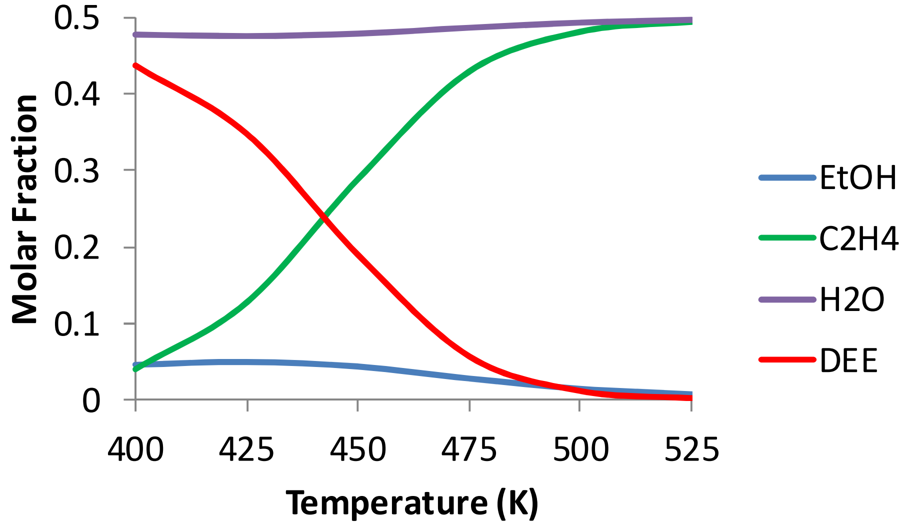
P = 0.1 bar



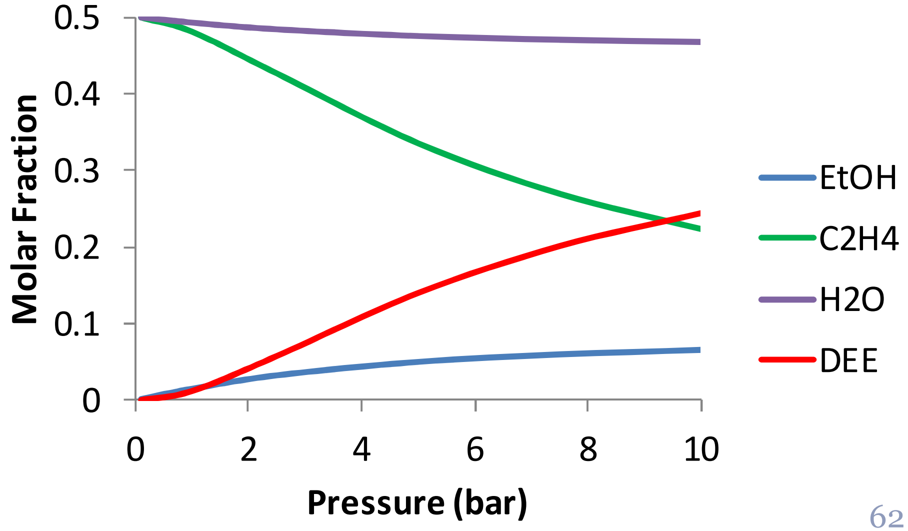
T = 475 K



P = 1 bar

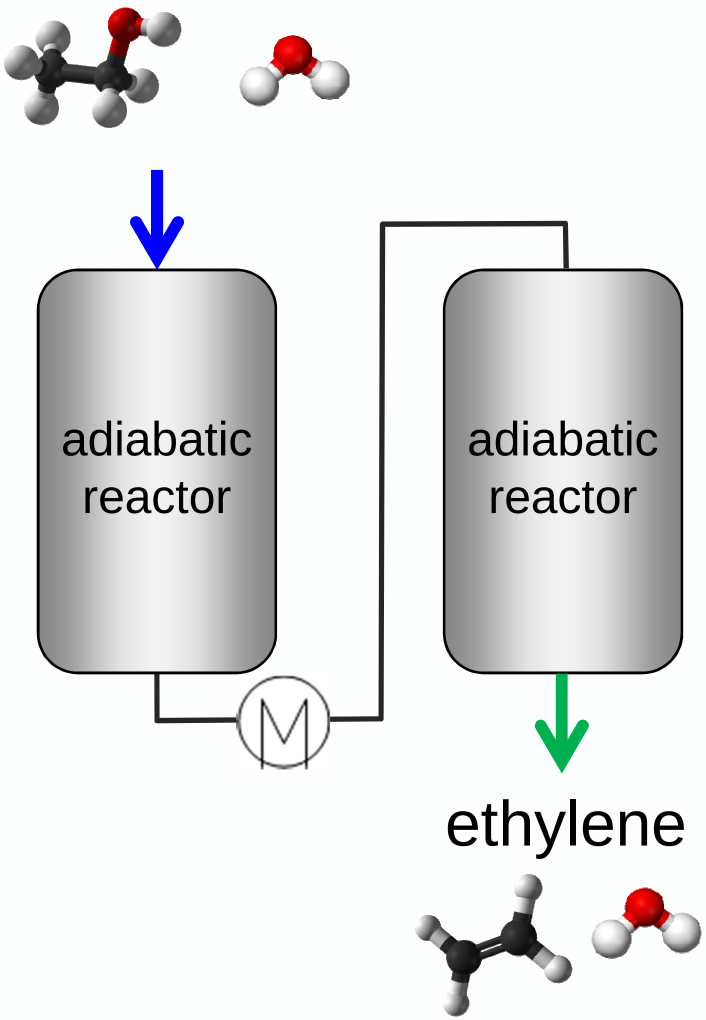


T = 500 K



Industrial dehydration reactor

bio-ethanol (aqueous ethanol solution)



Design specifications[1]	
T_{in} (K)	673
P (kPa)	530
Ethylene production (kT y^{-1})	220
Ethanol content (wt.%)	26
Catalyst mass (ton)	6

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

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

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

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

Reactor model equations

Continuity equations for surface species k and gas-phase components i :

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

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 $W=0$

Energy equation:

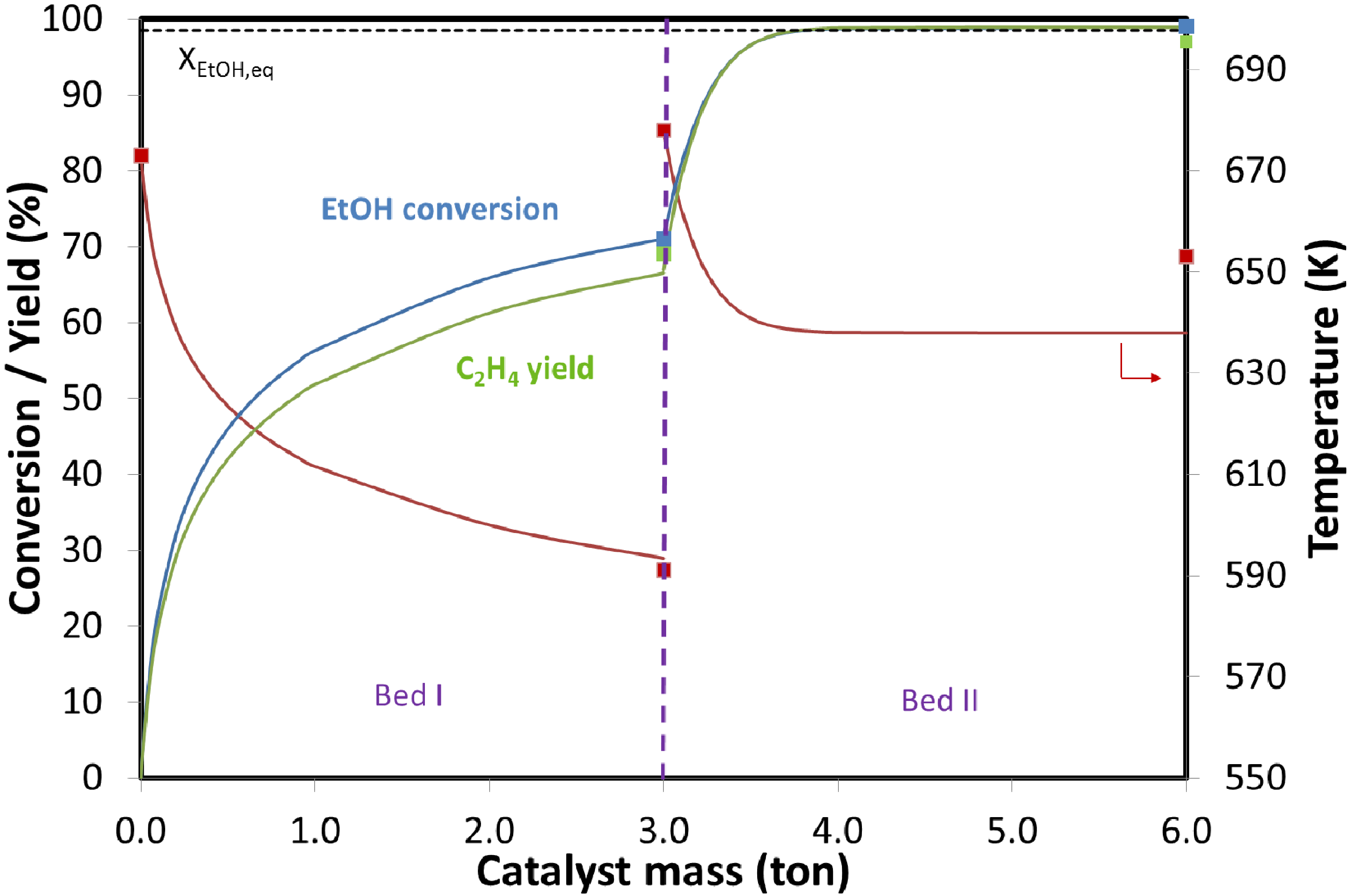
$$G c_p \frac{dT}{dW} = \sum_{i=1} \Delta H_{f,i}\, R_i C_t$$

$T = T^0$ 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 constant of elementary step j
- θ 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 capacity ($J\ kg^{-1}\ K^{-1}$)
- G mass flow rate (kgs^{-1})
- $\Delta H_{f,i}$ enthalpy of formation of component *i* ($J\ mol^{-1}$)

Industrial multibed adiabatic operation



Overview

- Introduction
- Ethanol dehydration on zeolites
  - First principles kinetic model development
  - Experimental validation
  - Effect of zeolite framework
  - Industrial reactor scale
- Conclusions

Conclusions

- 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

Acknowledgements

- Long Term Structural Methusalem Funding by the Flemish Government – grant number BOF09/01M00409
- Interuniversity Attraction Poles Programme
- Fund for Scientific Research (FWO) – Flanders
- Prof. A. Verberckmoes
- Dr. V. Galvita, dr. C.M. Nguyen, dr. K. Alexopoulos
- M. John, K.Van der Borght, D. Gunst

erc European Research Council

belspo

HPC UGENT

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:***

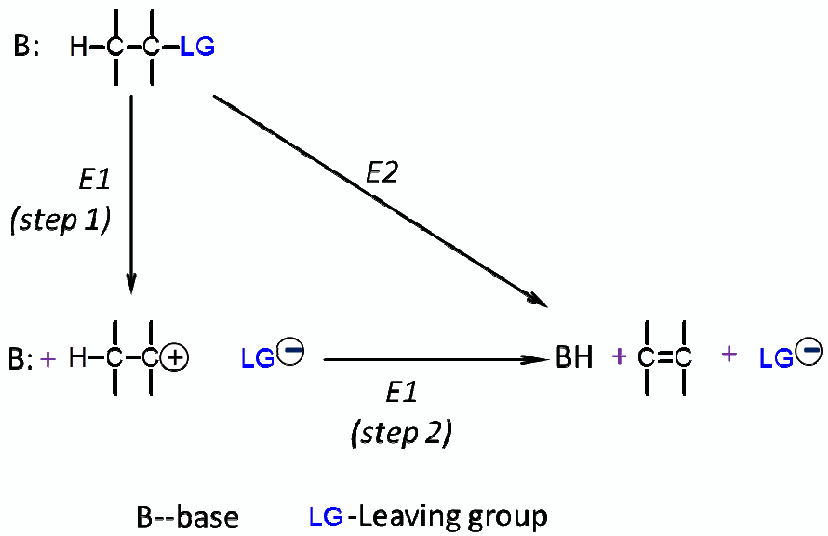
$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{k_B T} \right) = \frac{k_B T}{h} \frac{q^{\ddagger}}{q} \exp\left(-\frac{\Delta E_0^{\ddagger}}{k_B T} \right)$$

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

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

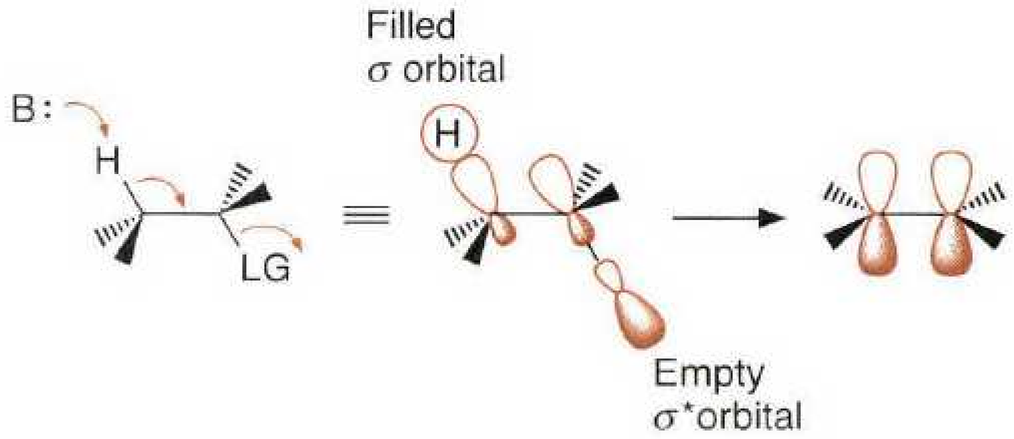
Glossary

- ***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.



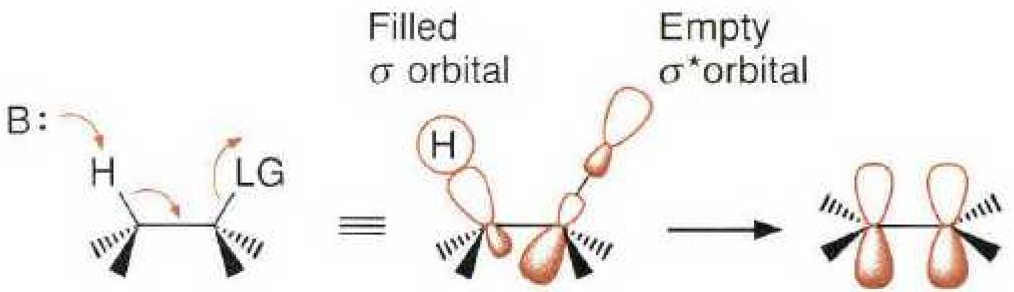
Glossary

- ***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)

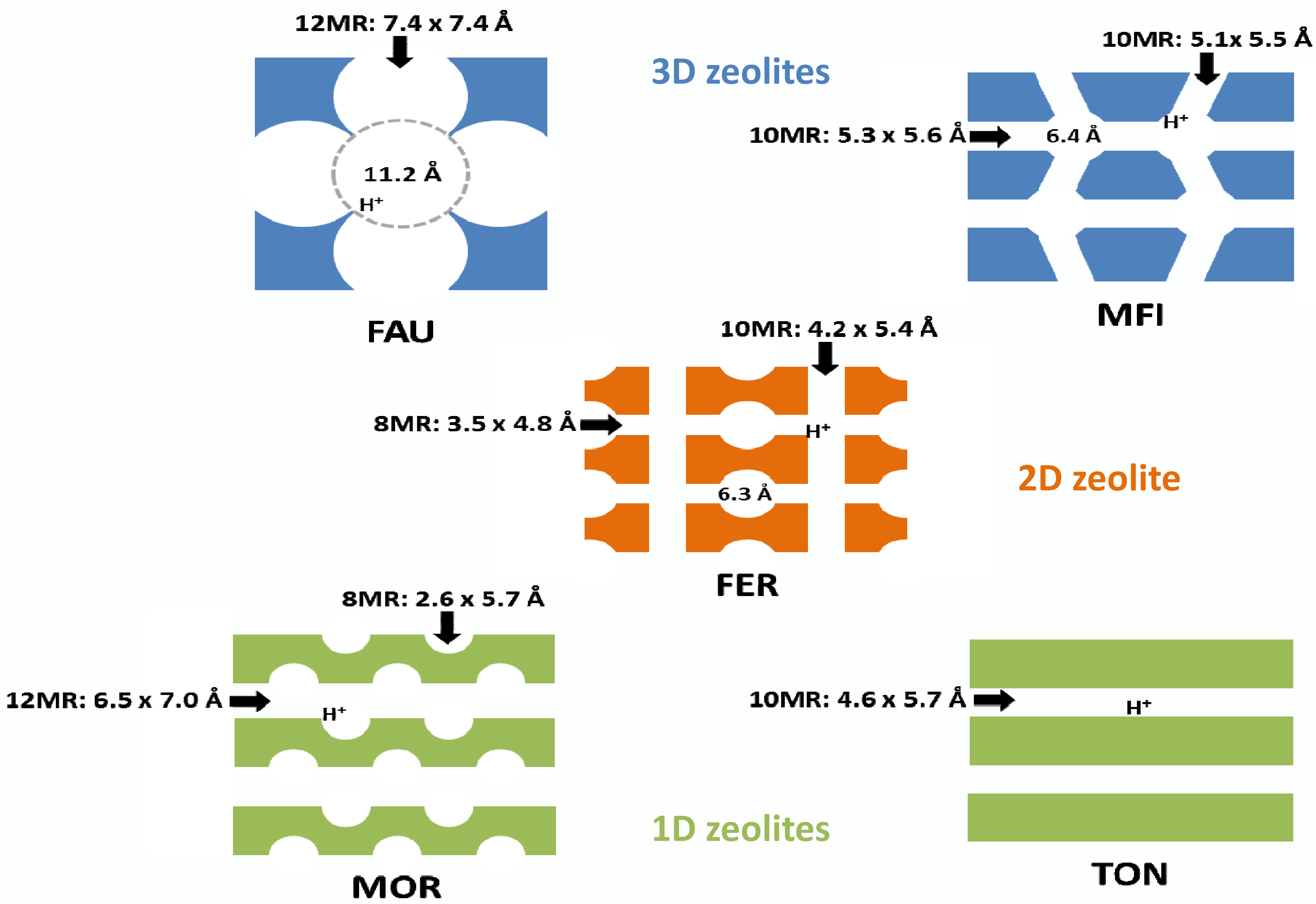


Glossary

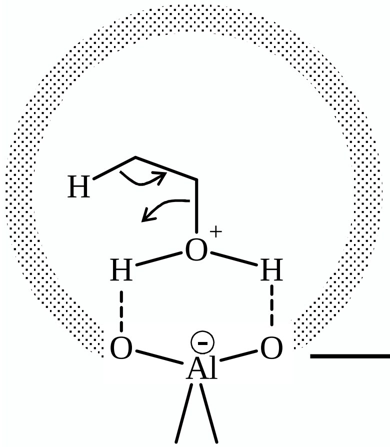
- ***SN1 (substitution, unimolecular)*** –In this reaction, the rate determining step involves a heterolytic cleavage of the bond between the leaving group and the carbon atom leading to formation of a carbenium ion which undergoes a substitution reaction with the nucleophile.

