

Modeling of acid catalyzed reactions: confronting ab initio to experimental kinetic data

Guy B. Marin

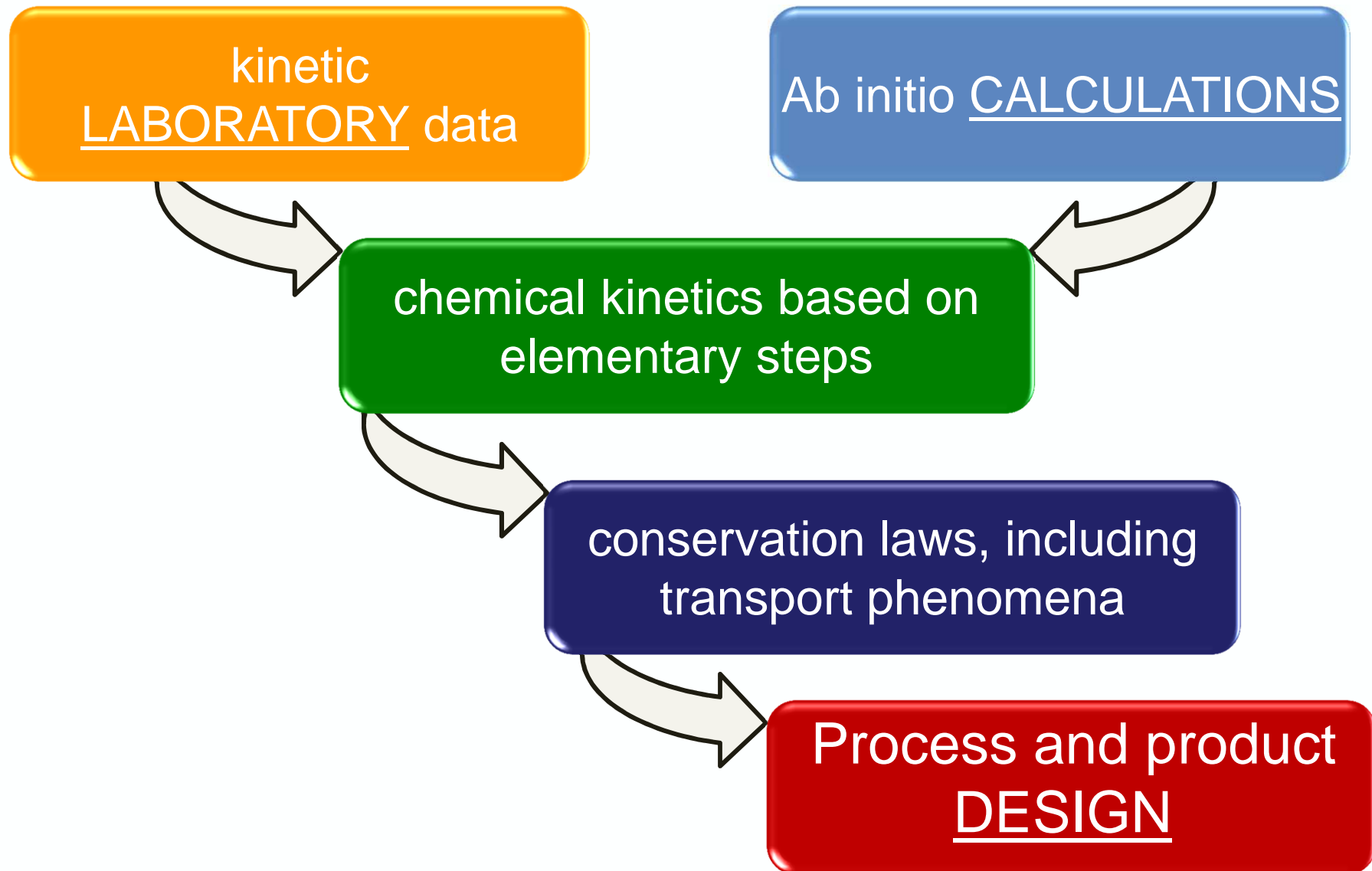
Laboratory for Chemical Technology, Ghent University

<http://www.lct.UGent.be>

Overview

- Introduction
- Bottom-up approach: alkylation of benzene
- Top-down approach: catalytic cracking
- Molecular modeling:
 - Adsorption of alkanes and alkenes
 - Conversion of alcohols
- Conclusions

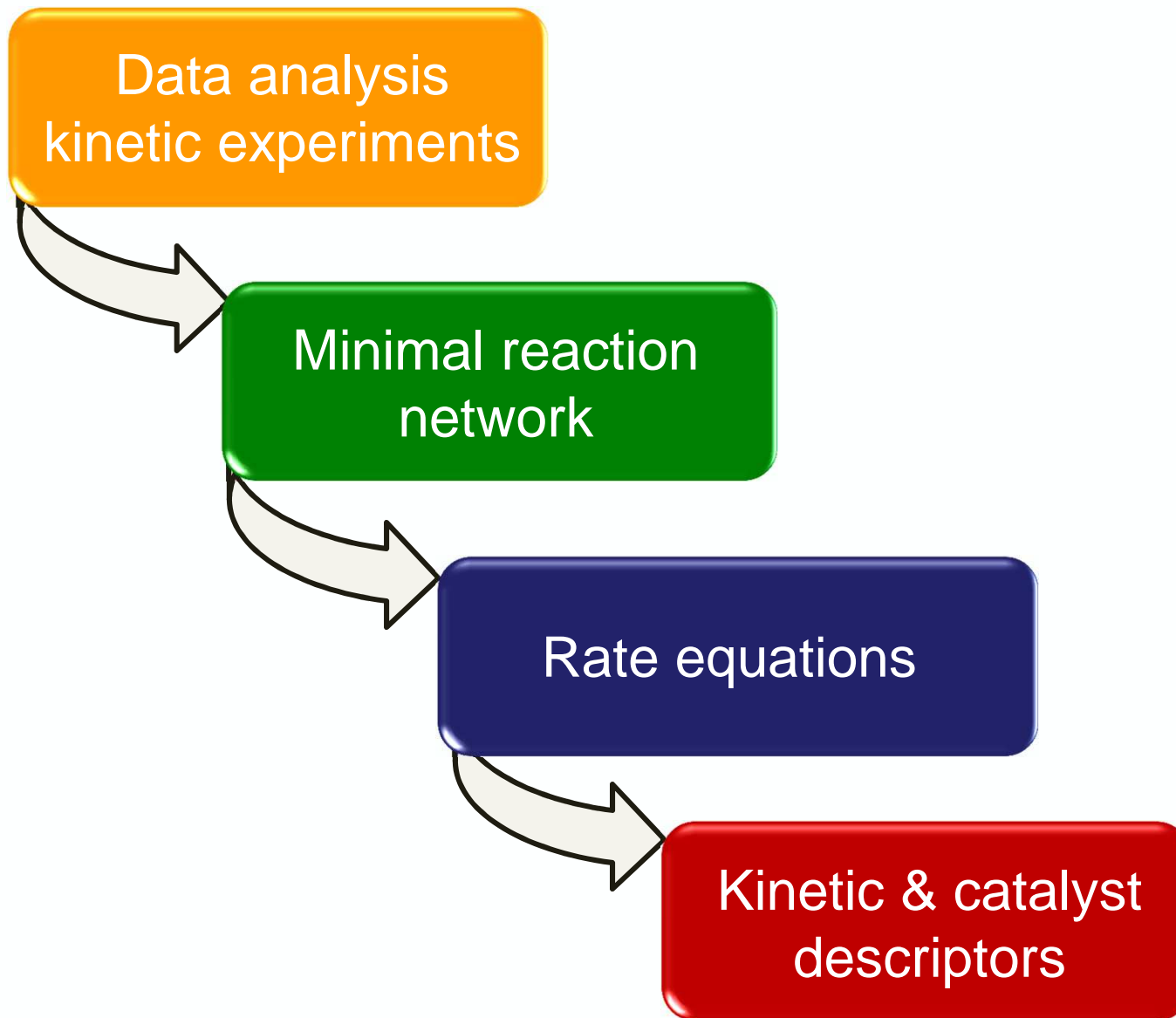
From molecule to process/product



Overview

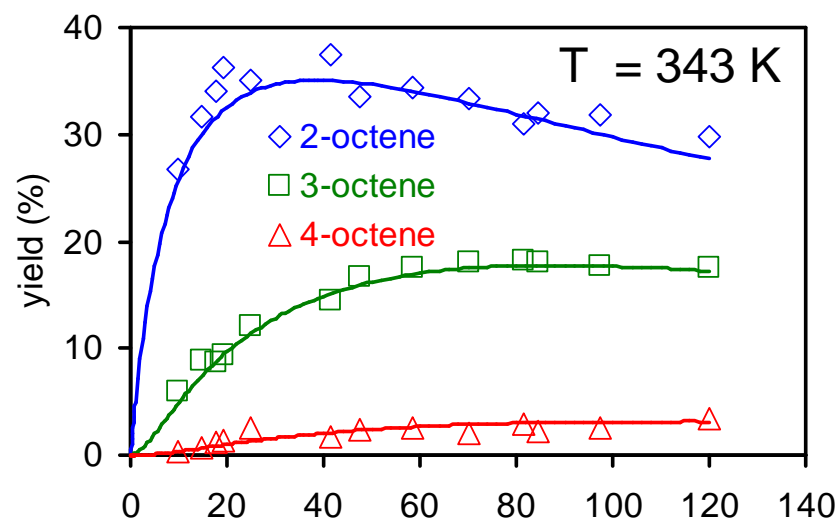
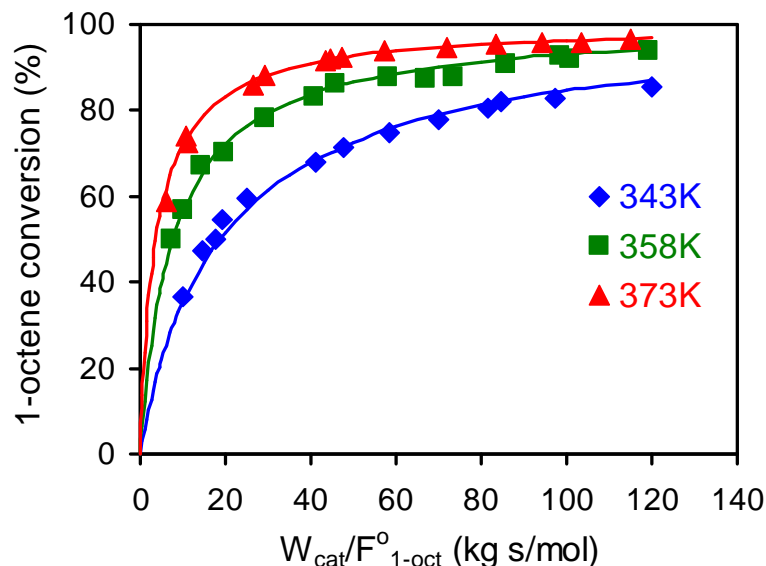
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Bottom-up approach

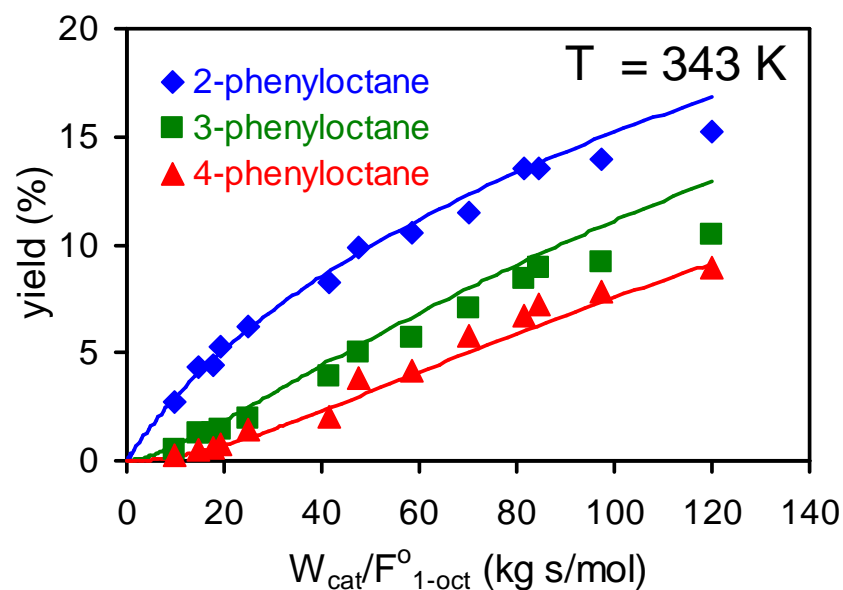


Alkylation: Conversion/yields versus space time

CBV760; B/O = 5 molar

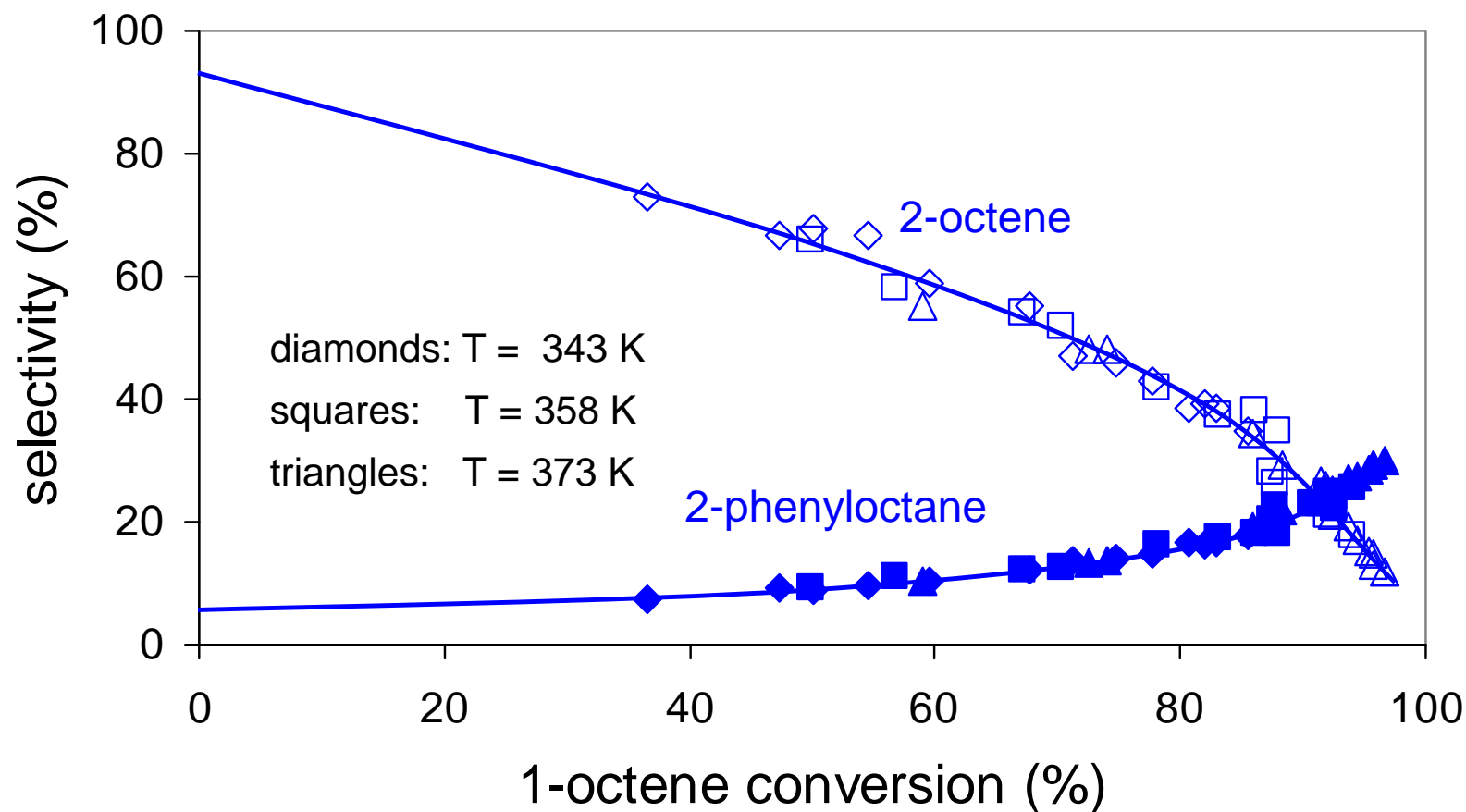


comparable time scales for
alkylation and olefin
isomerization



Product distribution

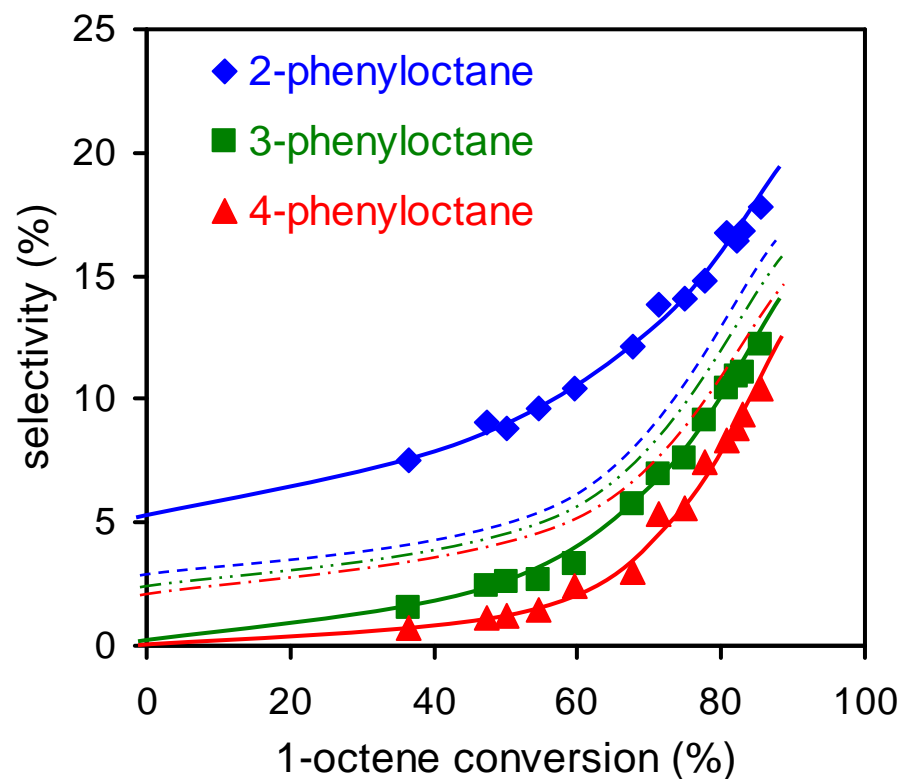
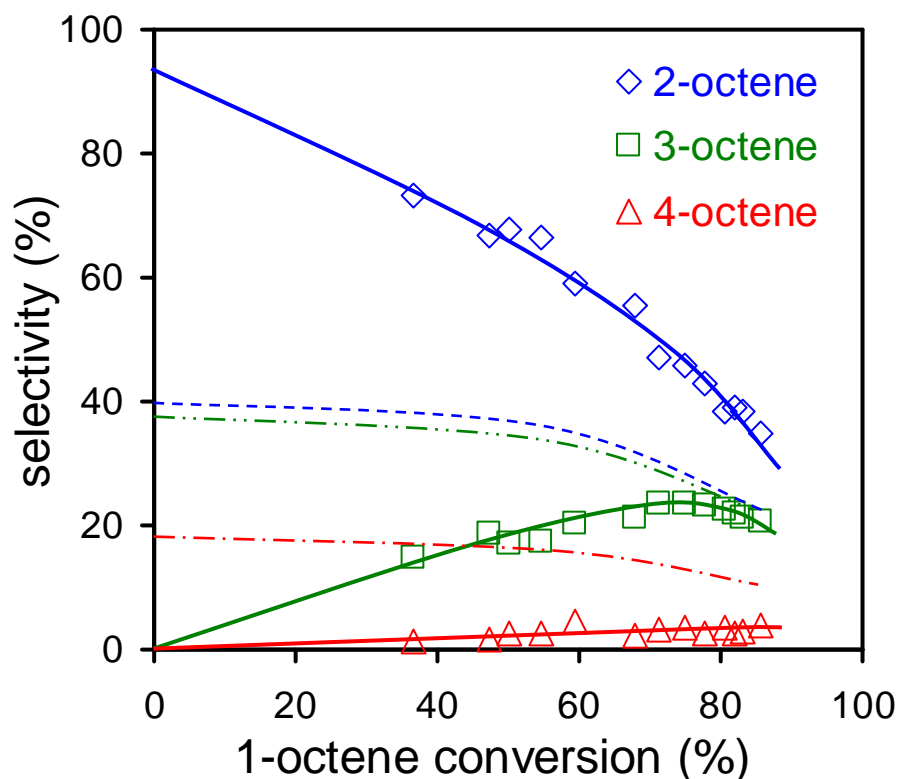
- Temperature influence: no effect on selectivity



CBV760 B/O = 5

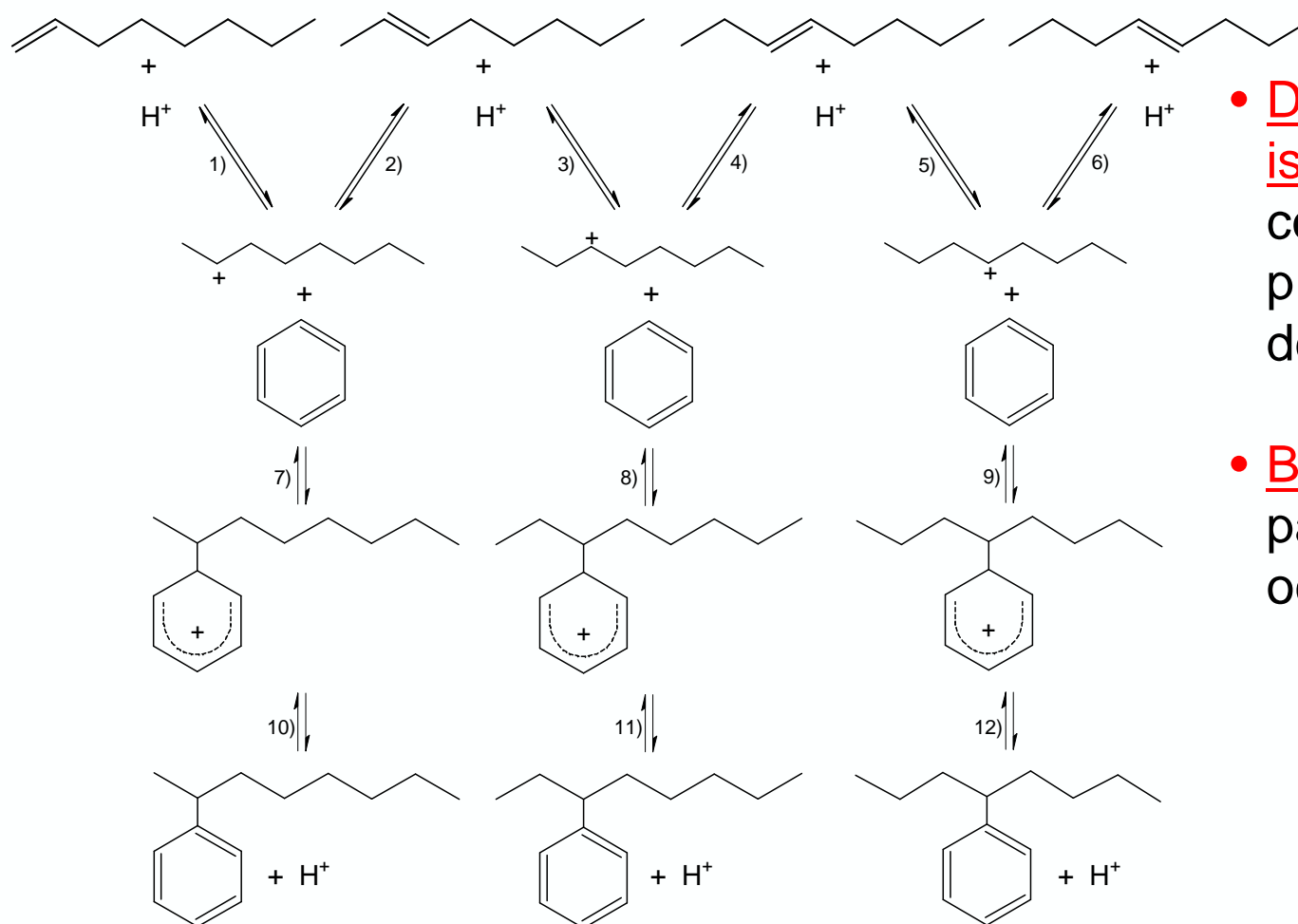
“Delplot” data analysis (1)

CBV760, $T = 343\text{K}$, $B/O = 5$ molar



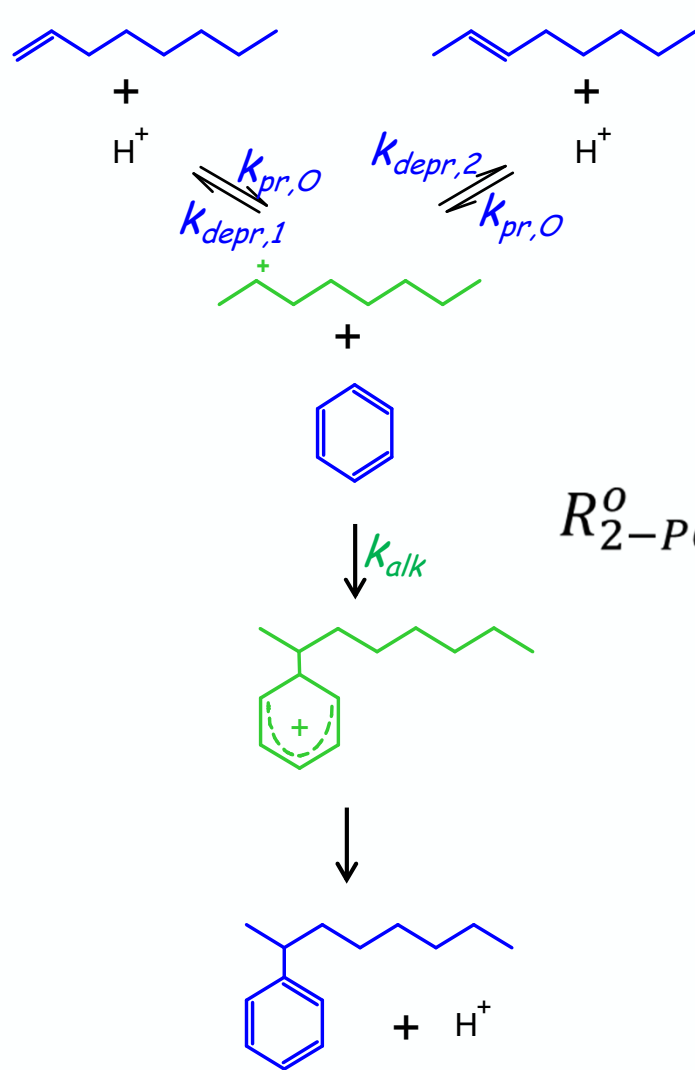
2-octene and 2-phenyloctane: primary products from 1-octene and benzene
octenes and phenyloctanes: internal equilibrium (dotted lines) not reached