- ***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°)

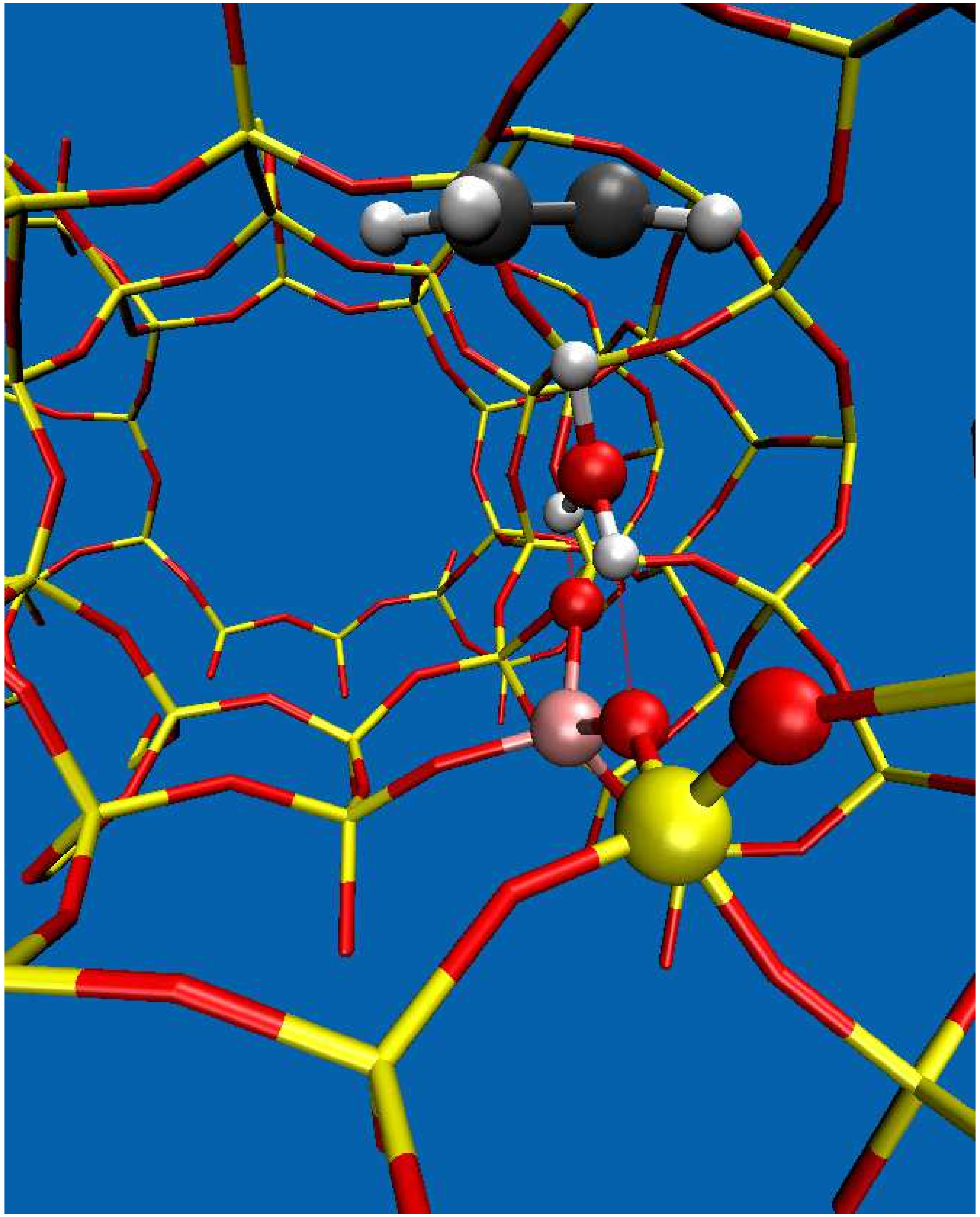
Zeolite topologies

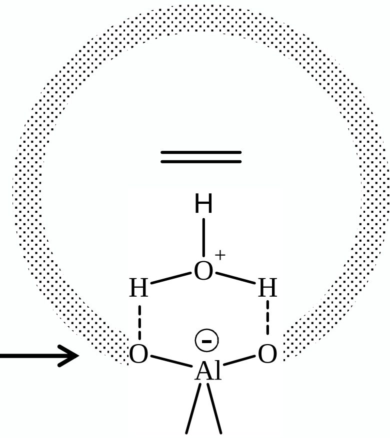


E1 like TS1



M1

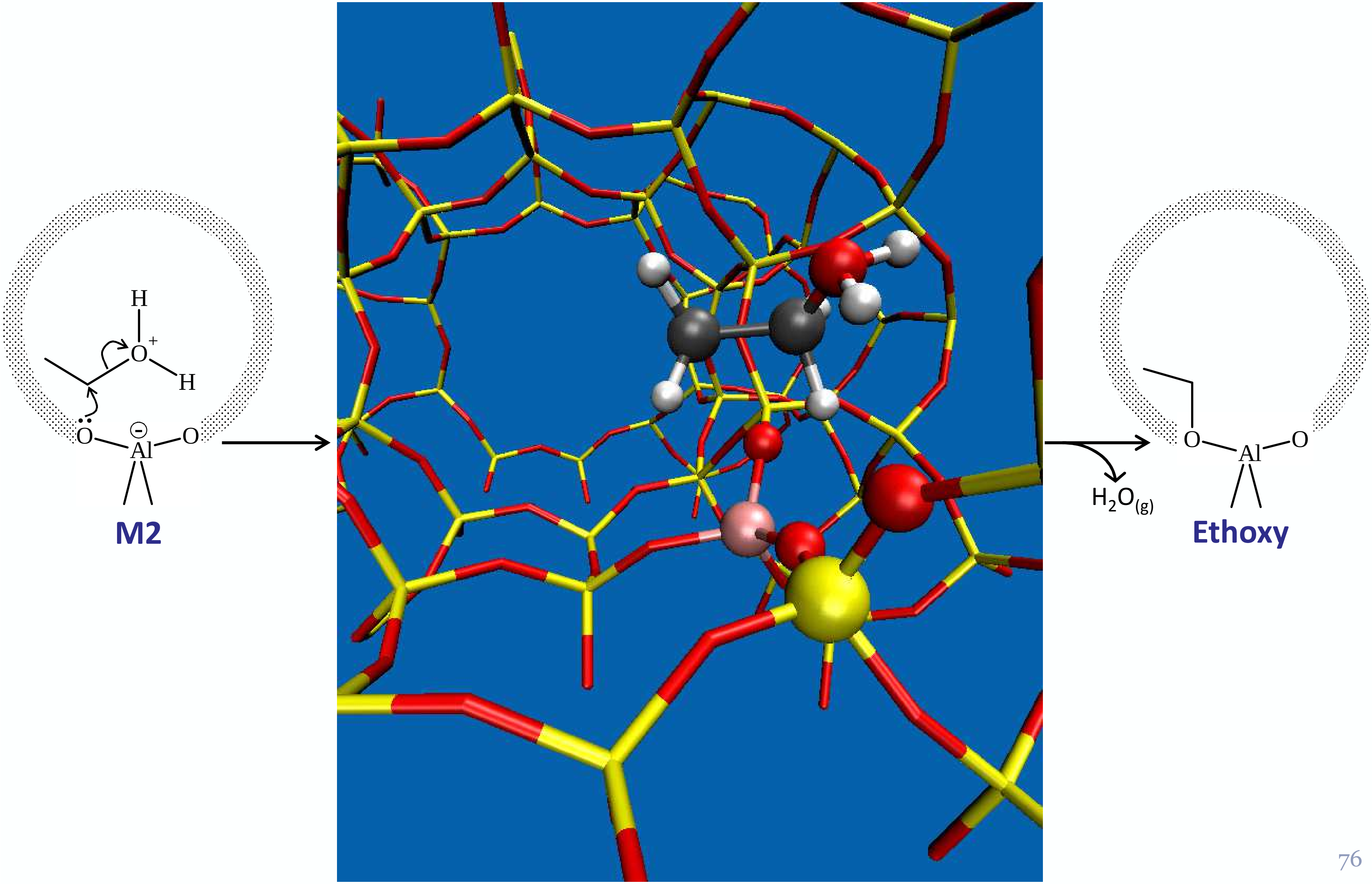




W

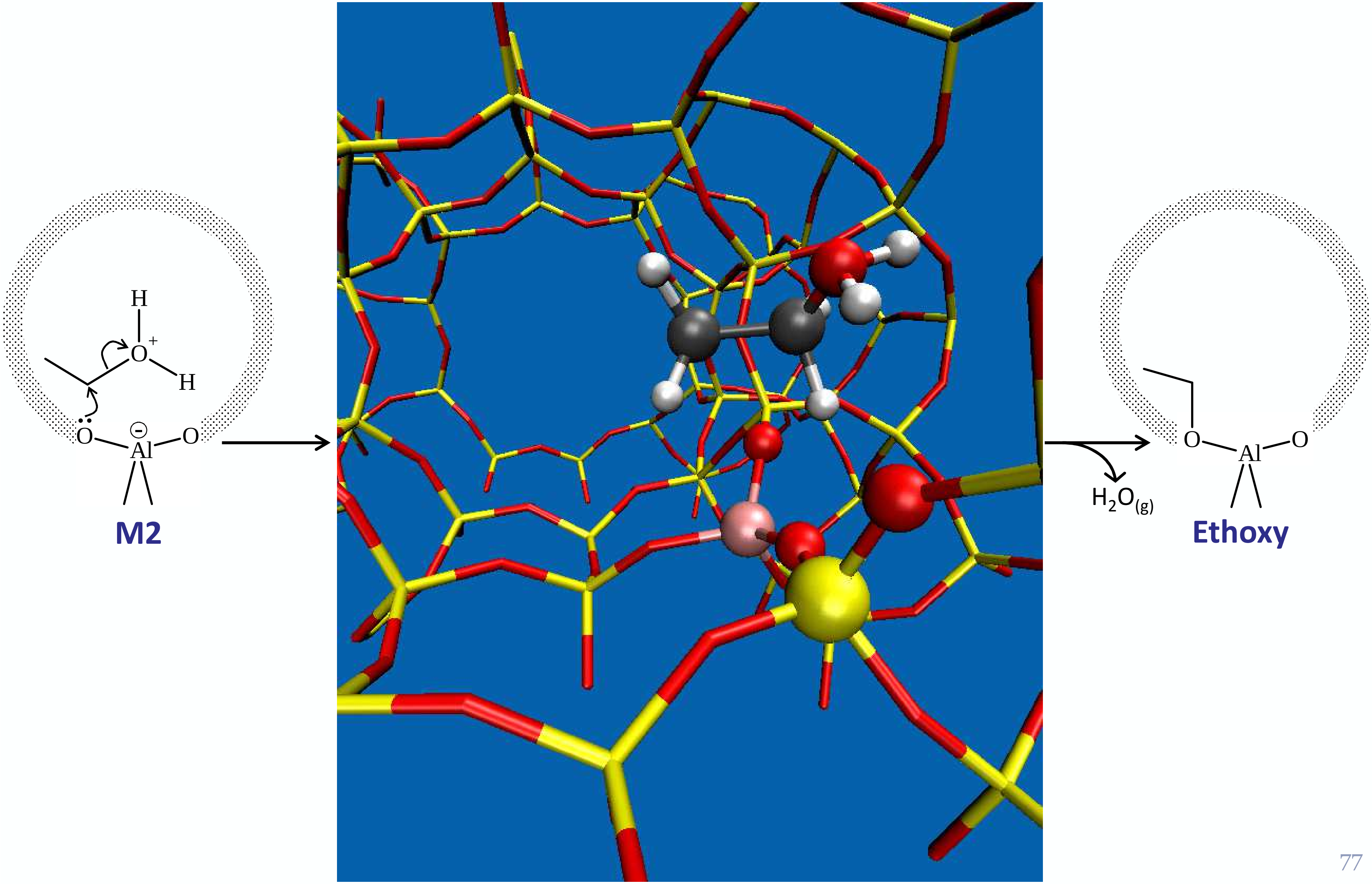
SN2

TS2



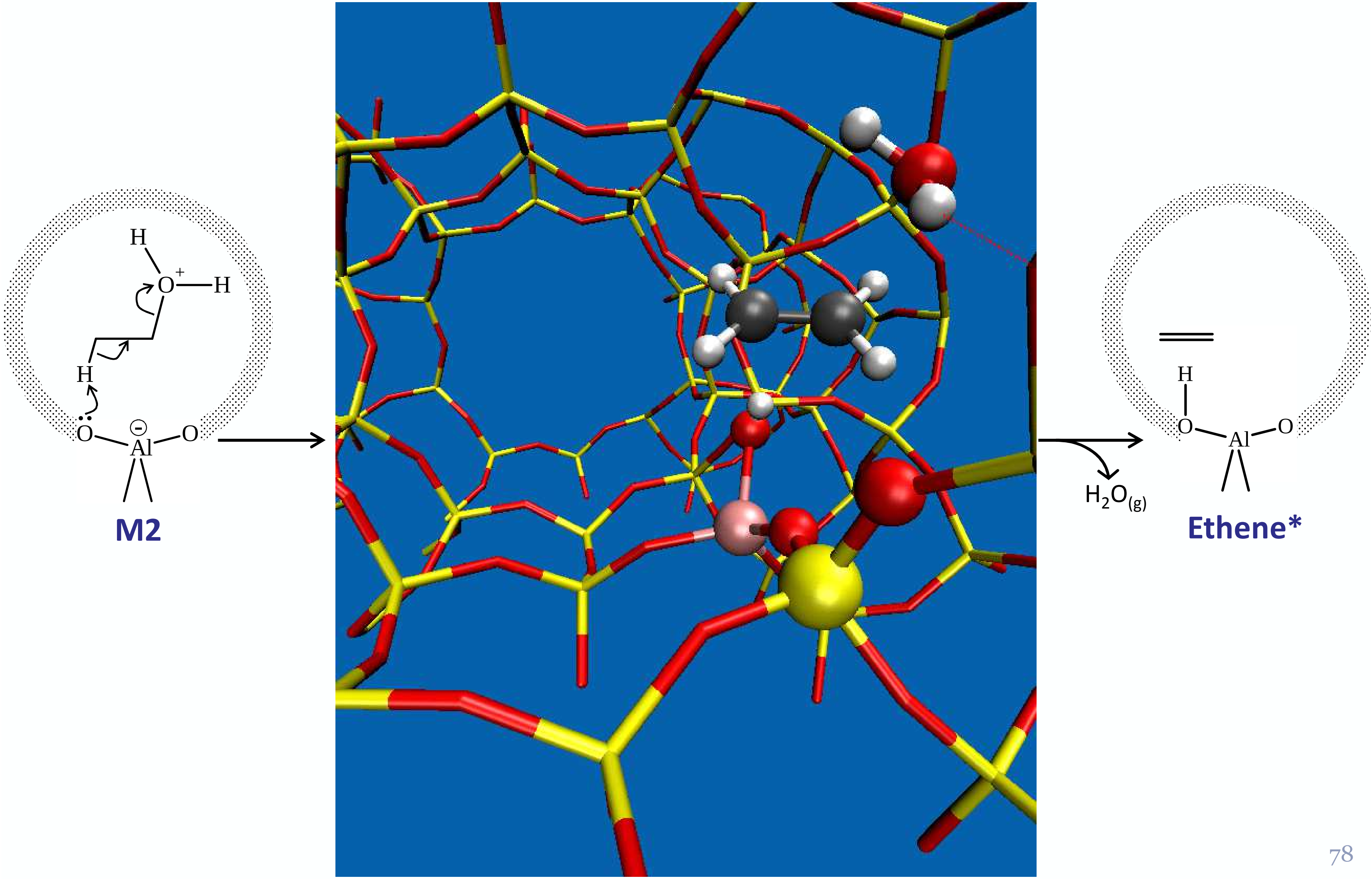
SN2

TS2



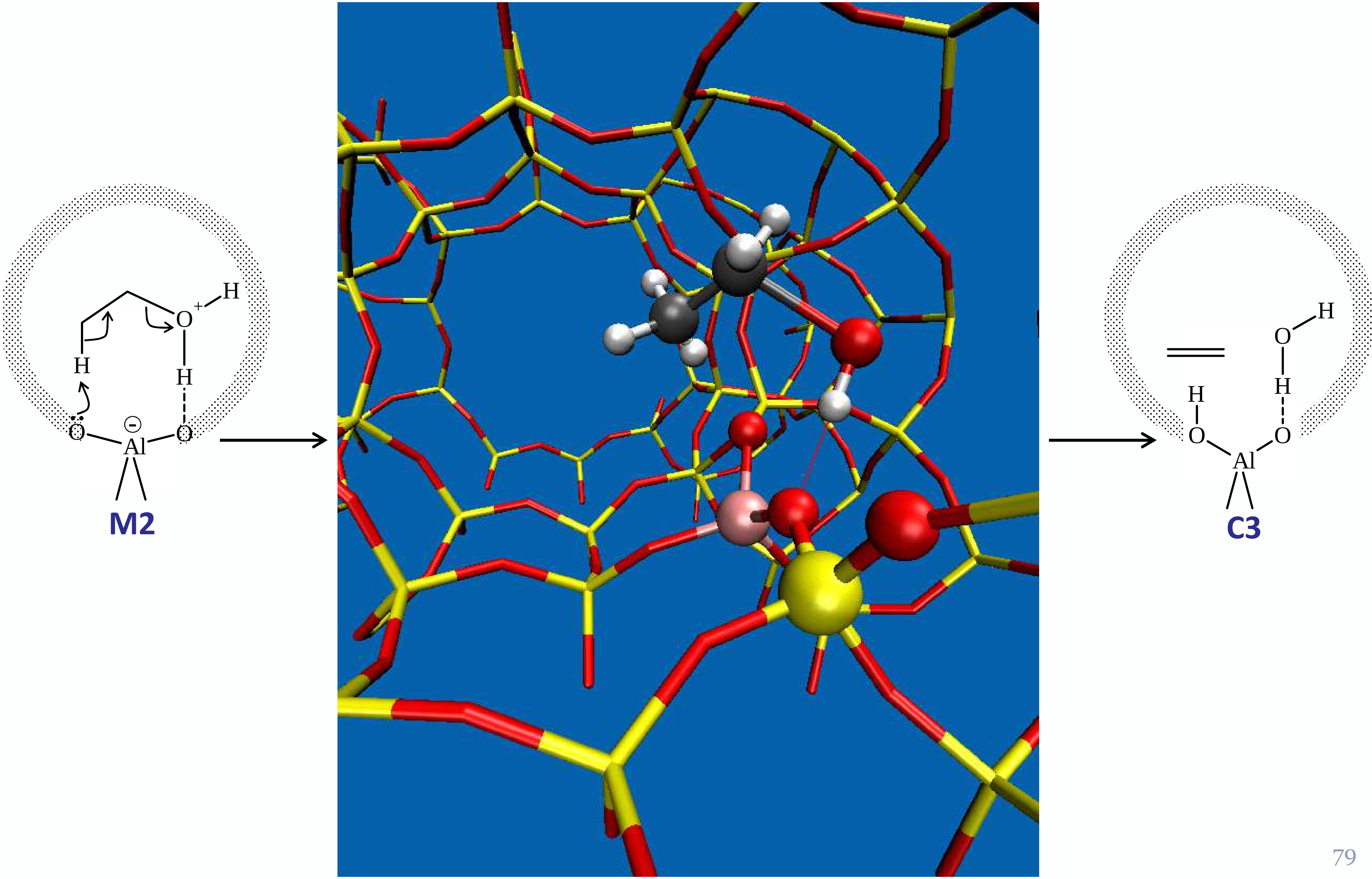
E2 (anti elimination)