Minimal reaction network



- Double-bond isomerization
consecutive protonation-deprotonation steps
- Benzene alkylation
parallel reaction of octyl-carbenium ions

Primary reaction network: rate equation

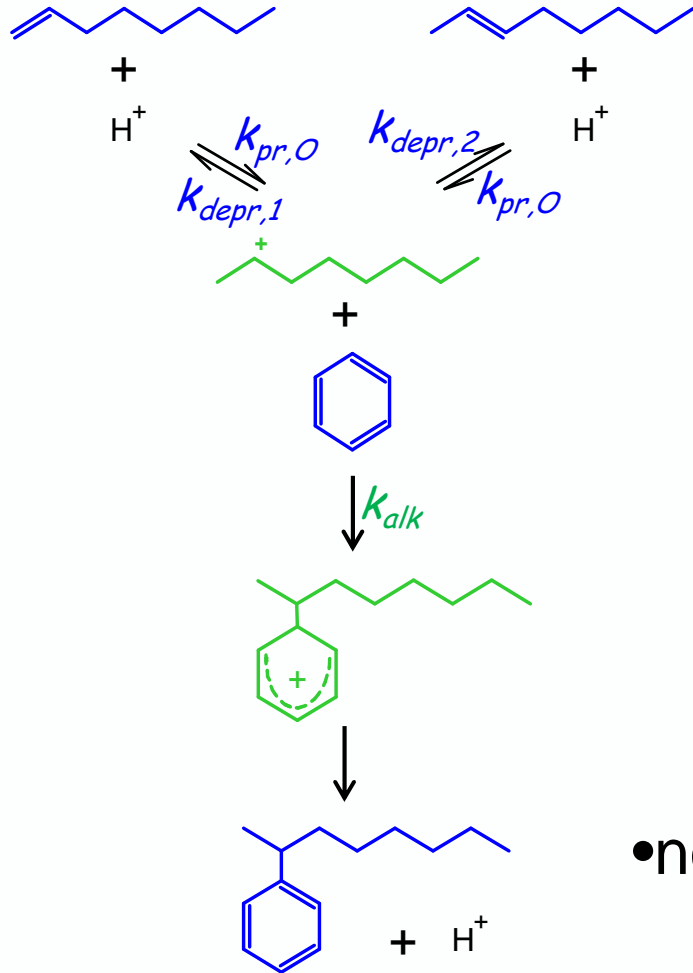


$$R_{2-PO}^o = \frac{k_{alk} K_{pr,O} C_t^o C_{1-oct}^o C_b^o}{1 + K_{iso,1} + K_{pr,O} C_{1-oct}^o + \frac{k_{alk} K_{pr,O}}{k_{pr,O}} C_b^o}$$

alkylation rate coefficient $\rightarrow k_{alk}$
 protonation equilibrium coefficient 1-octene: acid strength $\rightarrow K_{pr,O}$
 concentration of acid sites $\rightarrow C_t^o$
 equilibrium coefficient 1-octene_g \leftrightarrow 2-octene_g $\rightarrow K_{iso,1}$
 protonation rate coefficient $\rightarrow k_{pr,O}$

Thermodynamic consistency: $k_{de-pr,2} = k_{pr} \frac{K_{iso,1}}{K_{pr,O}}$

Initial selectivity ratio 2-PO/2-O



$$R_{2-PO}^o = \frac{k_{alk} K_{pr,O} C_t C_{1-oct}^o C_b^o}{1 + K_{iso,I} + K_{pr,O} C_{1-oct}^o + \frac{k_{alk}}{k_{pr}} K_{pr,O} C_b^o}$$

$$R_{2-O}^o = \frac{k_{de-pr,2} K_{pr,O} C_t C_{1-oct}^o}{1 + K_{iso,I} + K_{pr,O} C_{1-oct}^o + \frac{k_{alk}}{k_{pr}} K_{pr,O} C_b^o}$$

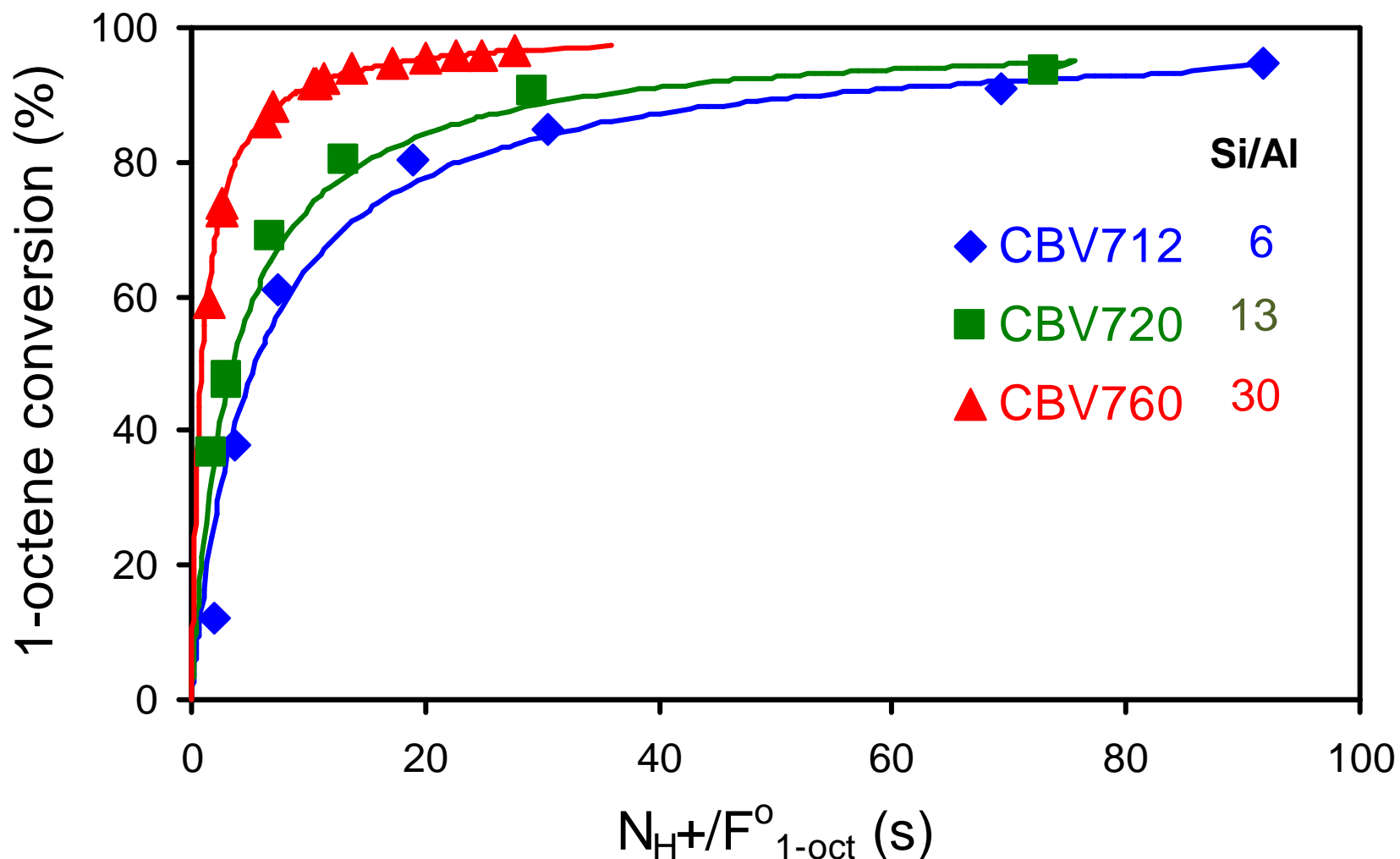
$$\frac{S_{2-PO}^o}{S_{2-O}^o} = \frac{k_{alk} C_b^o}{k_{de-pr,2}}$$

•no temperature influence on selectivity

$$\Rightarrow E_{a,alk} \cong E_{a,de-pr,2}$$

Influence acid properties of Y-zeolites (1)

$T = 373\text{K}$; $B/O = 5$



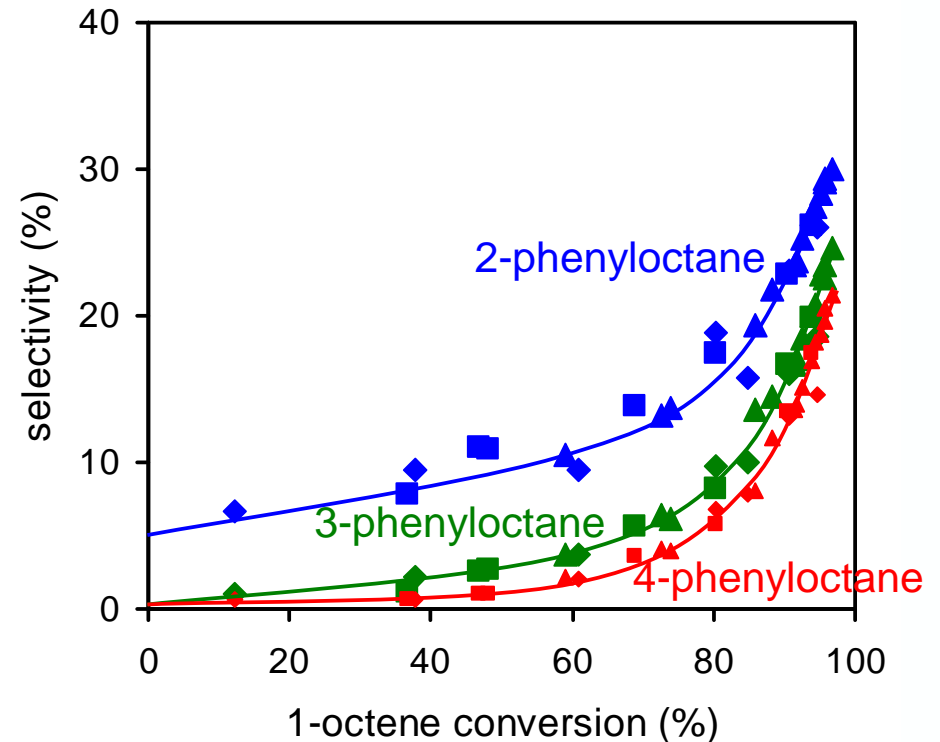
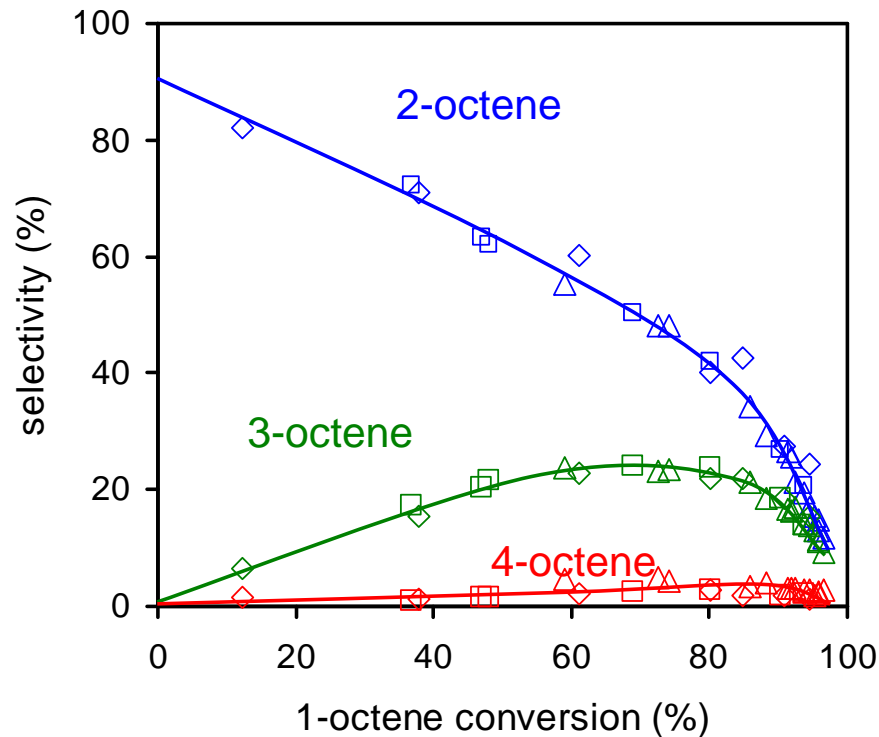
Influence acid properties of Y-zeolites (2)

$T = 373K$; $B/O = 5$

diamonds: CBV712

squares: CBV720

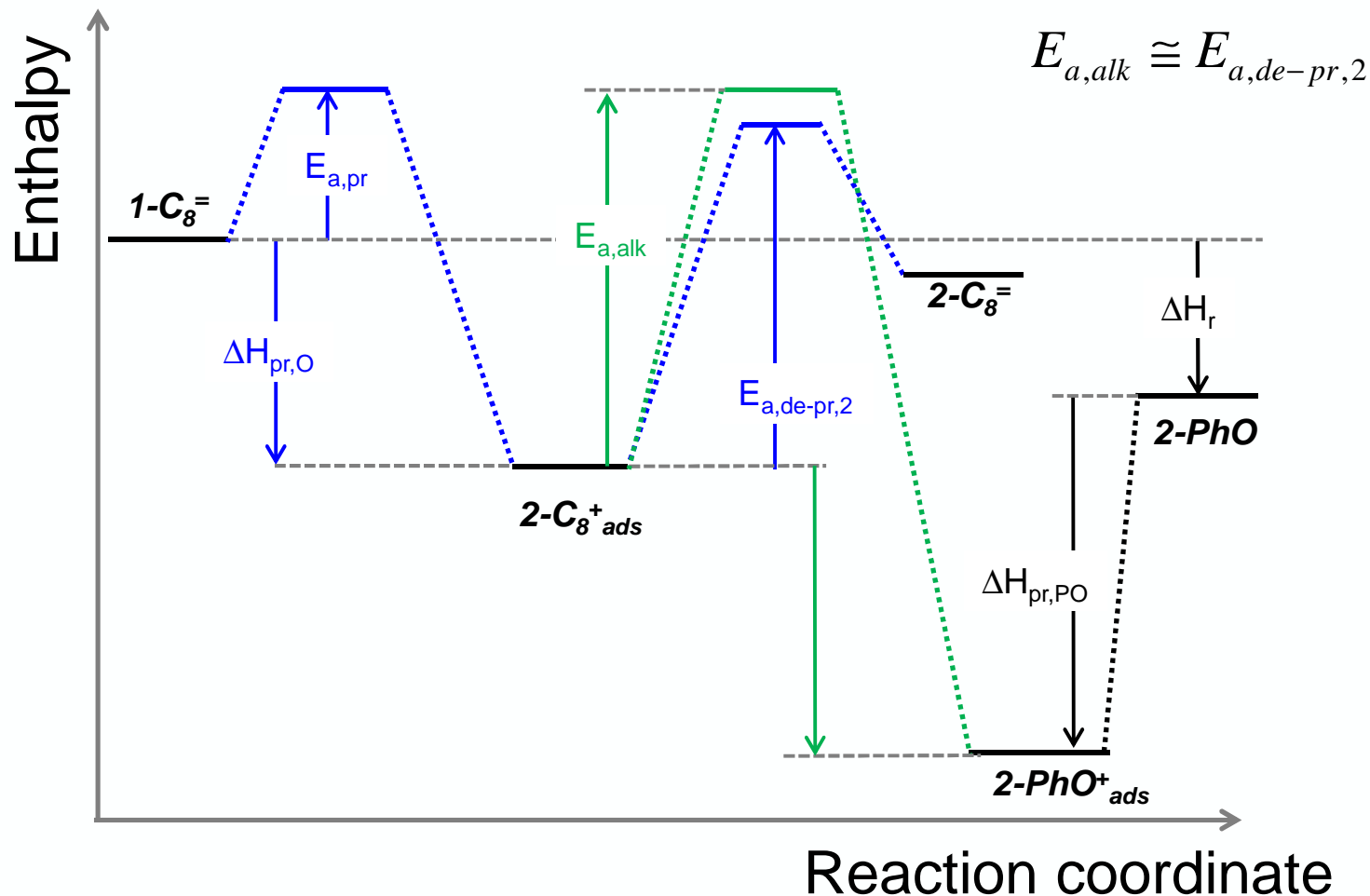
triangles: CBV760



e.g.: $S_{2-PO}^o = \frac{k_{alk} C_b^o}{k_{pr,1}}$ \rightarrow All intermediates and transition states are affected in the same way

Enthalpy diagram

Standard protonation enthalpy $\Delta H_{pr,O}$: measure for average acid site strength



Enthalpy diagram: influence acid strength

- Experimental observations

- no influence of temperature on selectivity $\Rightarrow E_{a \text{ deprot}} = E_{a \text{ alkylation}}$
- no influence of catalyst on selectivity $\Rightarrow \Delta_{\text{cat}} E_{a \text{ deprot}} = \Delta_{\text{cat}} E_{a \text{ alkylation}}$

- Thermodynamic consistency

- $\Delta H_{\text{iso,O(liq)}}$ independent of catalyst \Rightarrow single $\Delta_{\text{cat}}(\Delta H_{\text{pr,O}})$
- $\Delta H_{\text{r(liq)}}$ independent of catalyst $\Rightarrow \Delta_{\text{cat}}(\Delta H_{\text{alk}}) = \Delta_{\text{cat}}(\Delta H_{\text{pr,PheO}}) - \Delta_{\text{cat}}(\Delta H_{\text{pr,O}})$

- Assumptions (compatible with observations)

- no influence of catalyst on reaction entropies and activation entropies
- single $\Delta_{\text{cat}}(\Delta H_{\text{pr,PheO}})$
- $\Delta_{\text{cat}}(\Delta H_{\text{pr,PheO}}) = \Delta_{\text{cat}}(\Delta H_{\text{pr,O}})$: **single $\Delta_{\text{cat}}(\Delta H_{\text{pr}})$**

**all intermediates and all transitions states are
influenced to the same extent by a change in catalyst**

Kinetic & catalyst descriptors

- Kinetic descriptors

Protonation rate coefficient: $k_{pr,O}$

Alkylation rate coefficient: k_{alk}

- Catalyst Acidity descriptors

Acid site densities: C_t (experimentally determined)

Octene protonation equilibrium coefficient: $K_{pr,O}$

Phenyloctane protonation equilibrium coefficient: $K_{pr,PO}$

Difference in standard protonation enthalpy: $\Delta_{cat}(\Delta H^{\circ}_{pr})$

- Parameter estimation: regression to experimental data

$$S_{(b)} = \sum_1^{nob} \sum_1^{nresp} (\hat{y}_{i,j} - y_{i,j})^T \Sigma^{-1} (\hat{y}_{i,j} - y_{i,j}) \xrightarrow{b} Min. \quad \begin{array}{l} nob = 78 \\ nresp = 8 \end{array}$$

Parameter Estimates (kJ/mol)

- Kinetic descriptors (CBV760-reference)

$$E_{a,pr} = 45.8 \pm 1.9$$

$$E_{a,alk} = 69.6 \pm 1.6$$

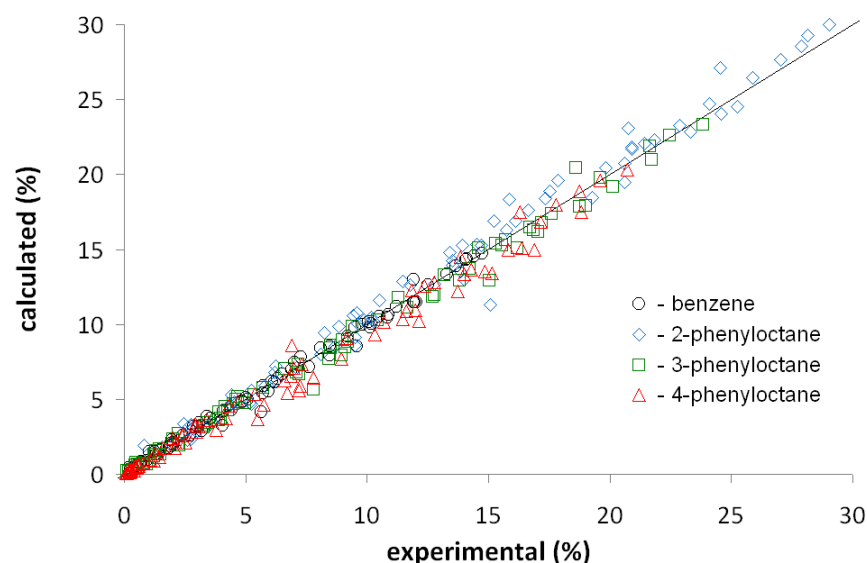
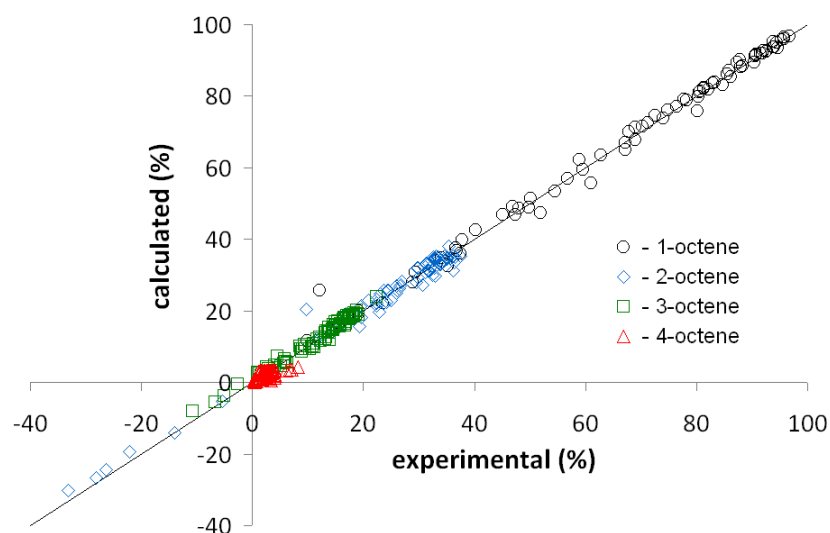
- Catalyst descriptors

$$\Delta H_{pr,O,CBV760} = -32.5 \pm 0.1$$

$$\Delta H_{pr,PO,CBV760} = -92.2 \pm 30.8$$

$$\Delta_{cat}(\Delta H_{pr})_{CBV720} = 4.8 \pm 0.2$$

$$\Delta_{cat}(\Delta H_{pr})_{CBV712} = 6.7 \pm 0.2$$



Summary: experimental data

- Double-bond isomerization and benzene alkylation occur on comparable time scale
- Detailed product distribution for the alkylation of benzene with long chain olefins
- Reaction product ranking, i.e. primary, secondary, and tertiary, based on selectivity and conversion data

Summary: analysis

- Detailed **reaction network**, compatible with the observed product distribution and with carbenium ion chemistry
- Model with **limited number of kinetic parameters** that can be applied to Y zeolites with different acid properties
- **Catalyst descriptors**: average acid strength and number of acid sites

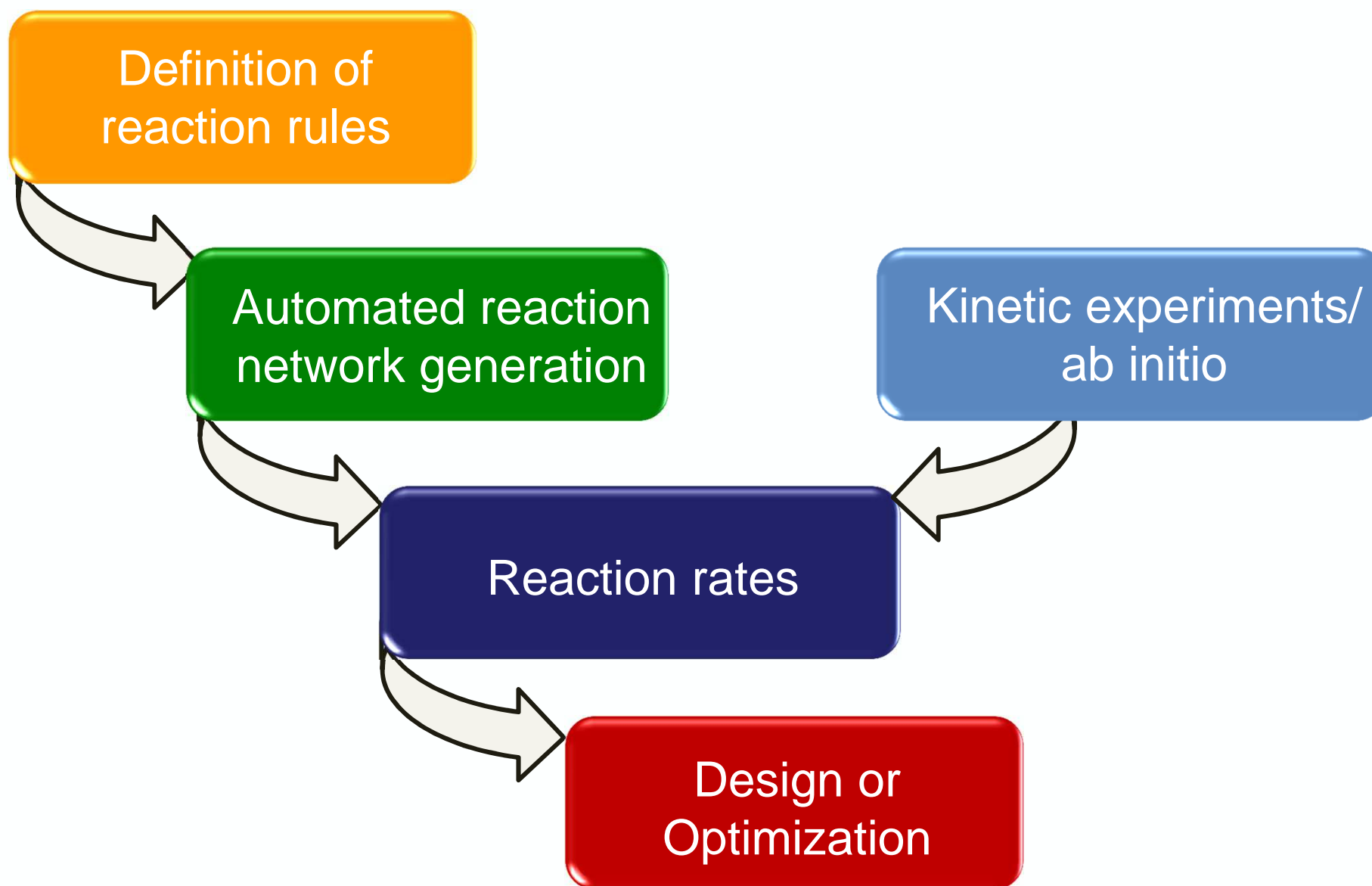
Conclusions: bottom up

- Experimental data
 - Intrinsic
 - Conversion versus space time
 - Selectivity versus Conversion
- Analysis
 - Reaction network
 - Reduction of number of kinetic parameters
 - Thermodynamic consistency
 - Catalyst descriptors