TS3



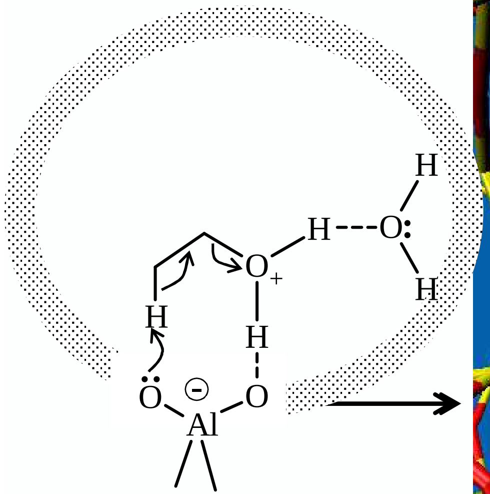
Syn elimination

TS4

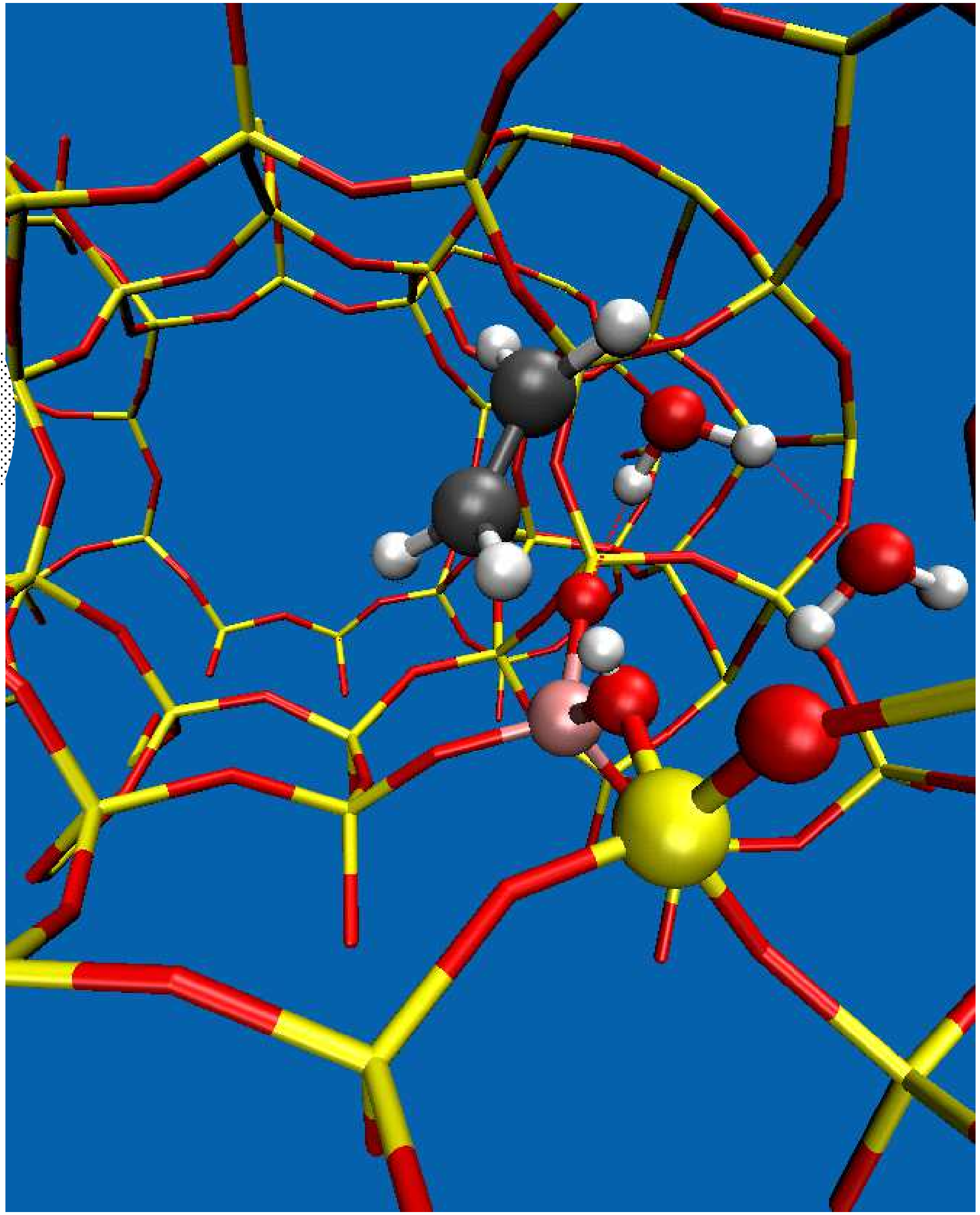


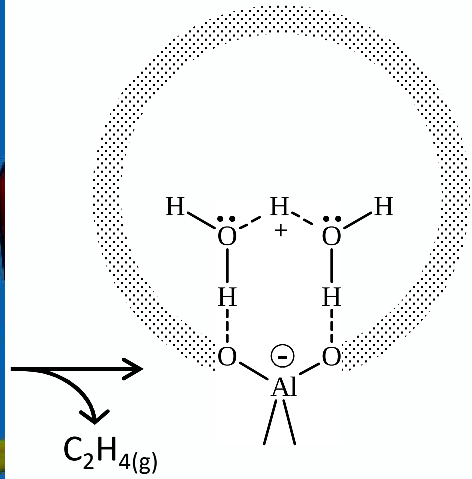
Syn elimination

TS5



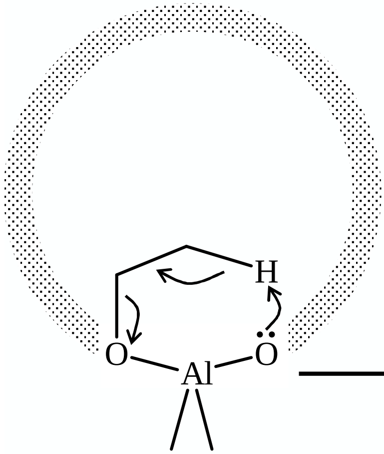
C2



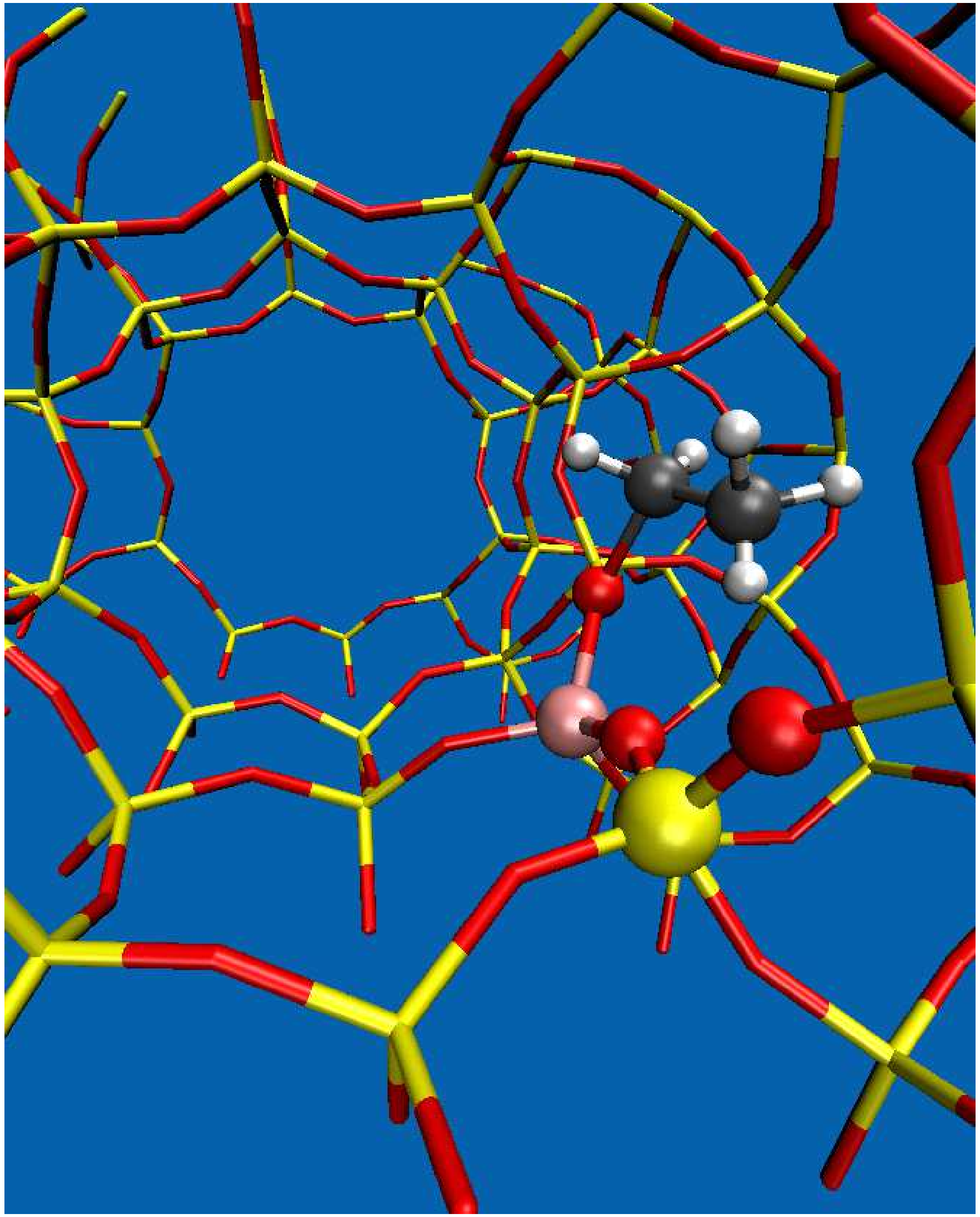


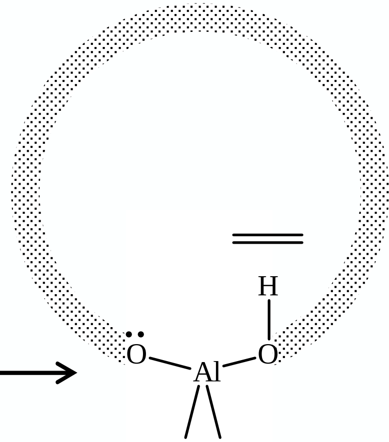
2W

TS6



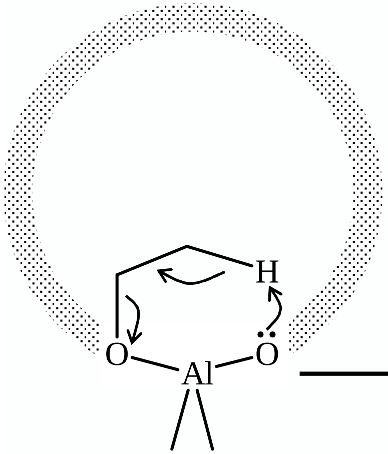
Ethoxy



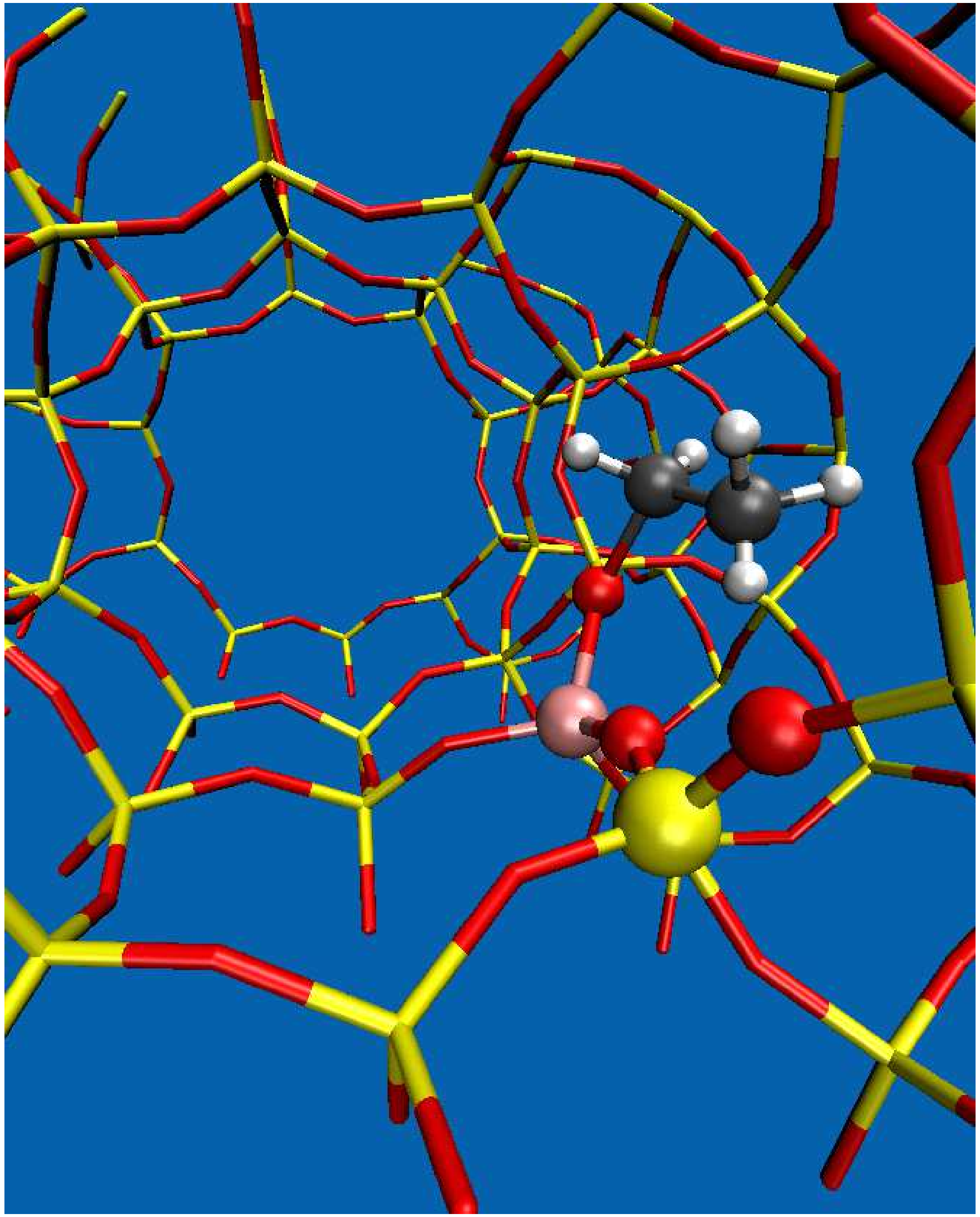


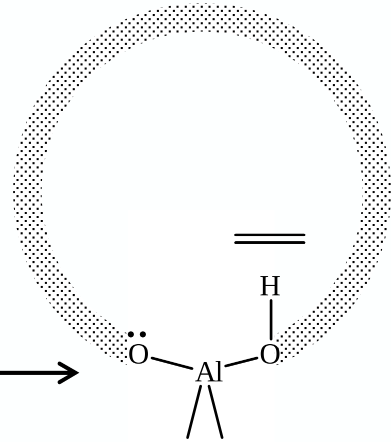
Ethene*

TS6



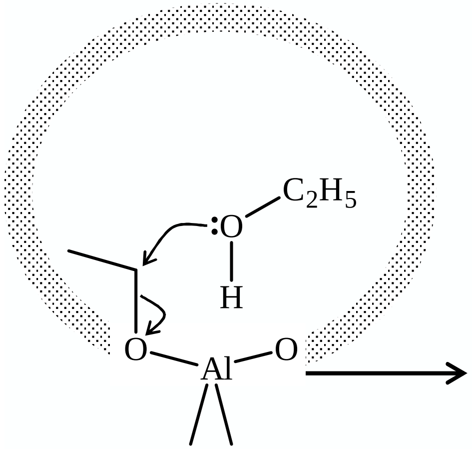
Ethoxy



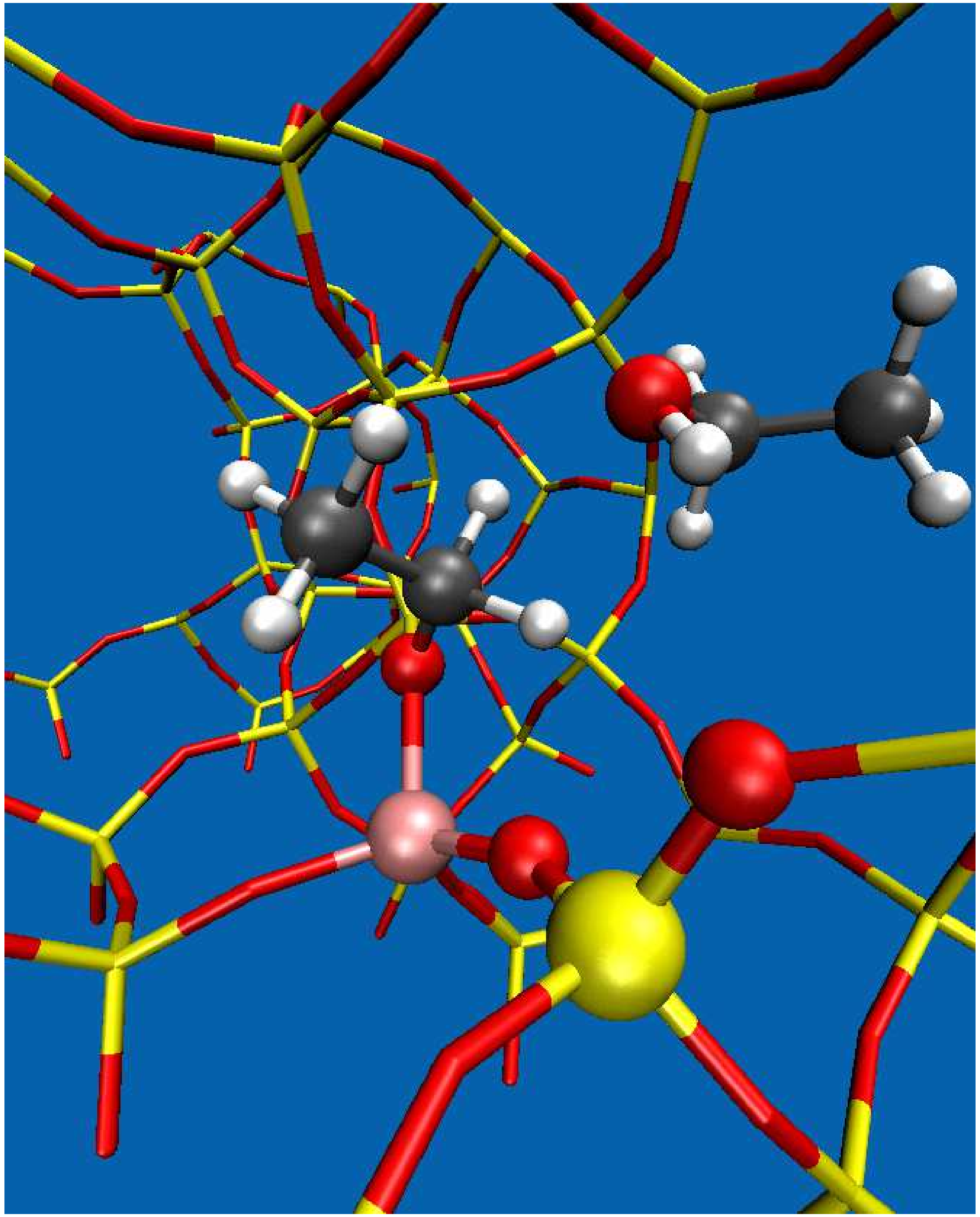


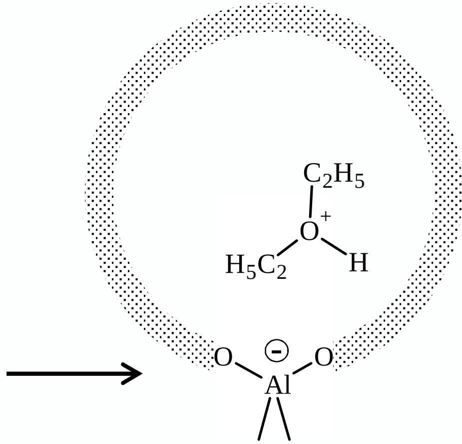
Ethene*

SN2 TS7



Ethoxy