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Top-down approach



Computer generation of reaction networks

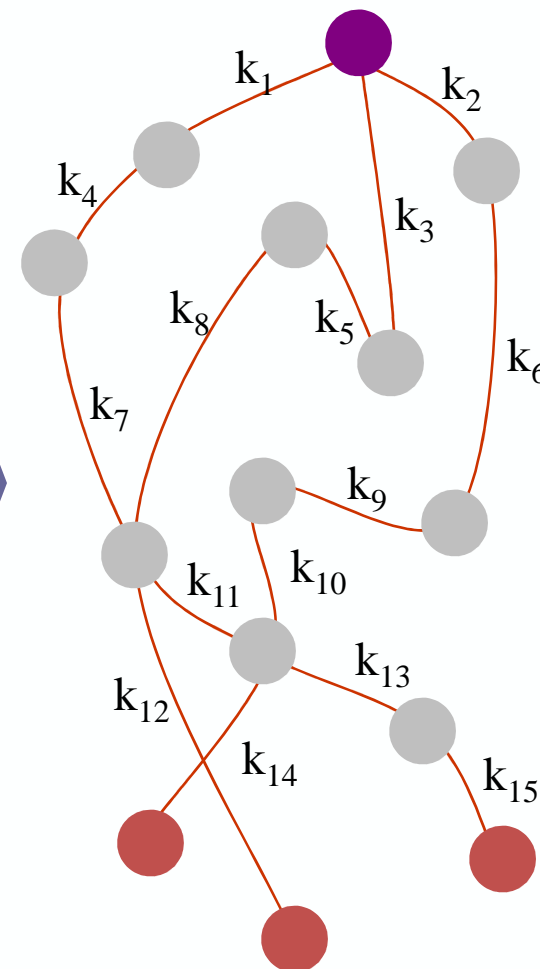
COMPUTER PROGRAM

Molecules

Elementary
Reaction Families

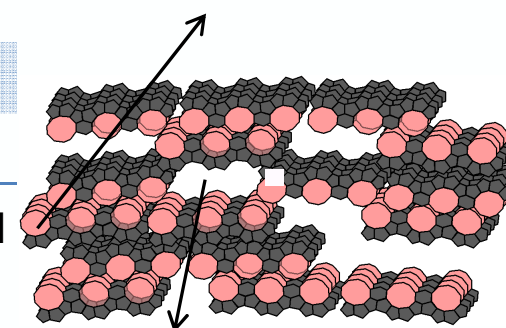
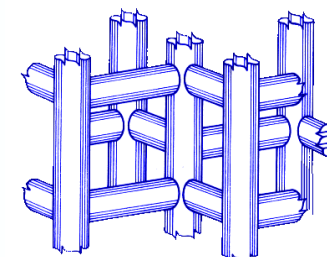
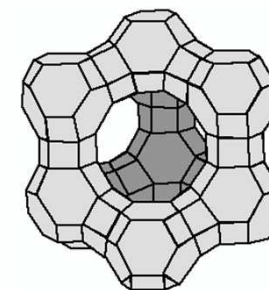
Reaction Rules

- Representation
- Species Uniqueness
- Mathematical Operations
- Termination Criteria
- Thermodynamics
- Kinetic Parameters



Catalytic cracking: catalysts

	catalyst	Si/Al bulk	Si/Al frame	C _t (mol NH ₃ /kg)	V _{micro} (cm ³ /g)
LZ-Y20	H-USY	2,6	30,0	0,99	0,19
Y62	NH ₄ -Y	2,6	2,6	3,49	0,34
CBV 500	NH ₄ -USY	2,6	3,9	1,50	0,27
CBV 720	H-USY	15	16,0	0,60	0,27
CBV 760	H-USY	30	100	0,23	0,25
CBV 3020	HZSM5/MFI	15	18,4	0,54	0,16
CBV 5524	NH ₄ -ZSM-5	25	25,2	0,35	0,18
CBV 8014	NH ₄ -ZSM-5	40	40	0,35	0,17
BIPOM1	BIPOM	50	47	0,13	0,64
BIPOM3	BIPOM	50	50	0,09	0,28



ultramicropore = MFI

supermicropore: BIPOM1: 1-2 nm
BIPOM3: 1-10 nm

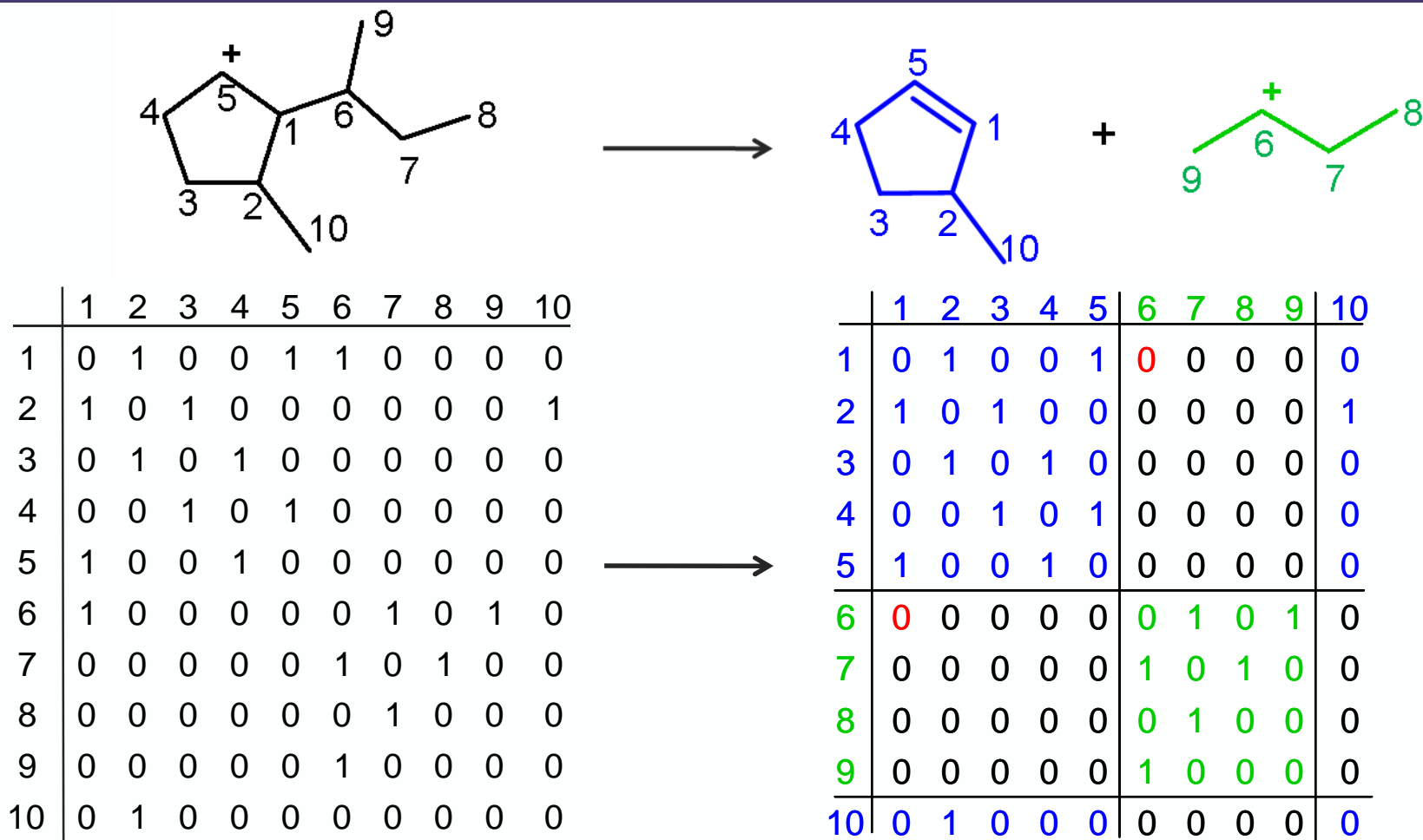
Catalytic cracking of CC(C)CC(C)C & C1CCCCC1

→ effect of acid properties and shape selectivity

Elementary reaction families

	alkanes	cycloalkanes
protolytic scission		
protonation/deprotonation		
β -scission/alkylation		
PCP isomerization		
hydride transfer		
ring contraction/expansion		

Hydrocarbons: matrix representation



e.g. n-C₁₉: 1981 alkanes , 25065 alkenes, 20437 carbenium ions

42600 (de)protonations, 12470 alkyl shifts, 15970 PCP branching and
6429 β -scissions

Rate constants: Single-Event MicroKinetics

Transition State Theory (TST):

$$k = \frac{\sigma_{\text{gl}}^{\text{reac}}}{\sigma_{\text{gl}}^{\neq}} \frac{k_{\text{B}}T}{h} \exp\left(\frac{\Delta\tilde{S}^{0,\neq}}{R}\right) \exp\left(-\frac{\Delta H^{0,\neq}}{RT}\right)$$

SEMK rate coefficients \tilde{k} : $k = \frac{\sigma_{\text{gl}}^{\text{reac}}}{\sigma_{\text{gl}}^{\neq}} \tilde{k} = n_{\text{e}} \tilde{k}(\text{m};n)$

symmetry reactant(s) and TS

- reaction family:
PCP, β -scission ...
- type: p, s, t

Arrhenius:

$$\tilde{k} = \tilde{A} \exp\left(\frac{E_{\text{a}}}{R}\right)$$

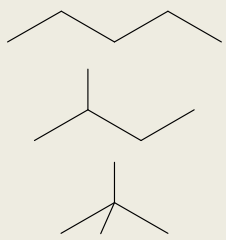
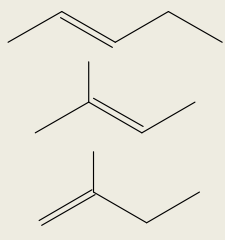
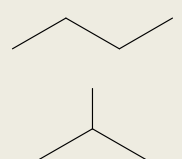
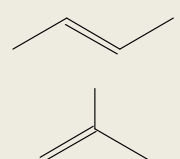
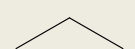
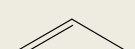


calculated based on TST and
statistical thermodynamics

estimated via regression to
experimental data

i-Octane: effect of framework

Product selectivities (mol%) at 15 mol% conversion of i-octane

7 kPa, 748 K

	par	ole	FAU		MFI	
C5			1	1	1	1
			12	3	2	1,5
			-	3	10	0,5
C4			5	23	6	5
			79	37	25	7
C3			4	32	38	39
C2			1	2	6	49
C1	CH ₄		7		48	

FAU: hydride transfer + β -scission \rightarrow **C4**

ZSM5/MFI: protolytic scission \rightarrow **C1 – C3**

\rightarrow Hydride transfer in MFI pores is hindered = *transition state shape selectivity*

SEMK cracking on MFI: shape selectivity descriptors

Transposition of SEMK model for cracking on FAU to MFI:

- account for acidity differences: C_t & $\Delta_{\text{cat}}(\Delta H_{\text{pr}})$
- account for transition state shape selectivity: suppression of rate of bimolecular hydride transfer reactions: $\Delta_{\text{cat}}E_{\text{a,htf}}$

estimated catalyst descriptors (kJ/mol):

	$\Delta_{\text{cat}}(\Delta H_{\text{pr}})$	$\Delta_{\text{cat}}E_{\text{a,htf}}$
CBV8014	$1,4 \pm 0,4$	$10,3 \pm 0,6$
CBV5524	$8,3 \pm 0,6$	10,3
CBV3020	$9,7 \pm 0,3$	10,3