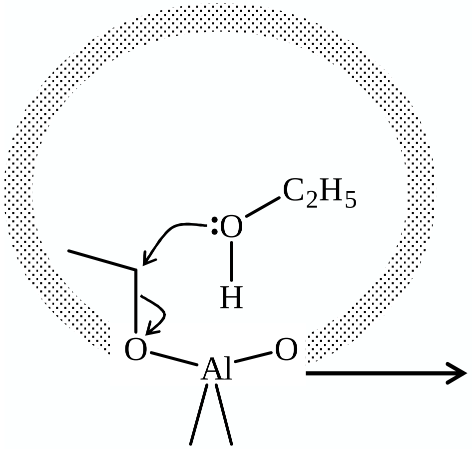




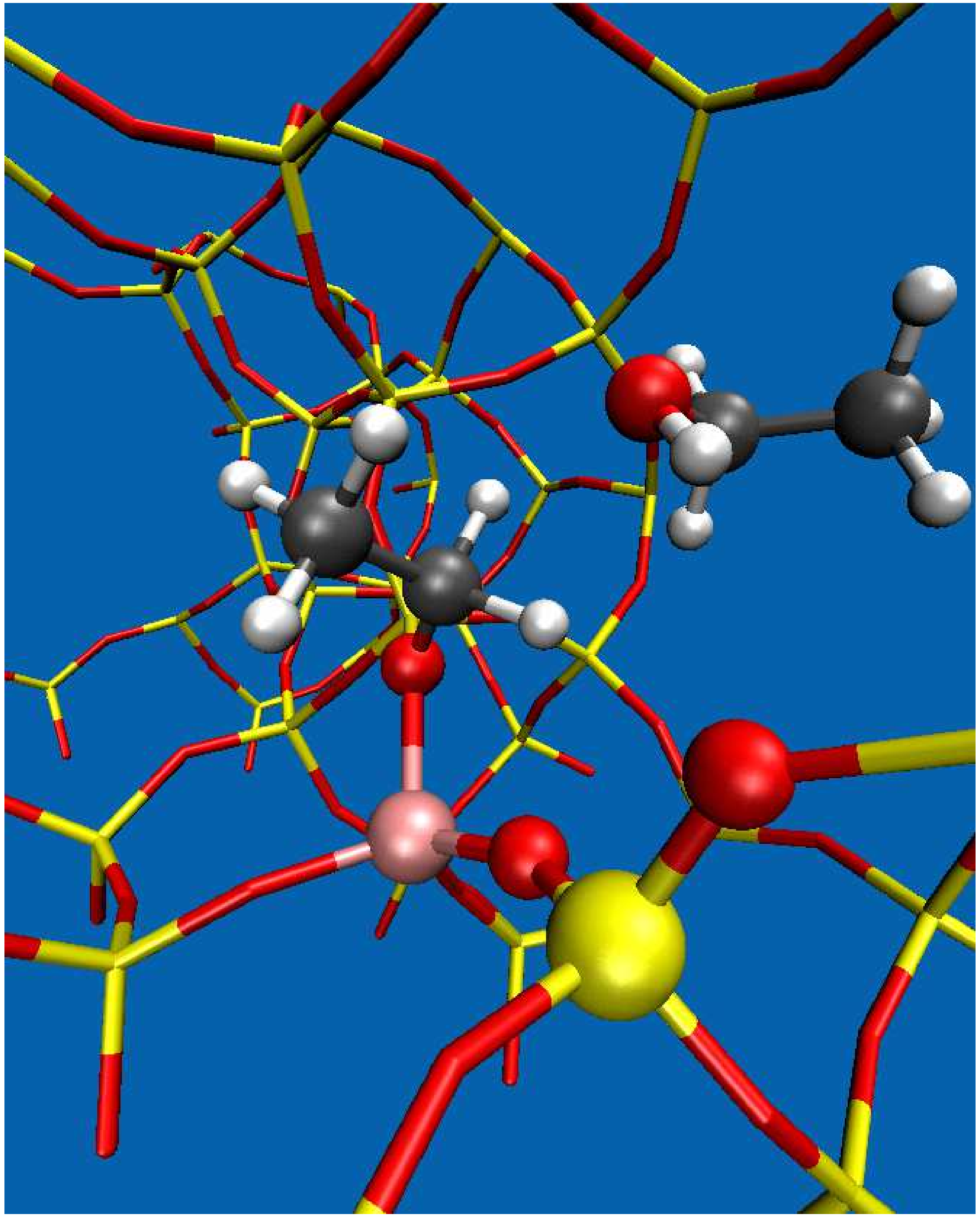
DEE*

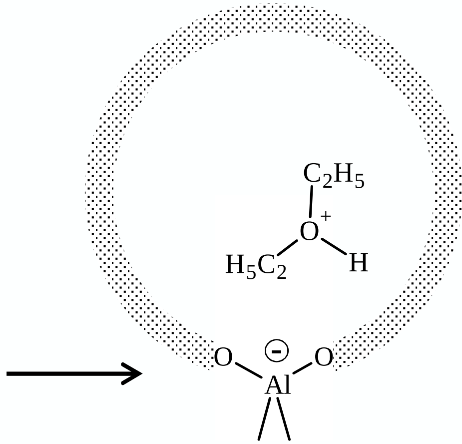
SN2

TS7



Ethoxy

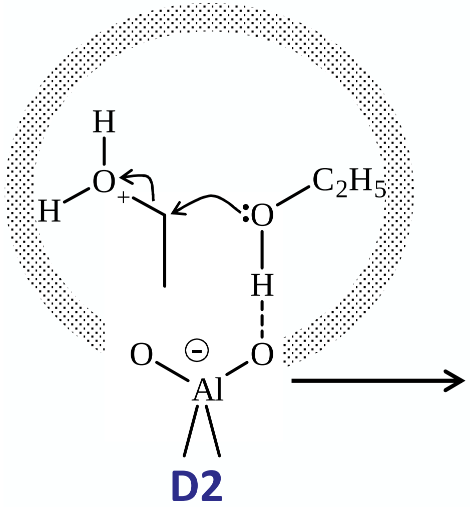


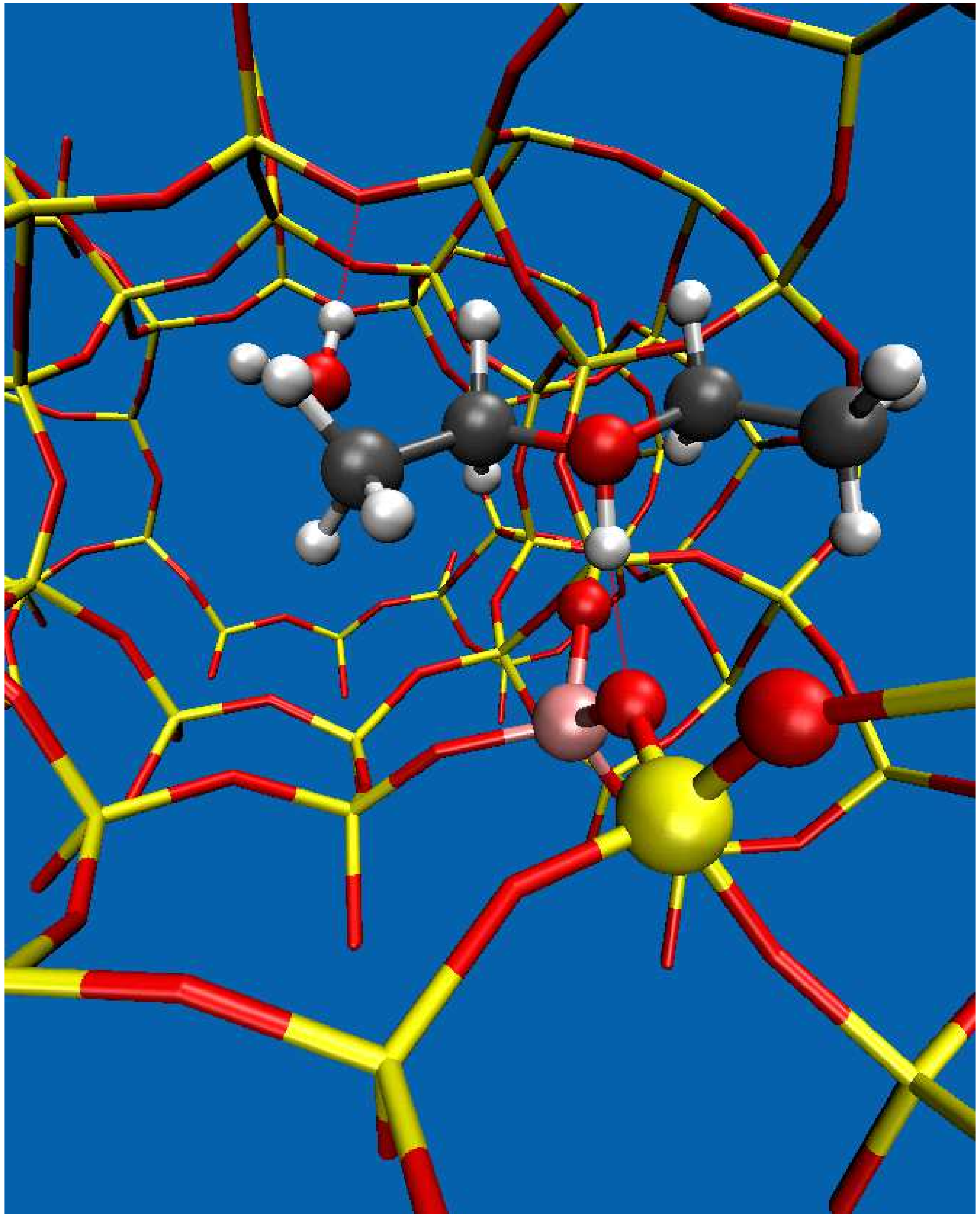


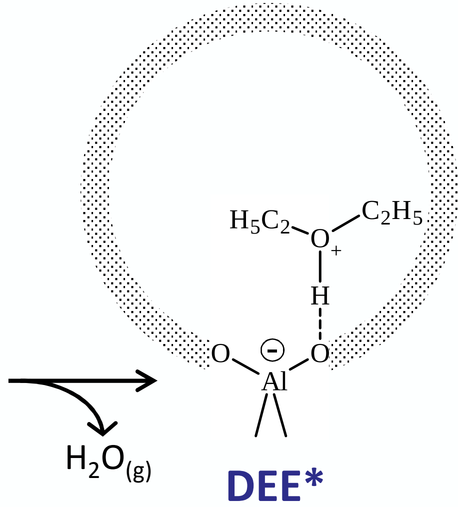
DEE*

SN2

TS8

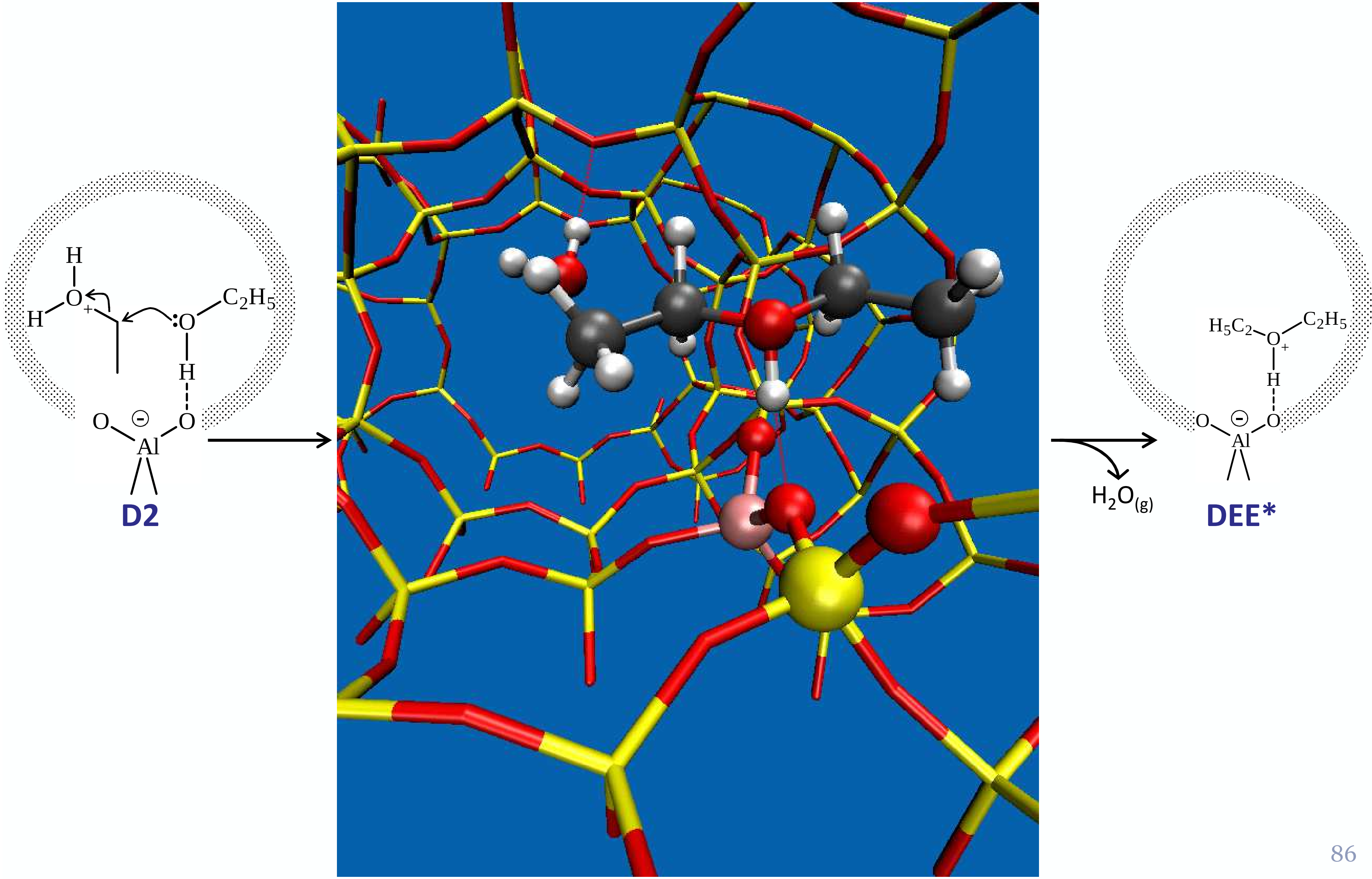




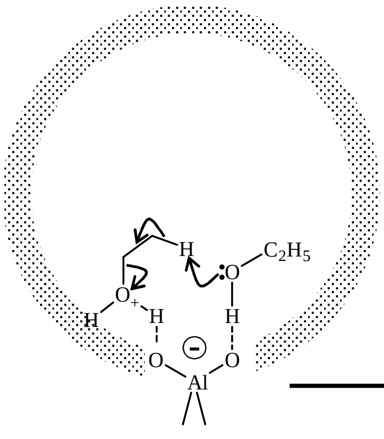


SN2

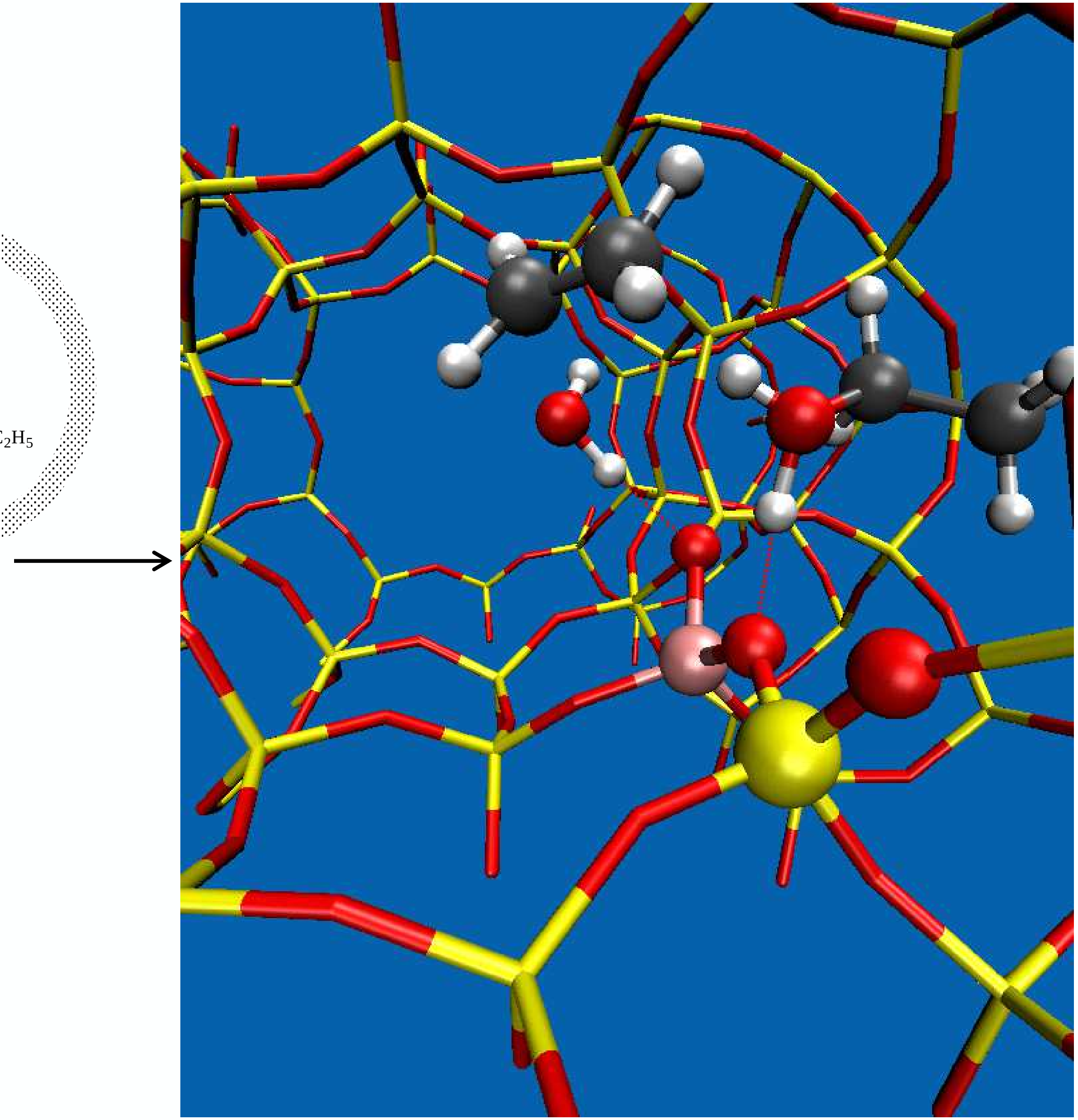
TS8

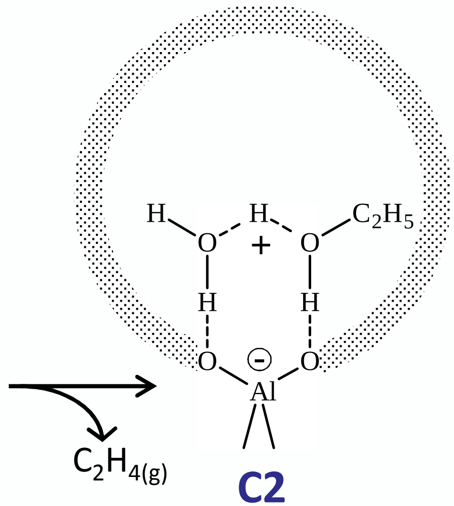


Ethanol-assisted syn-elimination TS9



D2

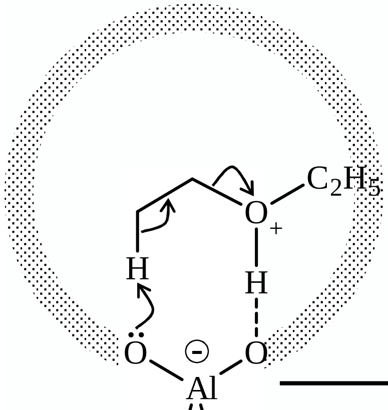




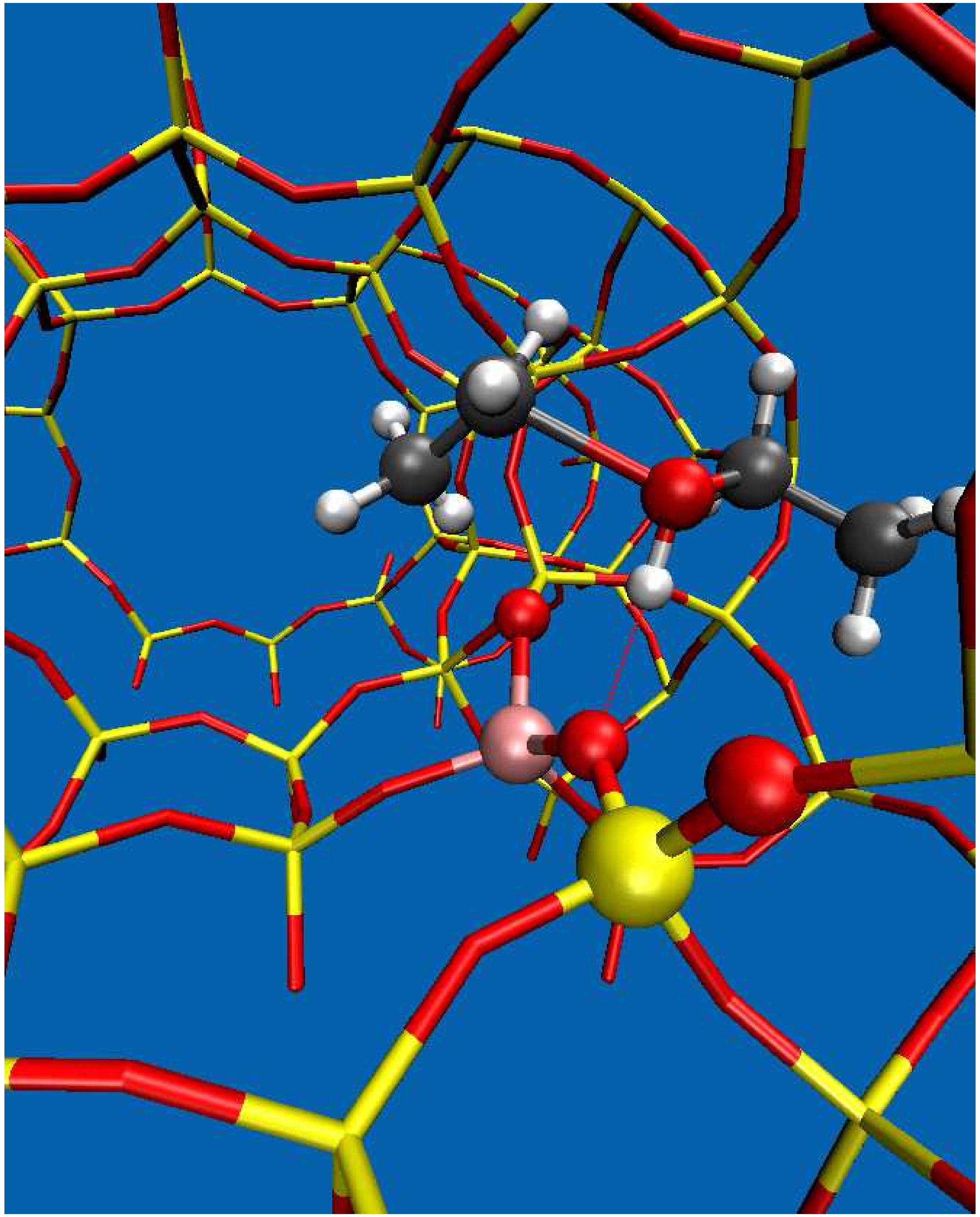
C2

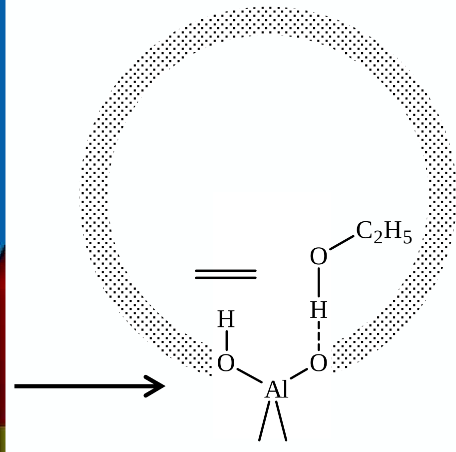
Syn elimination

TS10



DEE*

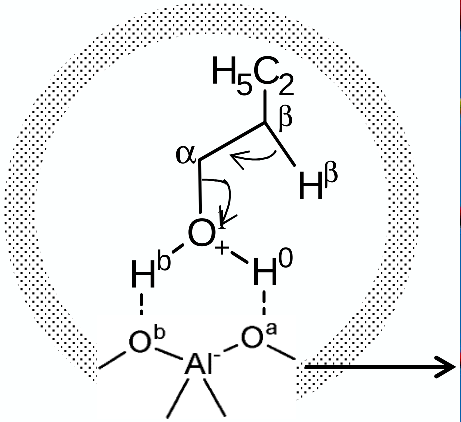




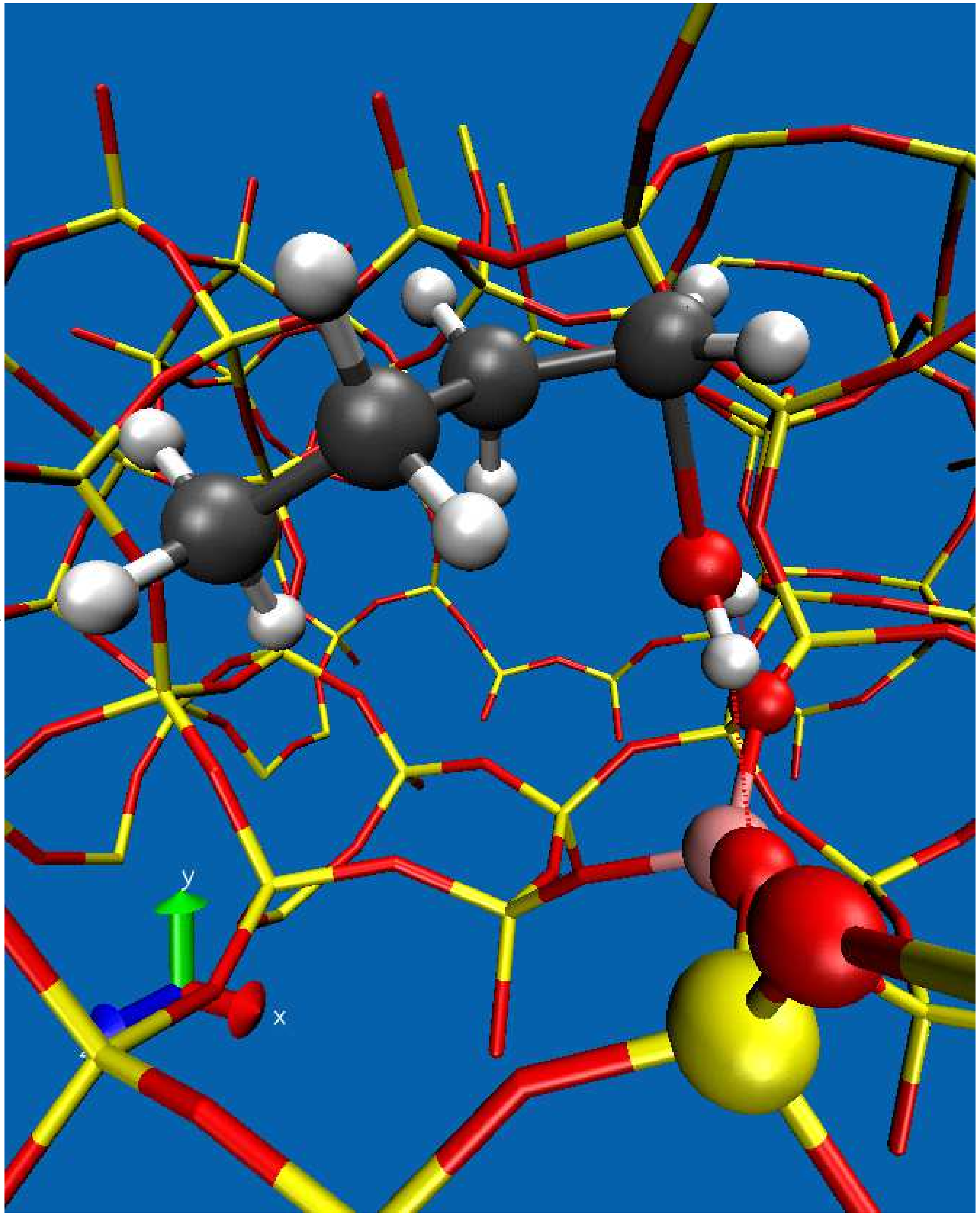
C1

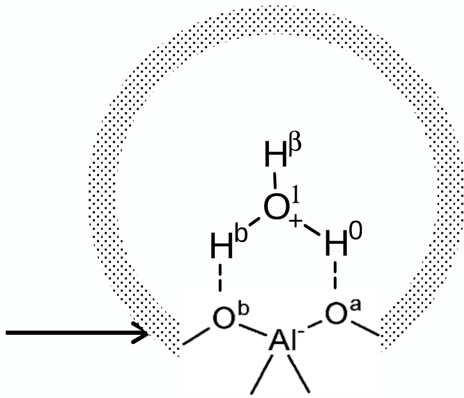
E1 like

TS1



M1

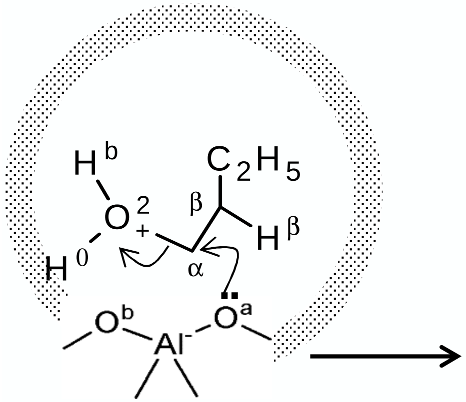




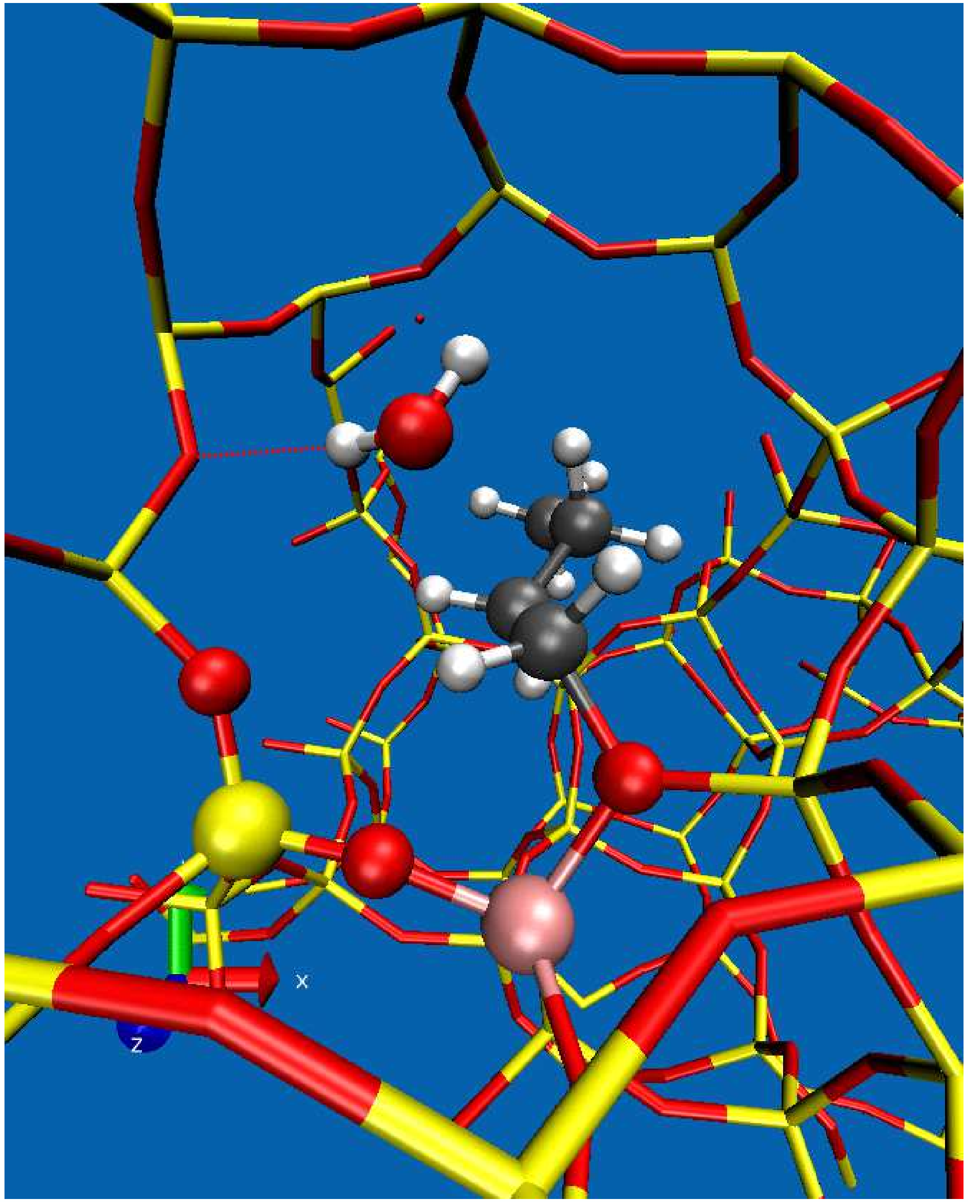
W

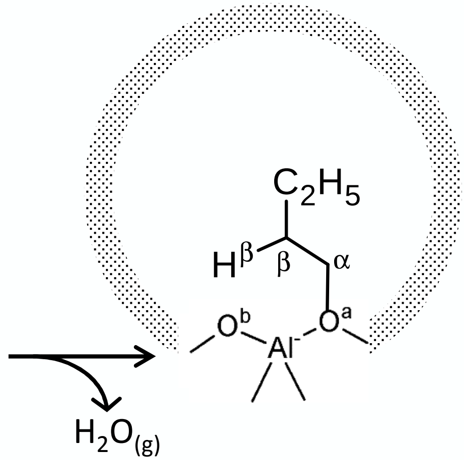
SN2

TS2



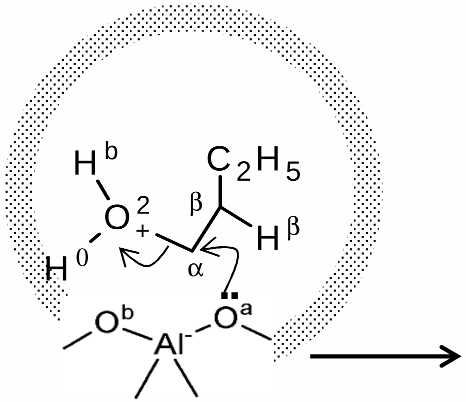
M2



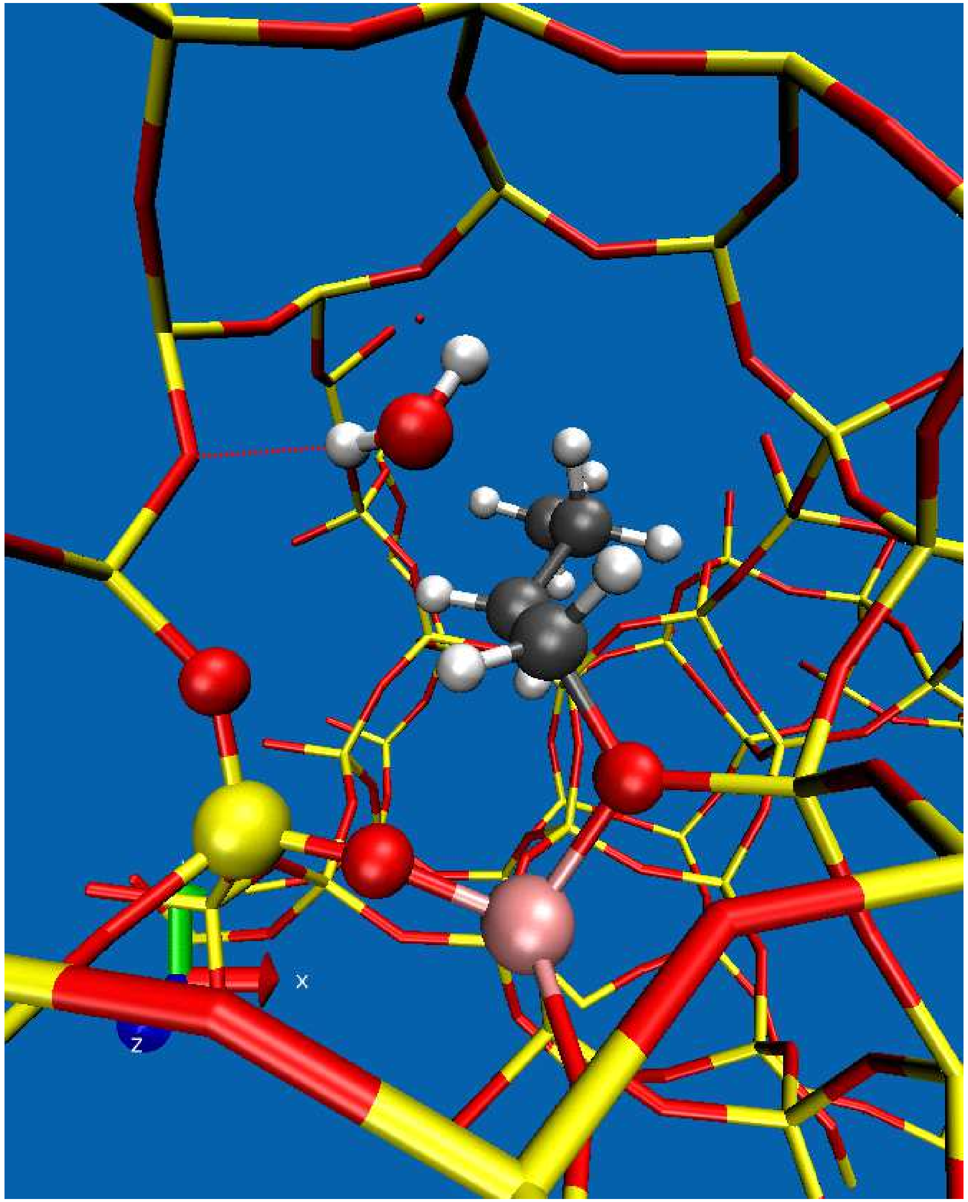


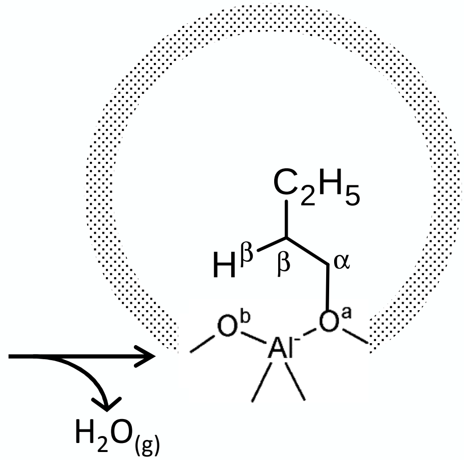
1-butoxide

SN2 TS2



M2

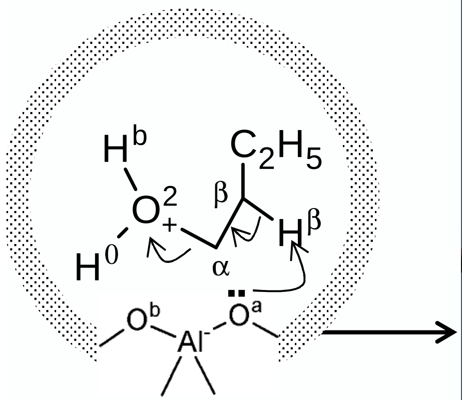




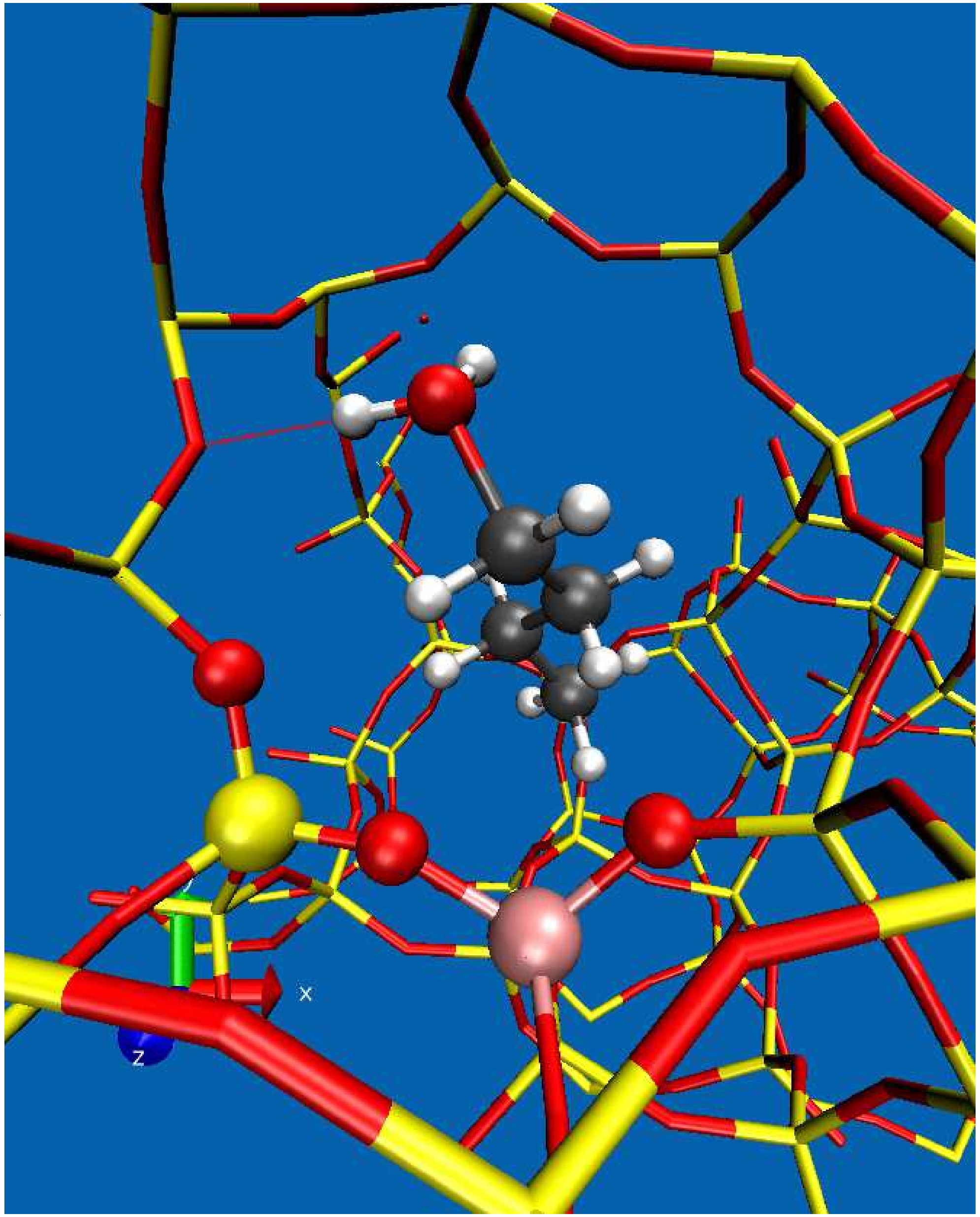
1-butoxide

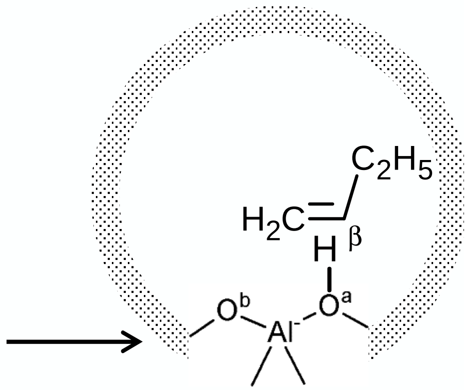
E2 (anti elimination)