Summary: model

- **Reaction network**
 - based on carbenium ion chemistry
 - computer aided generation of full reaction network
- **Kinetic descriptors**
 - reference Y zeolite
 - stability differences between secondary and tertiary intermediates as expected from carbenium ion chemistry
- **Catalyst descriptors**
 - acid strength affects the stability of intermediate species and transition states to the same extent
 - shape selectivity: activation energy for H transfer

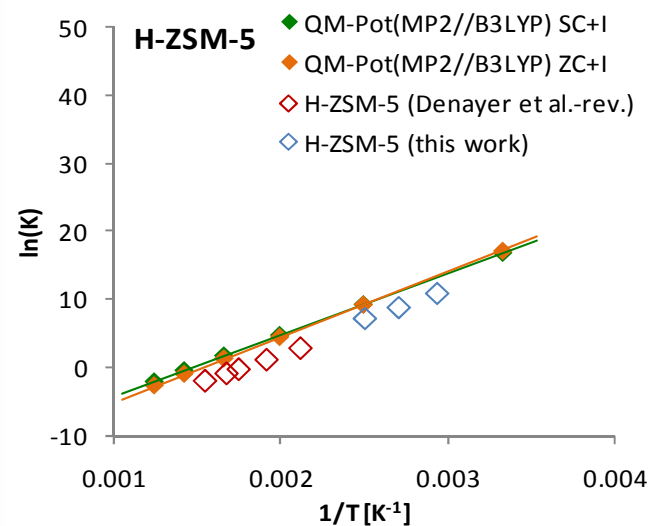
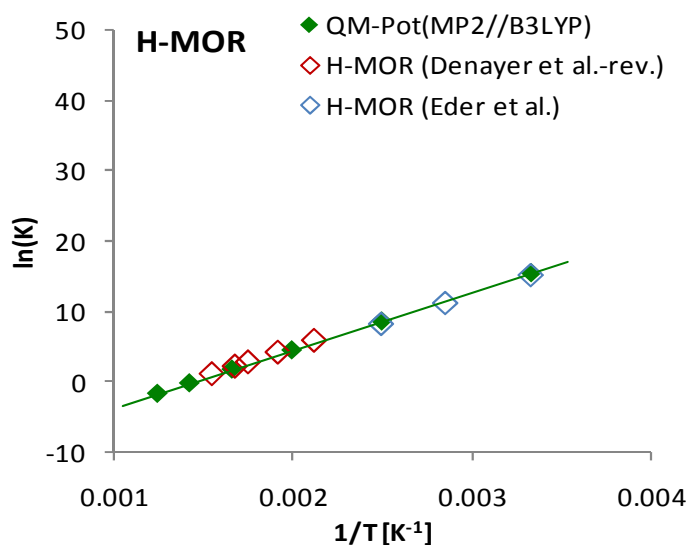
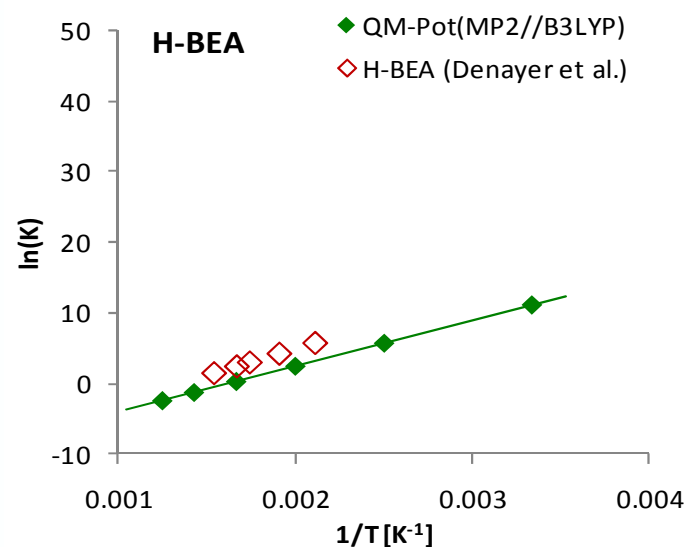
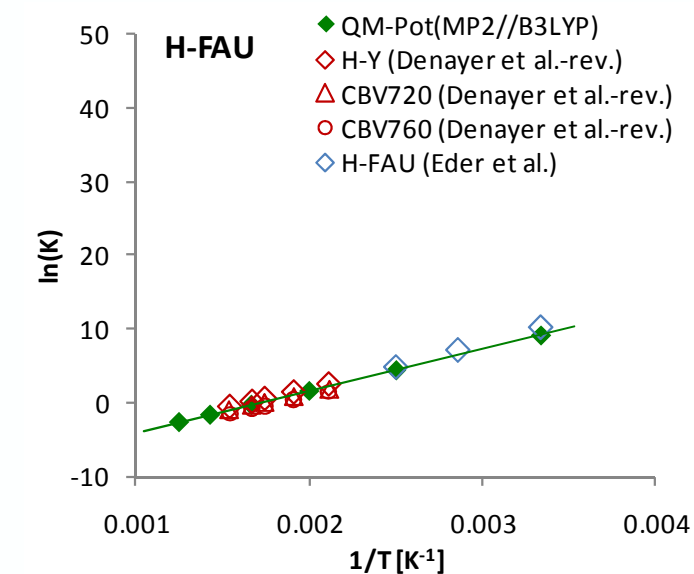
Conclusions: top down

- Model
 - Elementary reaction families
 - Computer generation of full reaction network
 - Kinetic and thermodynamic parameters
 - Limited number
 - Physico-chemical meaning: effects of catalyst
- Experimental data
 - Pure components versus complex mixture
 - Verification/validation: limited number

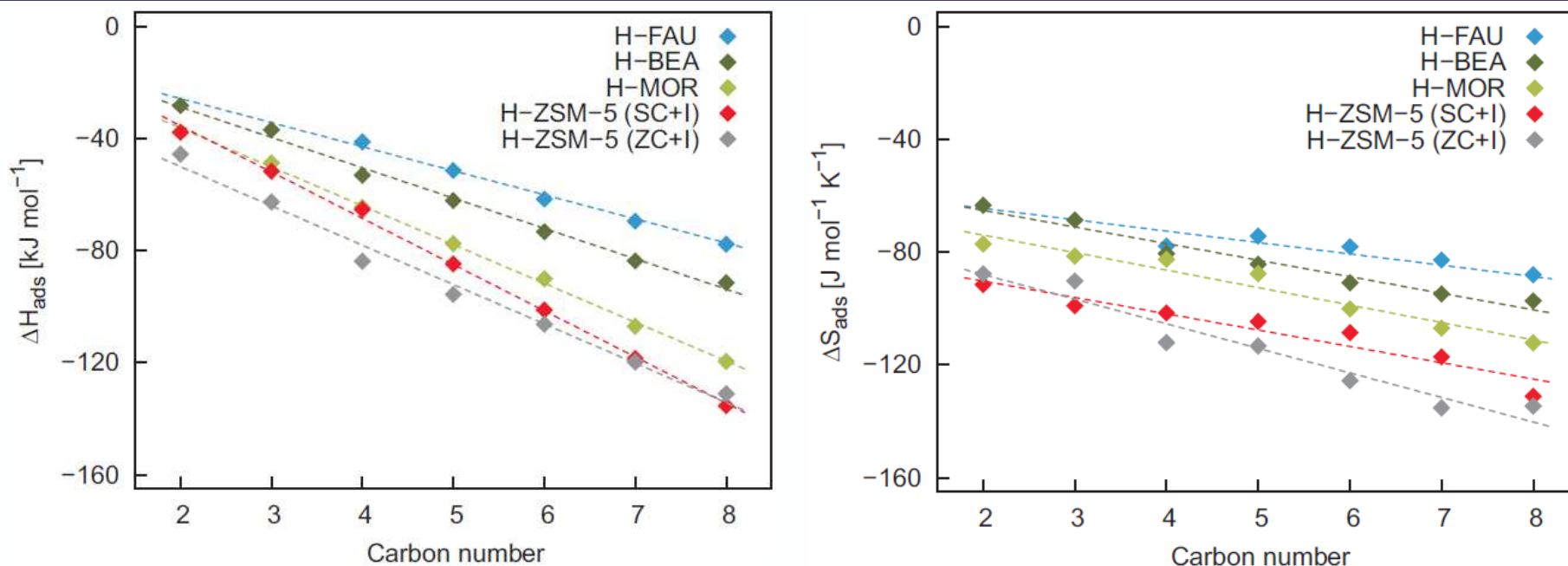
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n-Hexane: experimental versus ab initio



n-alkane physisorption

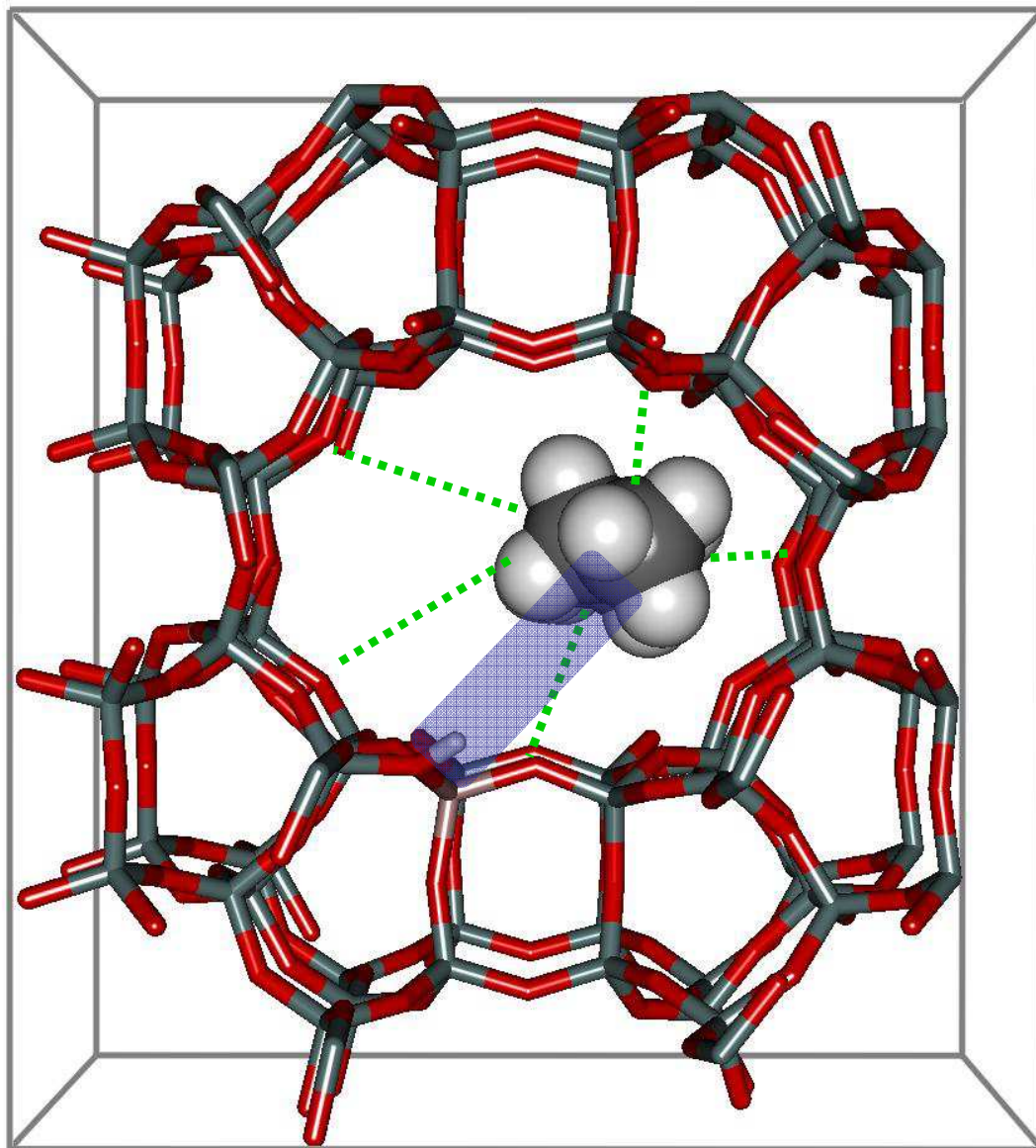


- Physisorption strength and entropy loss increase in the order: H-FAU < H-BEA < H-MOR < H-ZSM-5
- Physisorption strength and entropy loss increase with increasing carbon number