TS3



M2

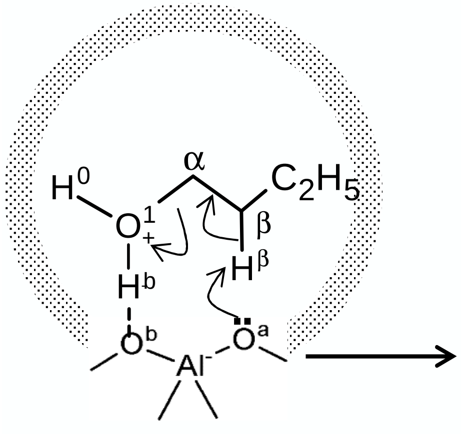




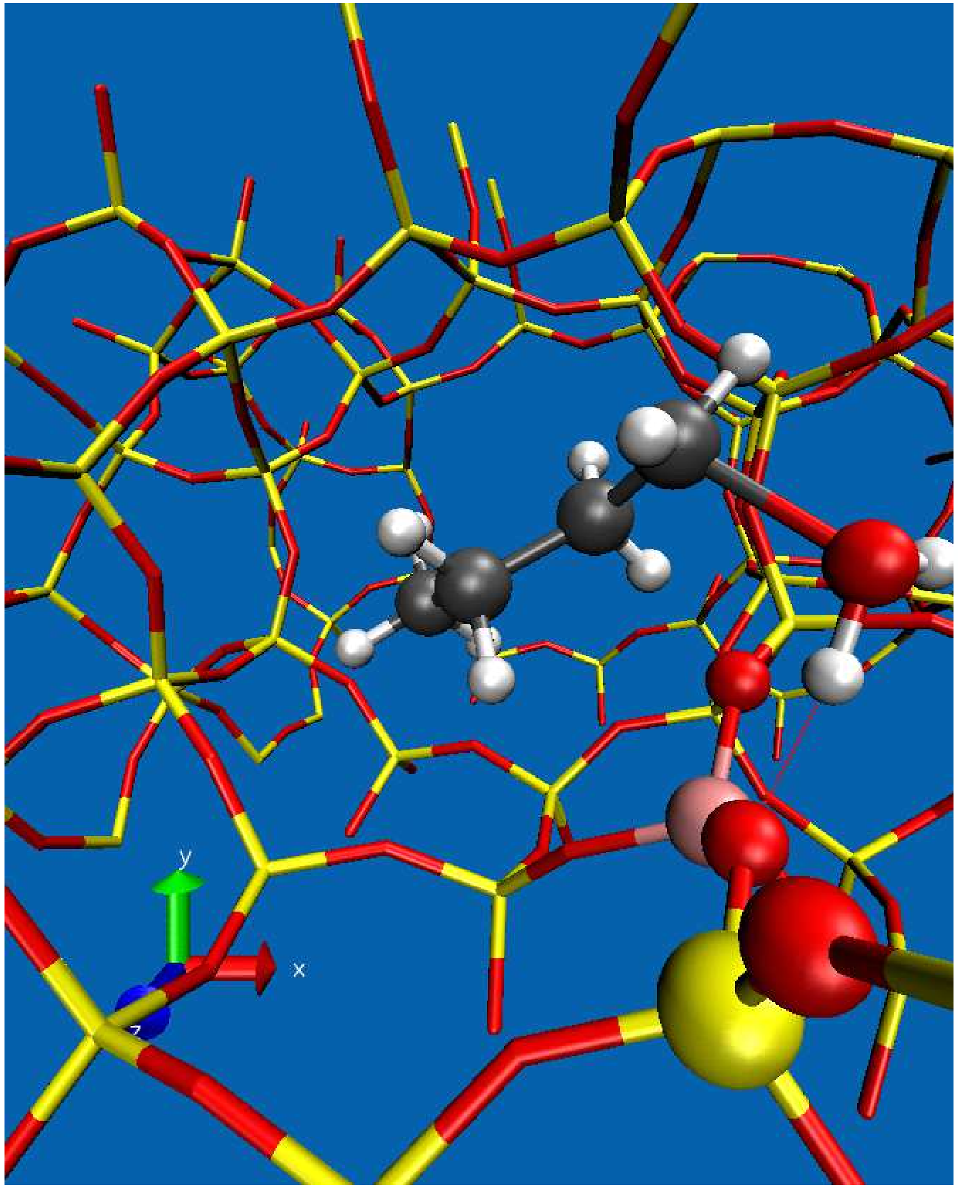
1-butene

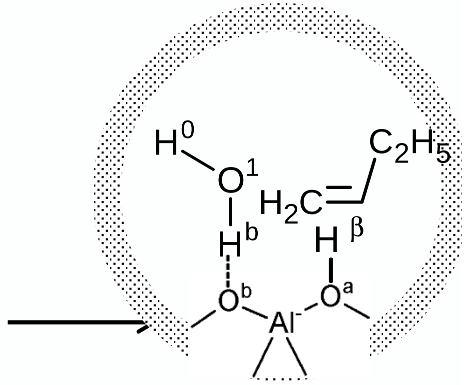
Syn elimination

TS4



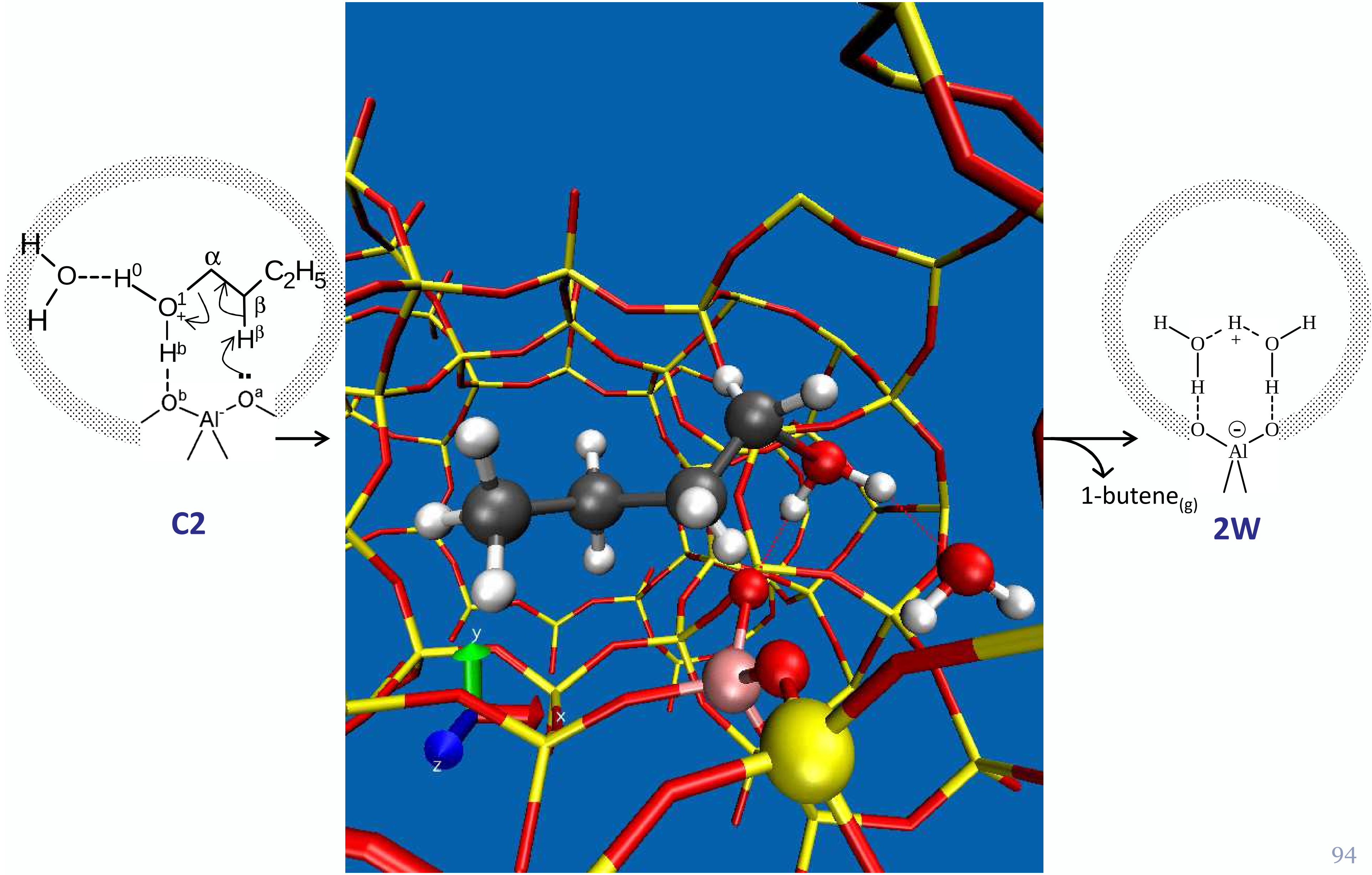
M2



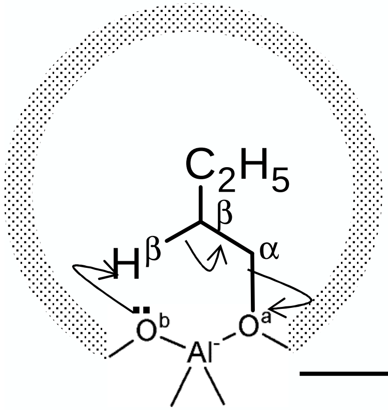


C3

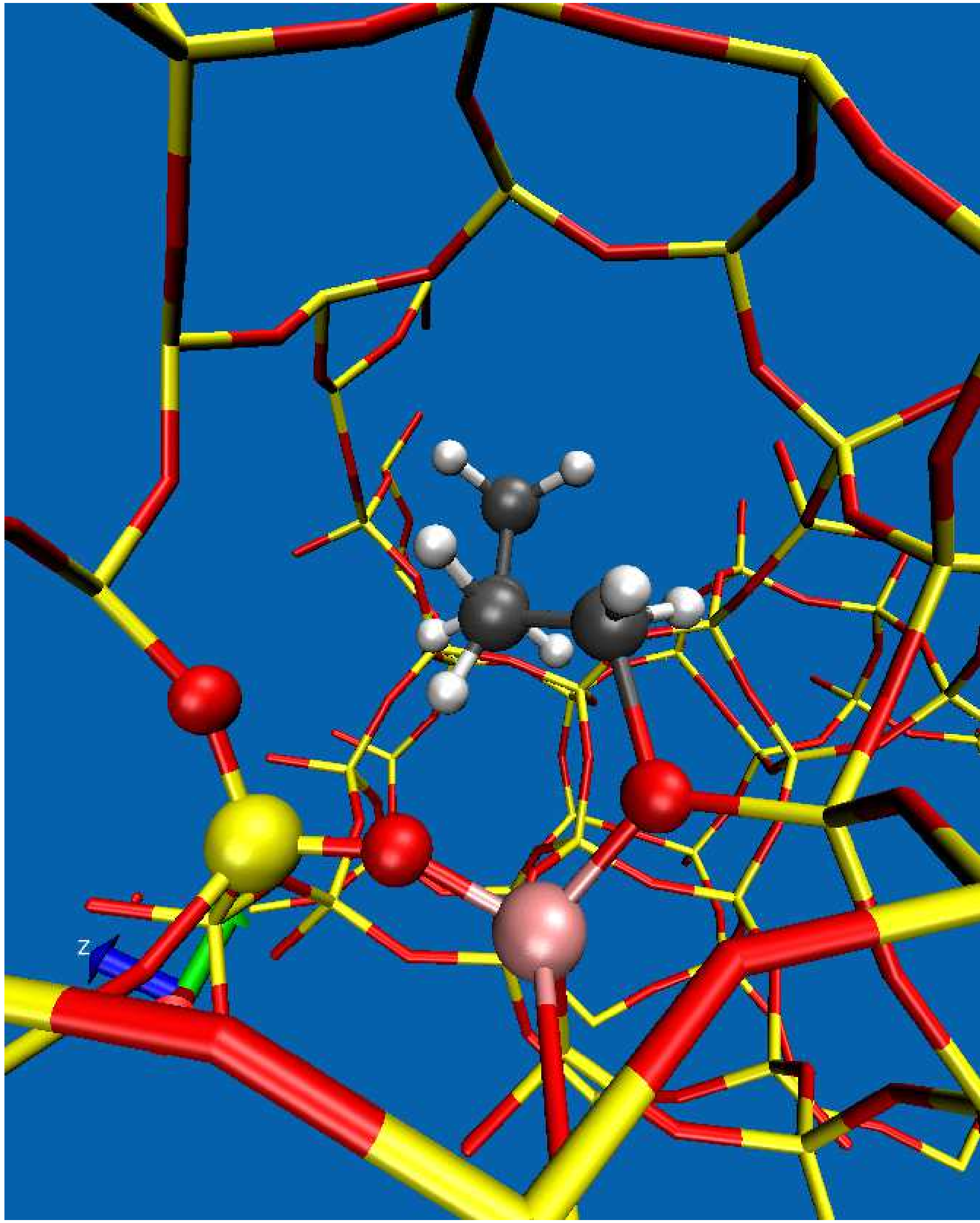
Syn elimination TS5

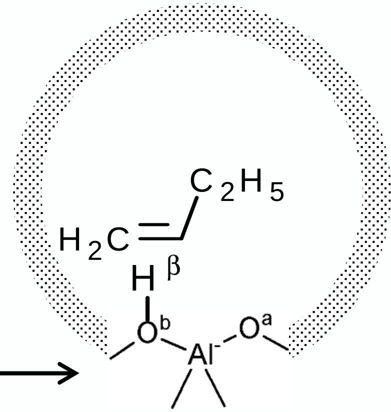


TS6



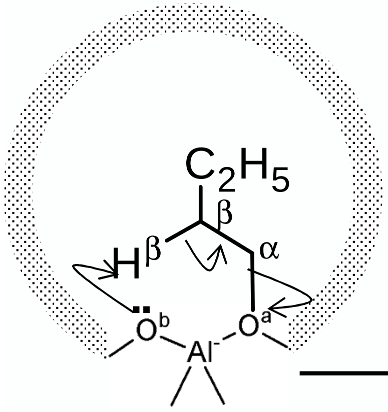
1-butoxide



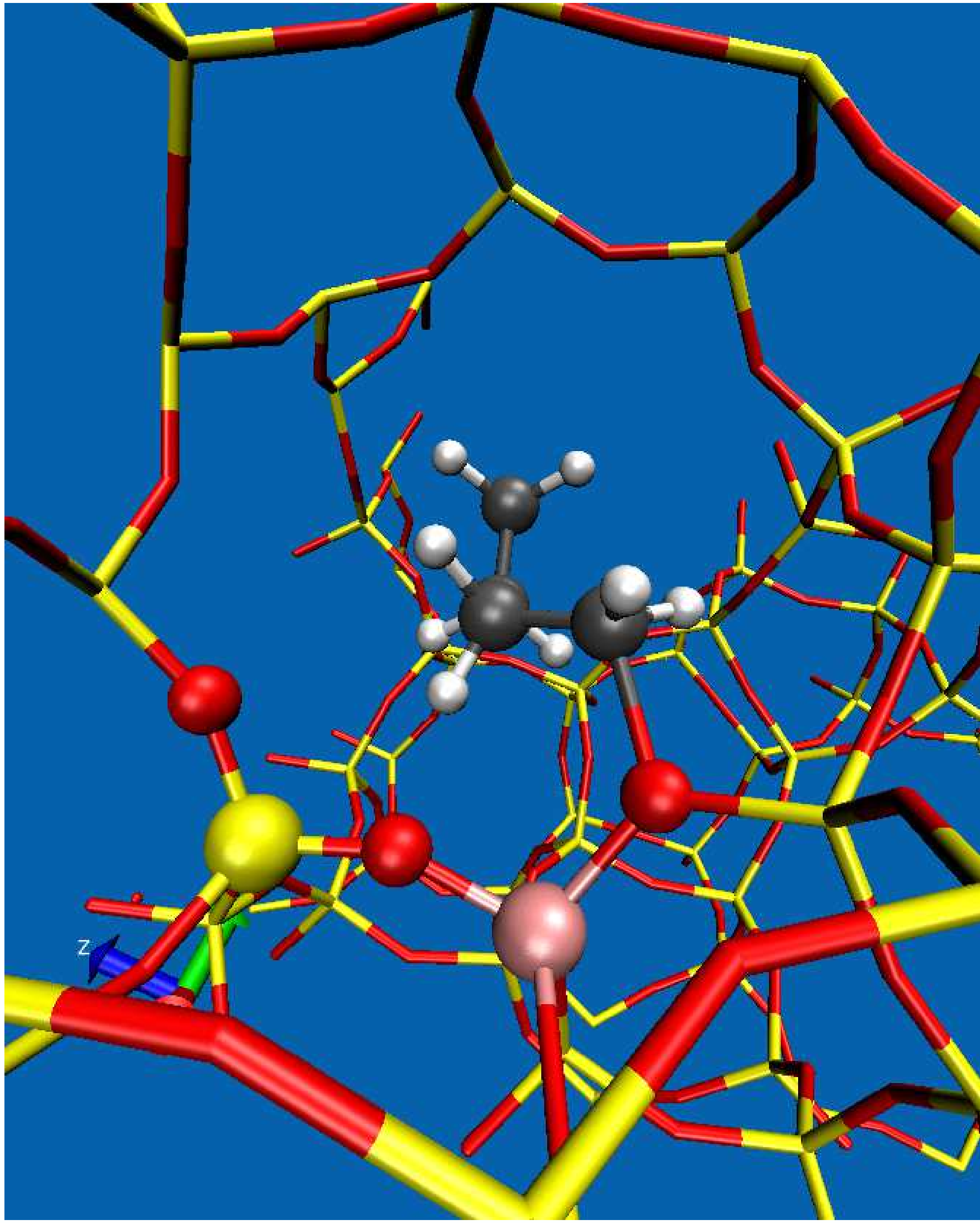