De Moor et al. (2011) *J. Phys. Chem. C*, 115, 1204–1219

De Moor et al. (2011) *J. Chem. Theory Comput.*, 7 (4), 1090–1101

n-alkane physisorption



Stabilizing contributions

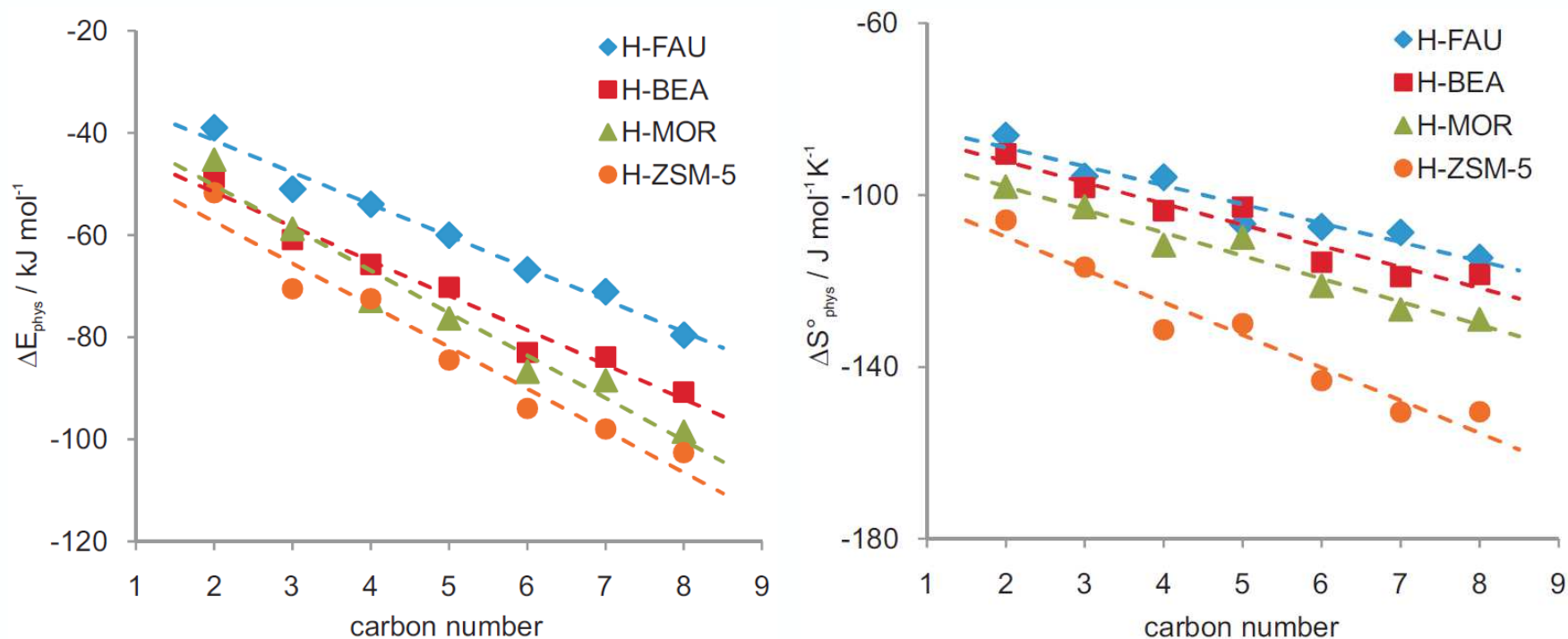
van der Waals interactions

- stabilizing
- increase with increasing CN
- depend on zeolite type

Weak interaction between acid proton and n-alkane

- stabilizing 5-10 kJ mol⁻¹
- independent of carbon number
- slightly depends on the zeolite type

Linear alkene physisorption

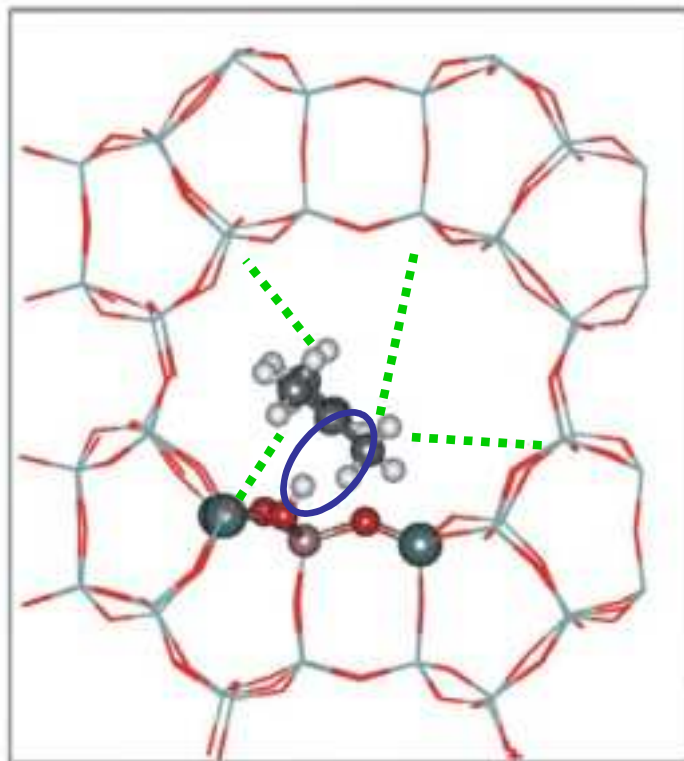


Physisorption strength and entropy loss

- increase with increasing CN
- increase in order: H-FAU < H-BEA < H-MOR < H-ZSM-5

Linear and branched alkene adsorption

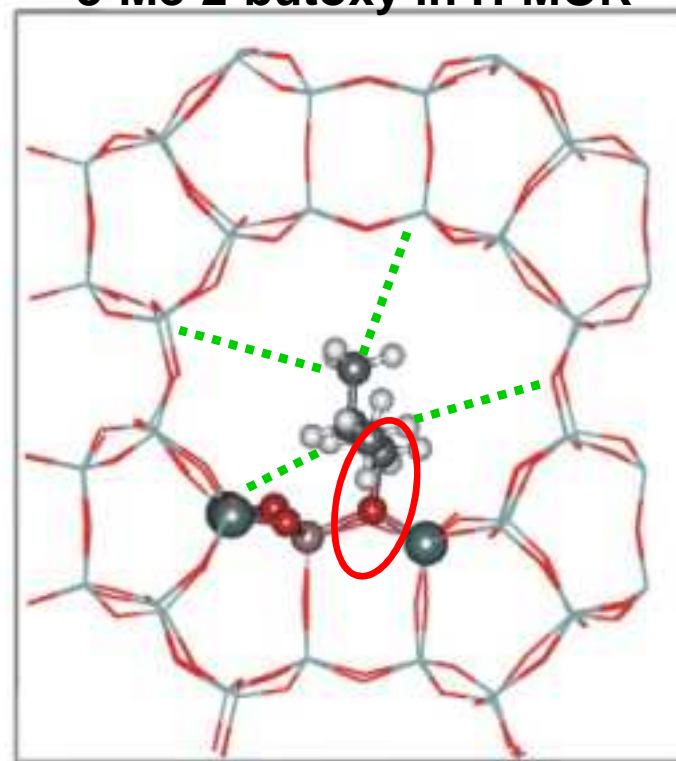
2-Me-2-butene in H-MOR



Physisorption

- van der Waals stabilization
- H^+ -alkene interaction (π -complex) ~20-30 kJ/mol

3-Me-2-butoxy in H-MOR



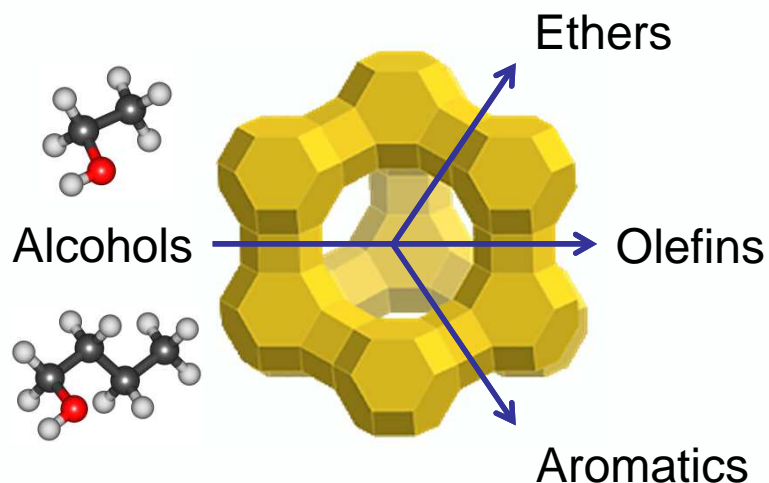
Chemisorption

- van der Waals stabilization
- C-O bond
- electrostatic contributions
- repulsion / zeolite deformation

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Zeolite-catalyzed alcohol conversion

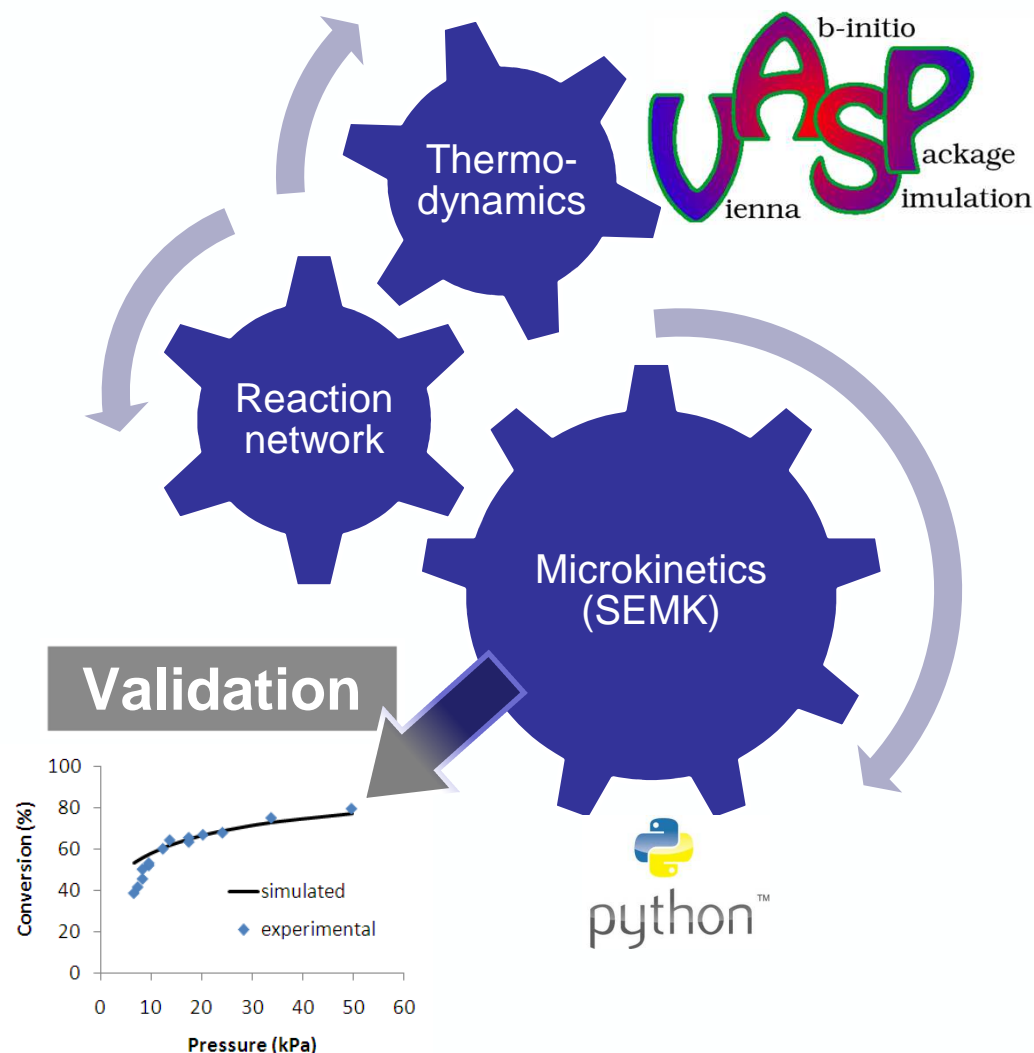


$T, P, W/F^\circ, \%H_2O$

Goal: Simulate the influence of **reaction conditions** and **zeolite framework** on product distribution