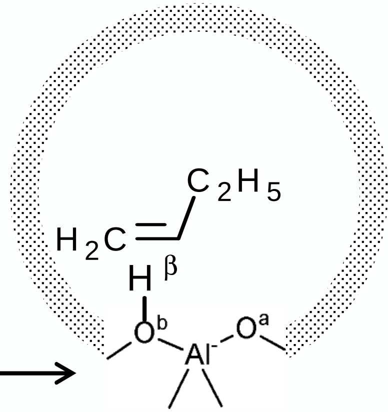
1-butene*

TS6



1-butoxide

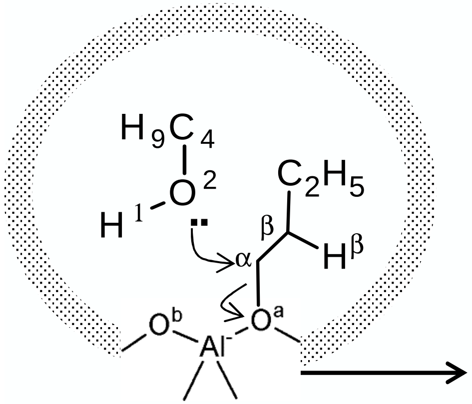




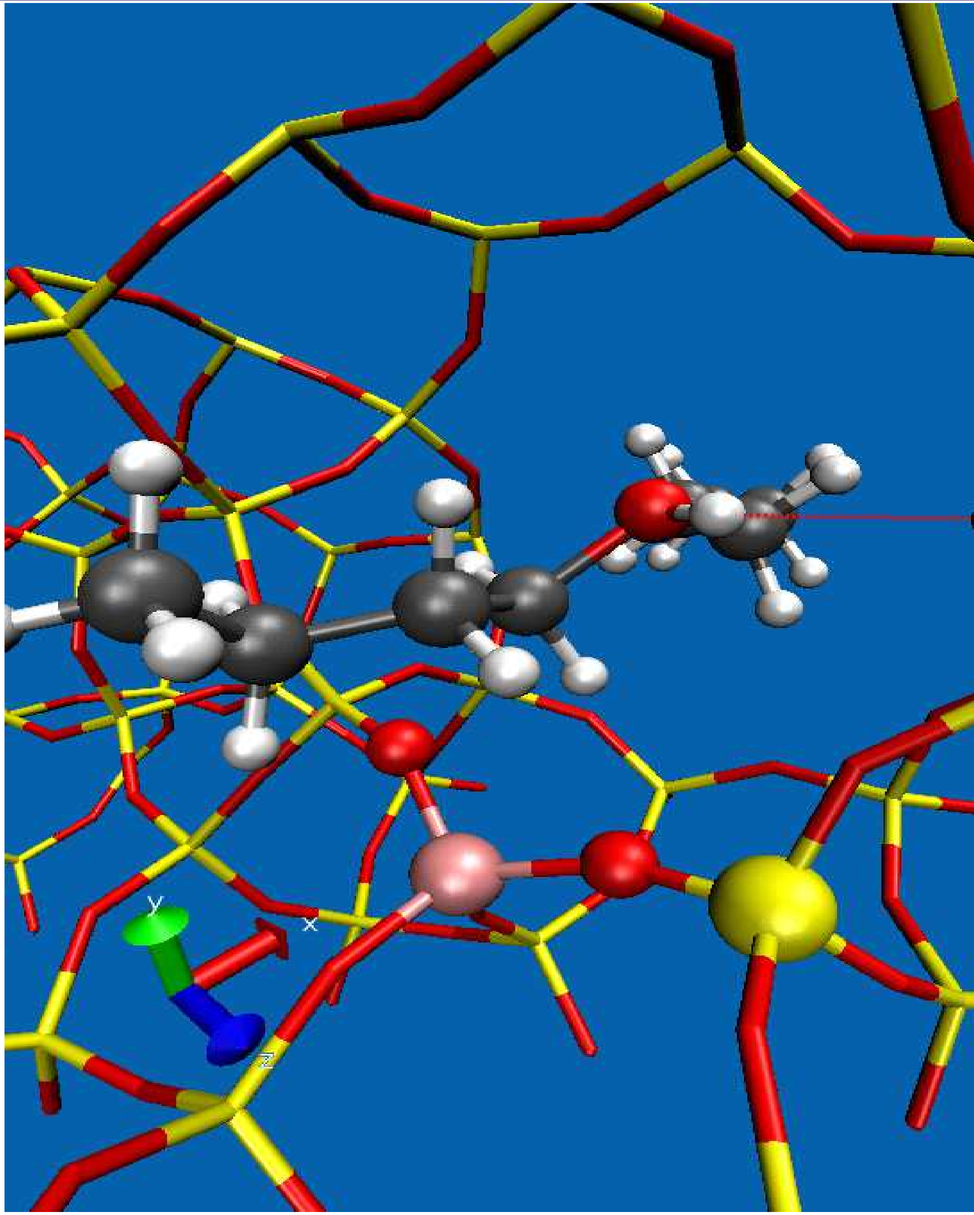
1-butene*

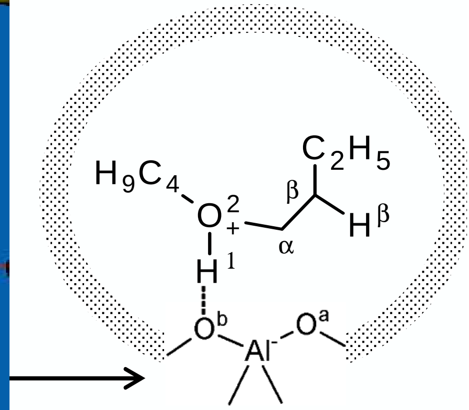
SN2

TS7



1-butoxide +
1-butanol (g)

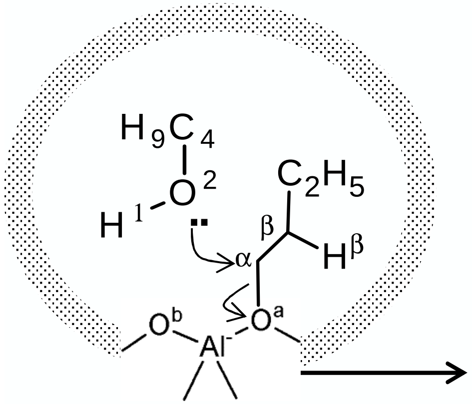




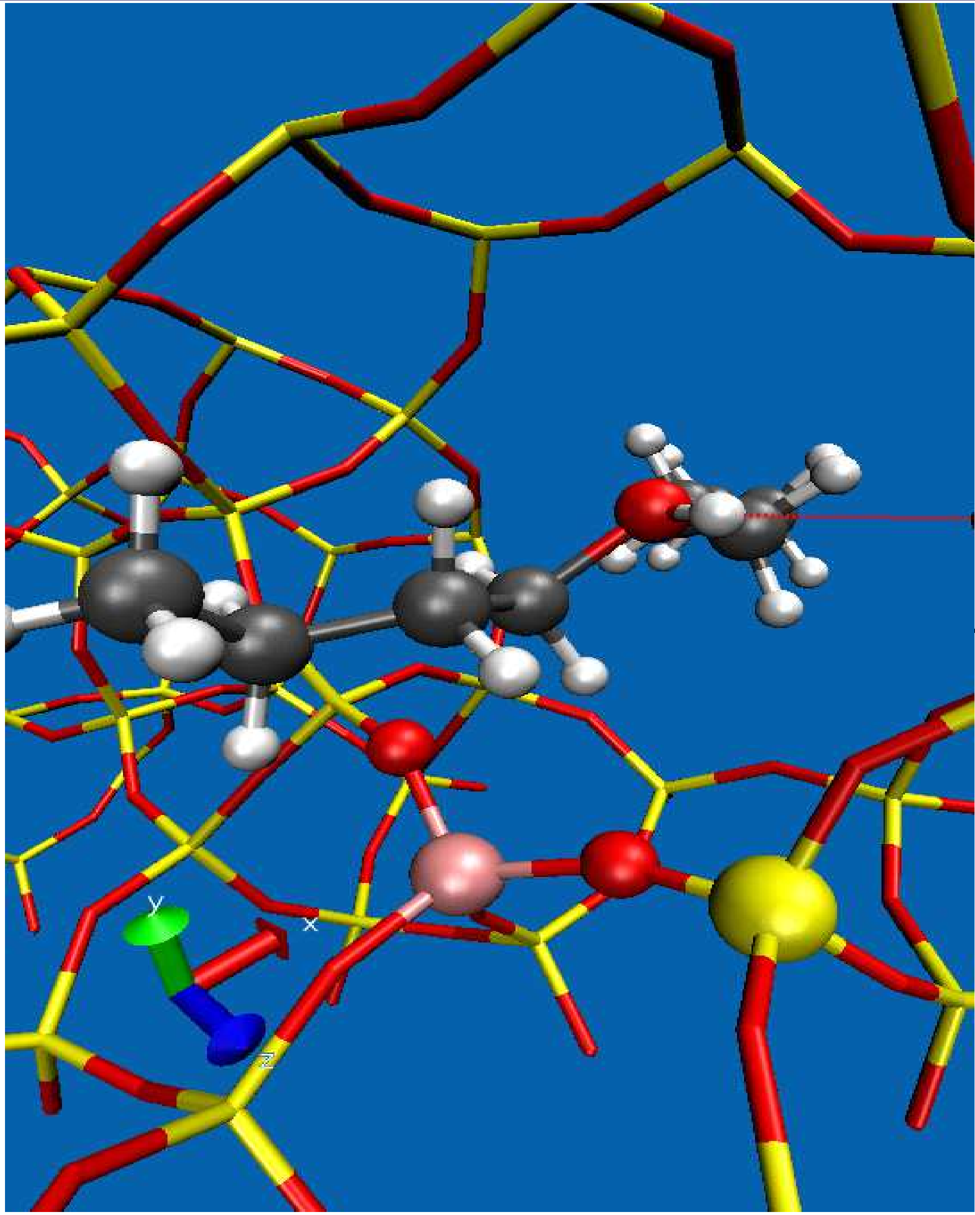
DBE*

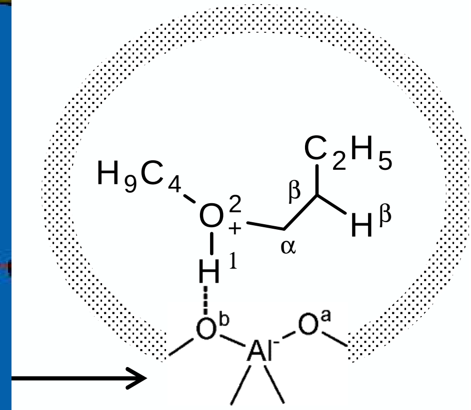
SN2

TS7



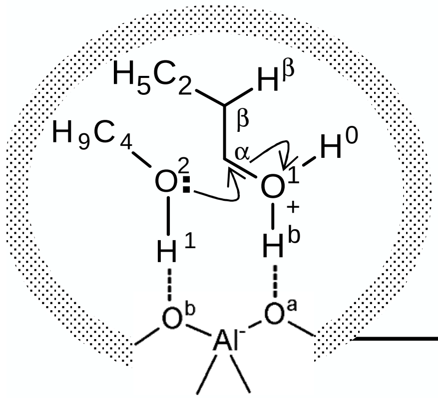
1-butoxide + 1-butanol (g)



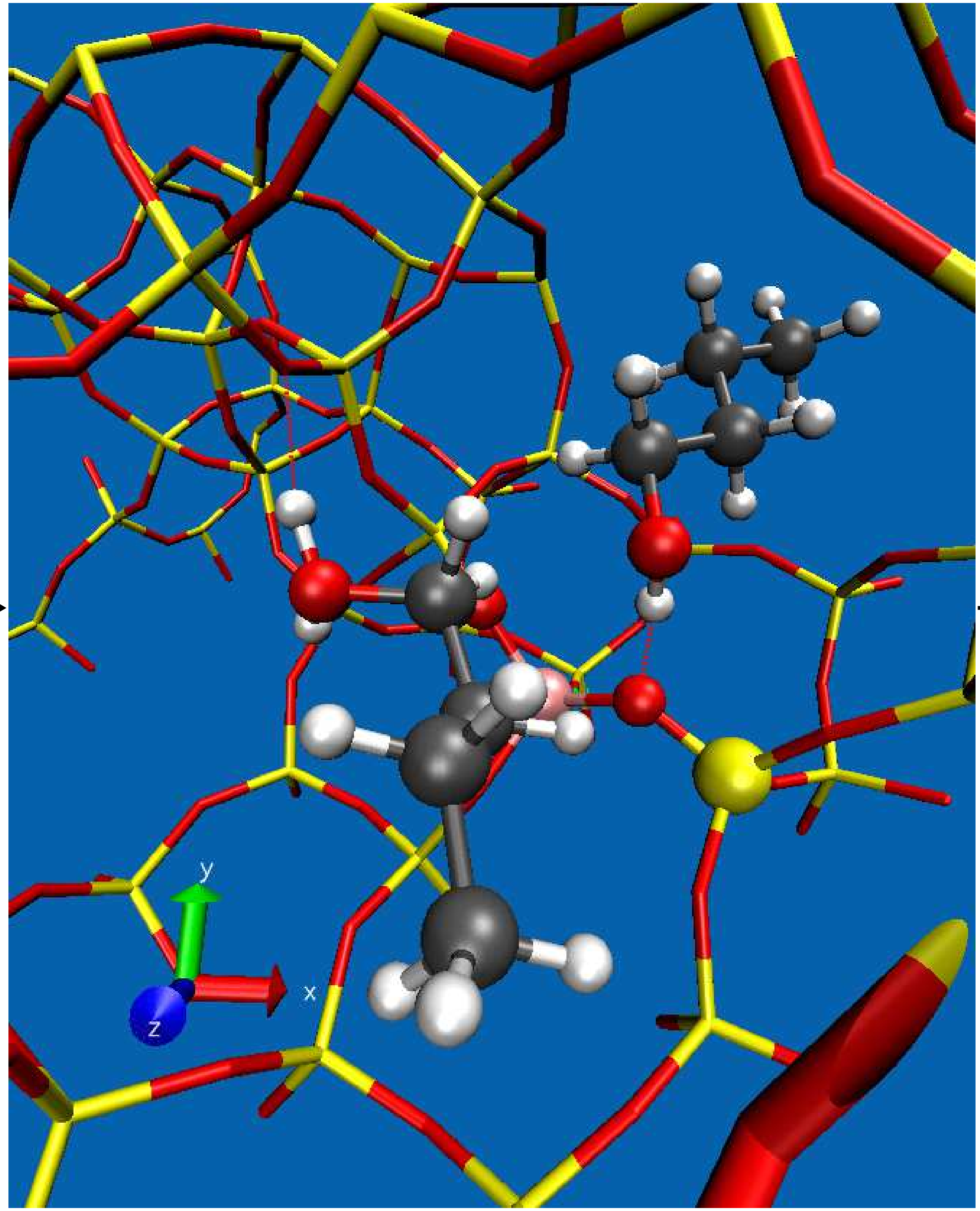


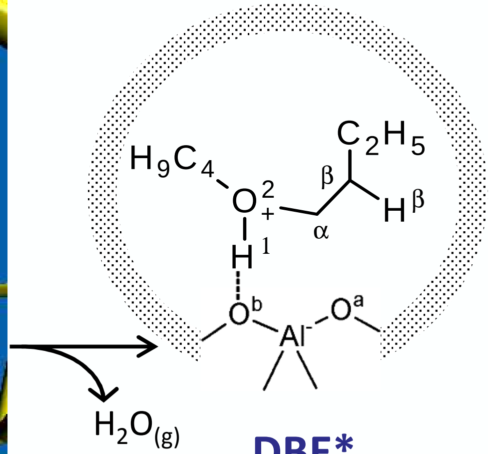
DBE*

SN2 TS8



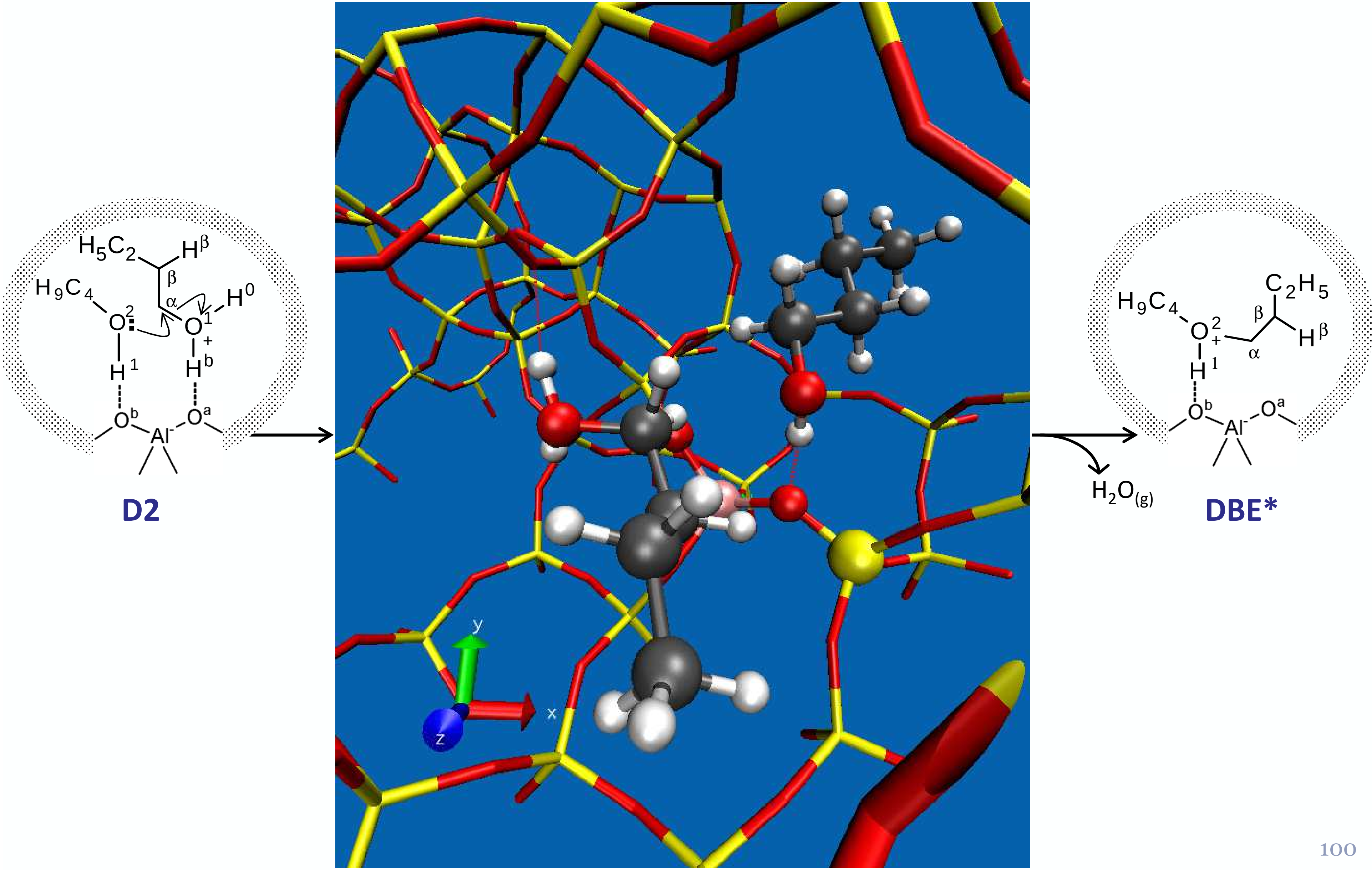
D2





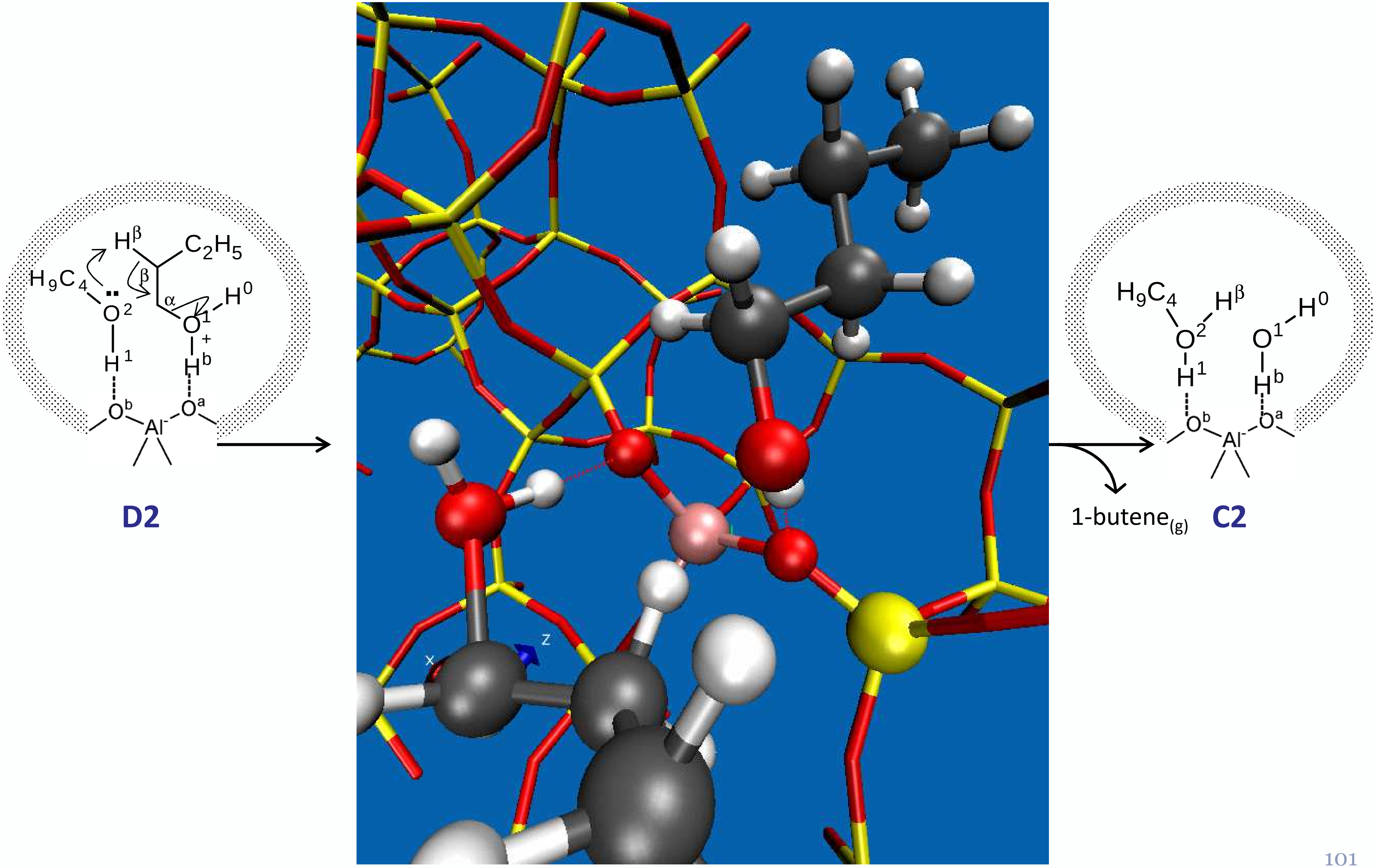
DBE*

SN2 TS8



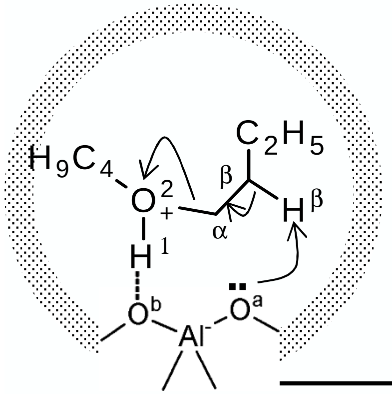
H5C2
Hβ
H9C4
β
α
H0
O2
O1
H1
Hb
Ob
Al-
Oa
D2
y
x
z
H2O(g)
H9C4
C2H5
O2
β
Hβ
α
H1
Ob
Al-
Oa
DBE*

butanol-assisted syn-elimination TS9

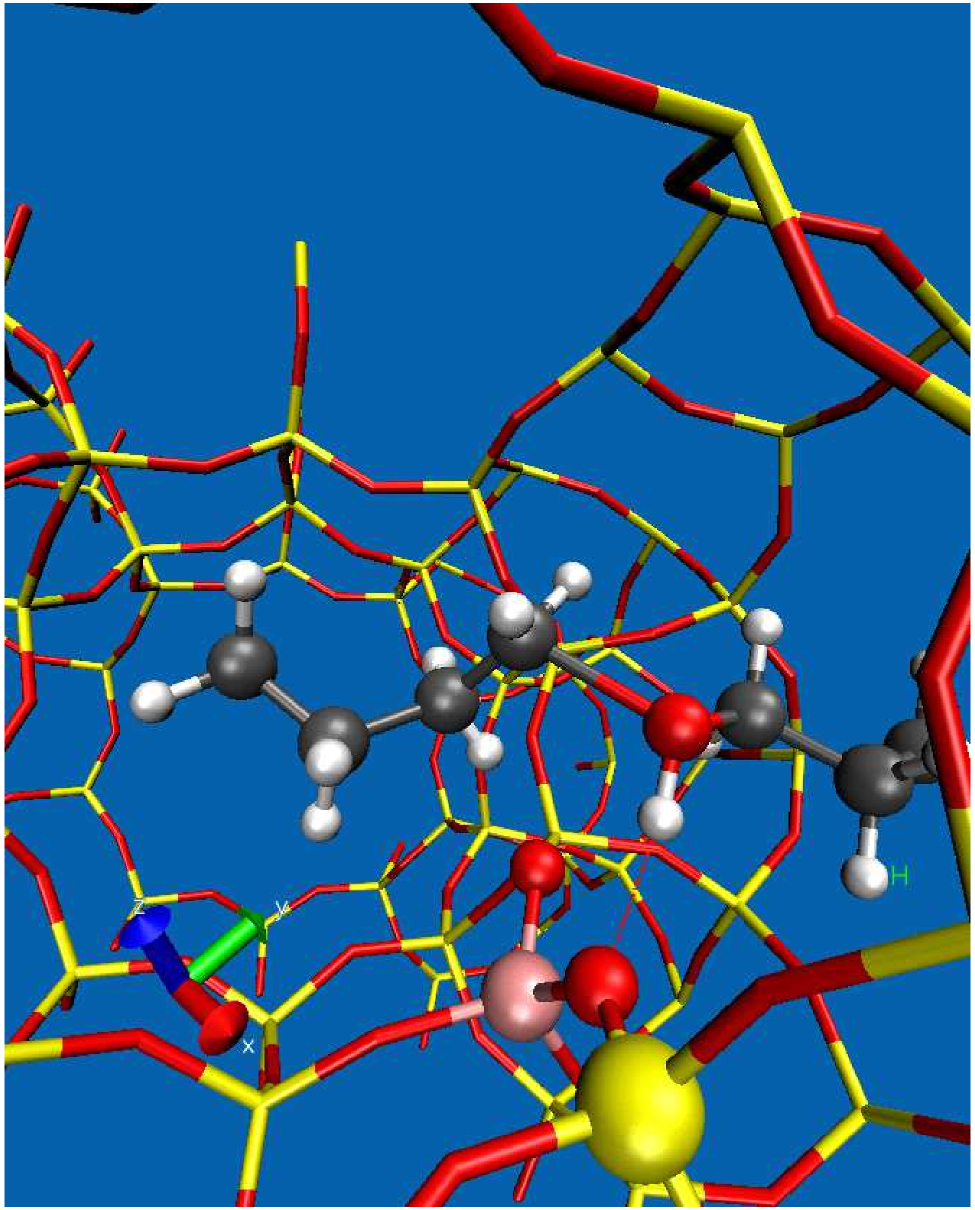


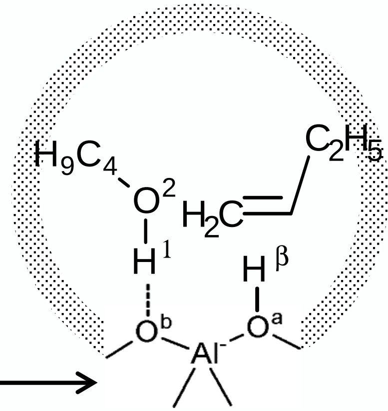
Syn elimination

TS10



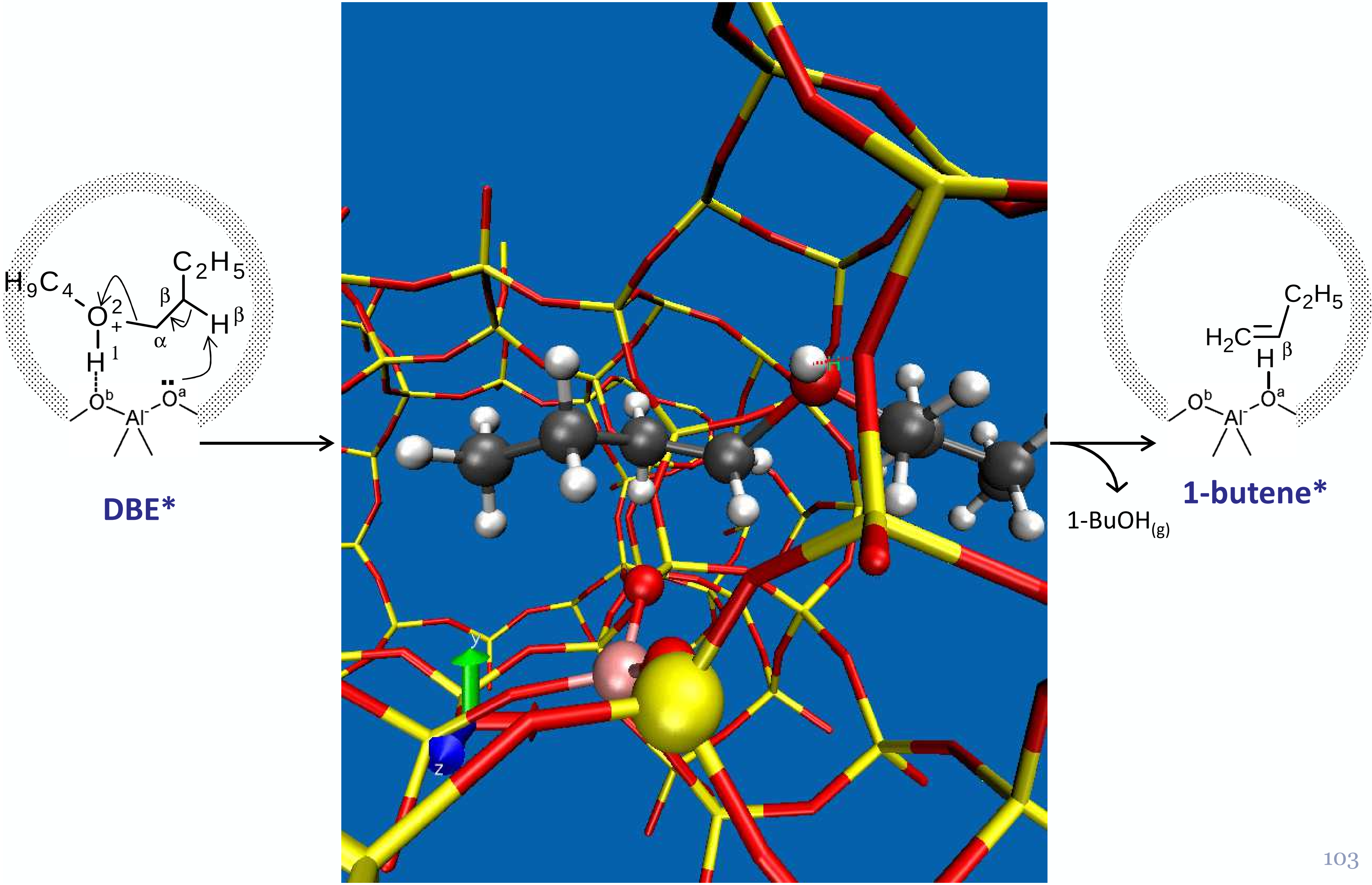
DBE*





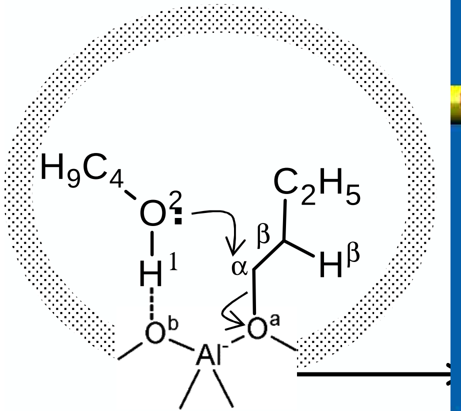
C1

TS11

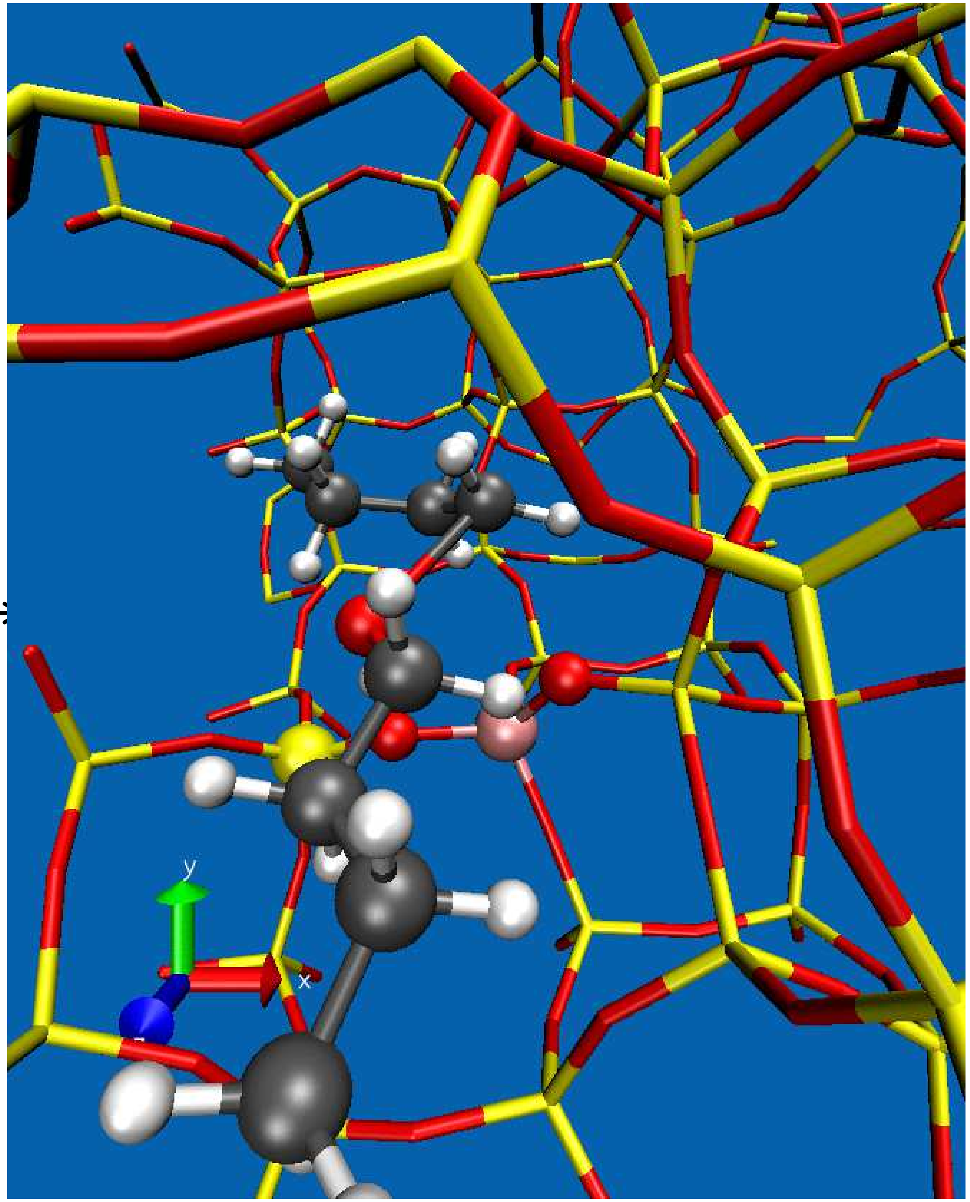


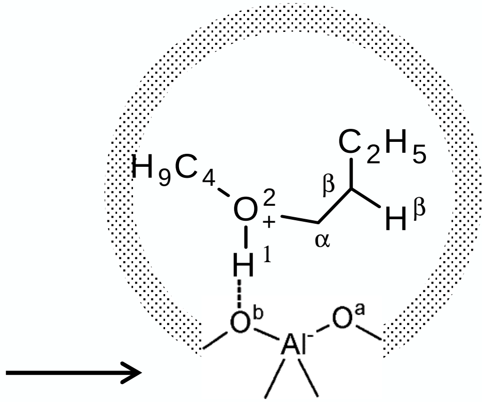
SN1

TS12



1-butoxide + 1-butanol *





DBE*