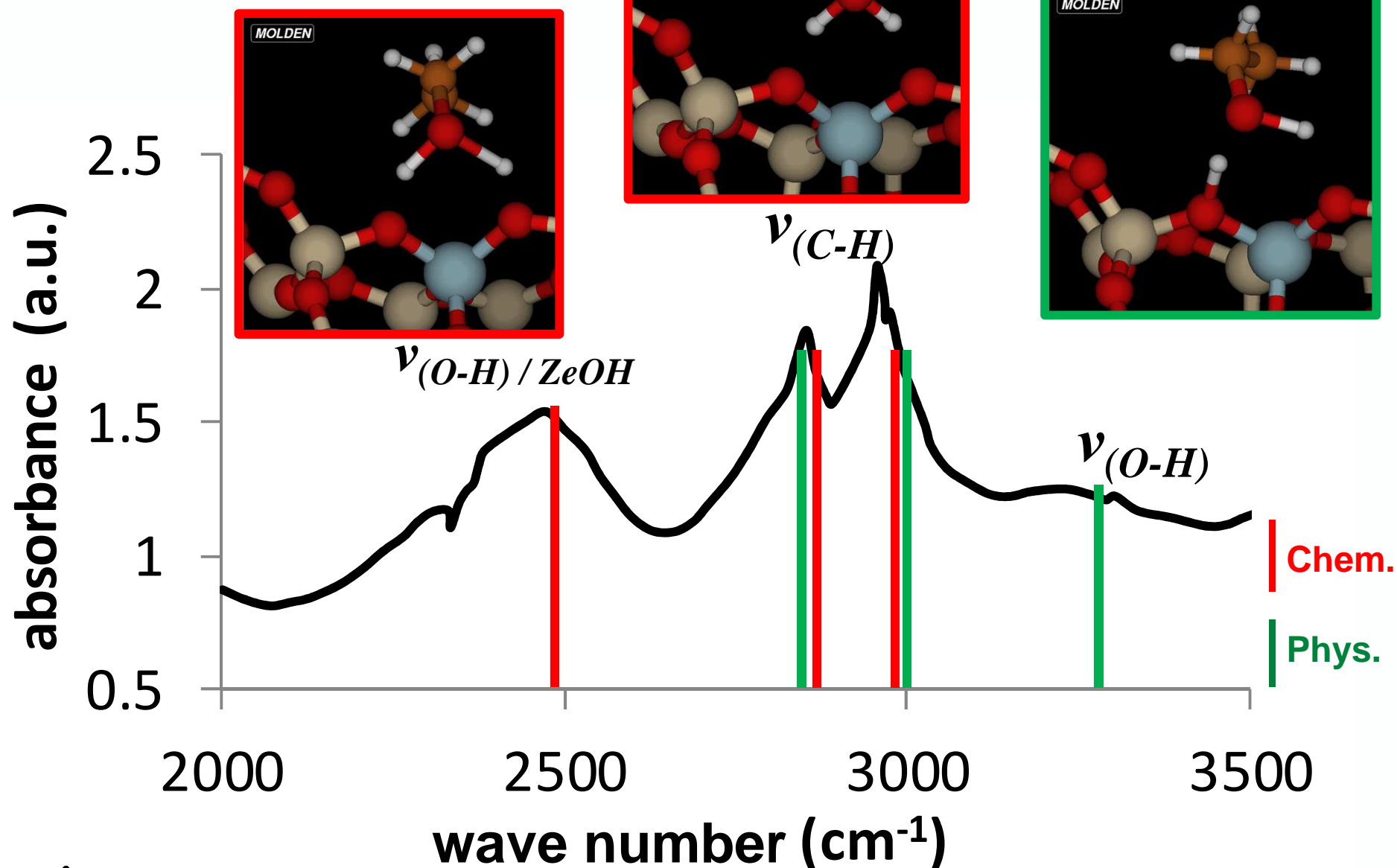
H-FAU H-ZSM-5
H-MOR H-ZSM-22

Methodology

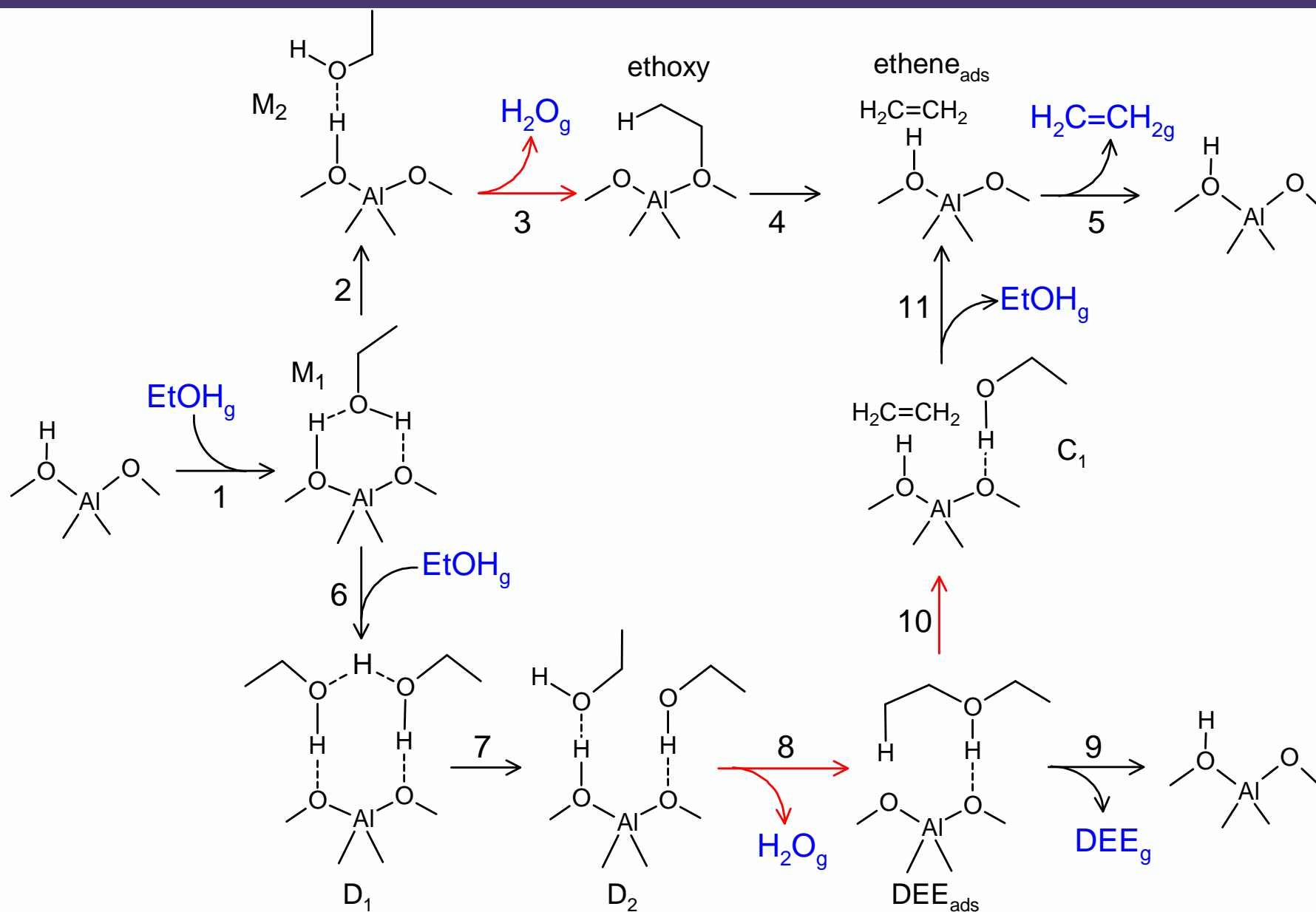


IR spectrum

Ethanol in ZSM5

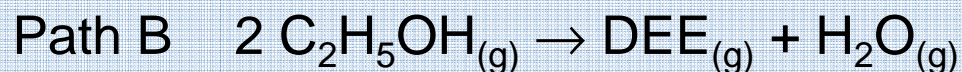
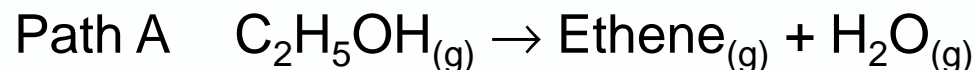


Ethanol: Ab Initio rate coefficients



Reaction paths and rate-determining steps

		A	B	C
(1)	$\text{C}_2\text{H}_5\text{OH}_{(g)} + * \leftrightarrow \text{M}_1$	1	1	0
(2)	$\text{M}_1 \leftrightarrow \text{M}_2$	1	0	0
(3)	$\text{M}_2 \rightarrow \text{Ethoxy} + \text{H}_2\text{O}_{(g)}$	1	0	0
(4)	$\text{Ethoxy} \leftrightarrow \text{Ethene}_{\text{ads}}$	1	0	0
(5)	$\text{Ethene}_{\text{ads}} \leftrightarrow \text{Ethene}_{(g)} + *$	1	0	1
(6)	$\text{M}_1 + \text{C}_2\text{H}_5\text{OH}_{(g)} \leftrightarrow \text{D}_1$	0	1	0
(7)	$\text{D}_1 \leftrightarrow \text{D}_2$	0	1	0
(8)	$\text{D}_2 \rightarrow \text{DEE}_{\text{ads}} + \text{H}_2\text{O}_{(g)}$	0	1	0
(9)	$\text{DEE}_{\text{ads}} \leftrightarrow \text{DEE}_{(g)} + *$	0	1	-1
(10)	$\text{DEE}_{\text{ads}} \rightarrow \text{C}_1$	0	0	1
(11)	$\text{C}_1 \leftrightarrow \text{Ethene}_{\text{ads}} + \text{C}_2\text{H}_5\text{OH}_{(g)}$	0	0	1



SEMK: Plug-flow reactor-outlet simulation

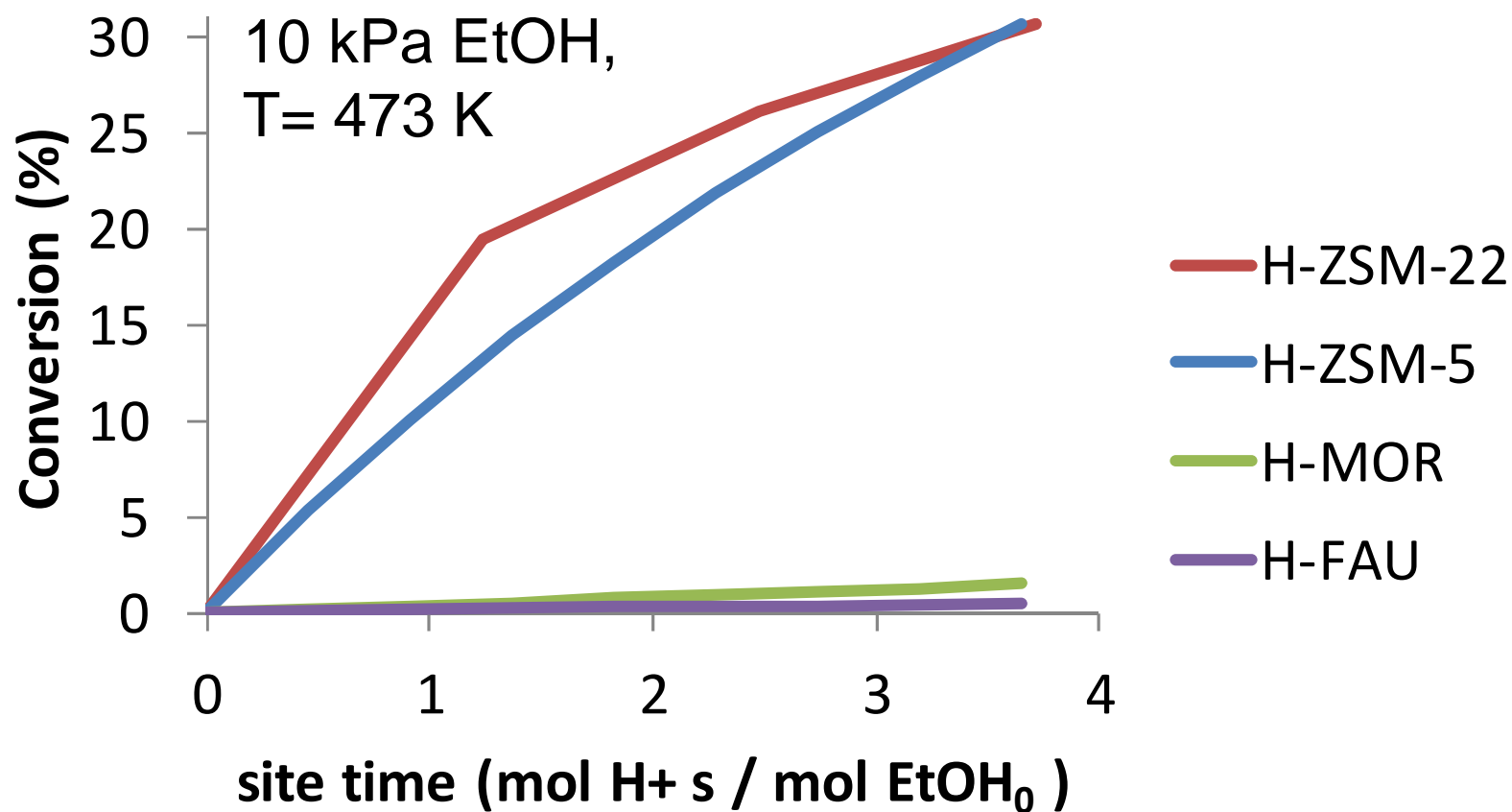
Plug flow reactor continuity equations for each gas-phase component i with QSSA for the surface species i^* :

$$R_{i^*} = \sum_j v_{ji^*} r_j = 0$$

$$\frac{dF_i}{dW} = C_t R_i = C_t \sum_j v_{ji} r_j \quad F_i = F_{i,0} \text{ at } W=0$$

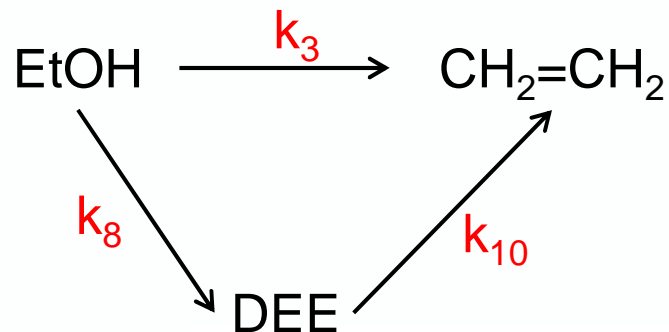
- F_i molar flow rate of component i (mol/s)
- W catalyst mass (kg)
- C_t acid site concentration (mol H^+ /kg)
- R_i net production frequency of component i (1/s)
- r_j turnover frequency of elementary step j (molecules/site/s = mol/mol H^+ /s)
- v_{ji} stoichiometric coefficient of component i in the elementary step j

Influence of zeolite framework



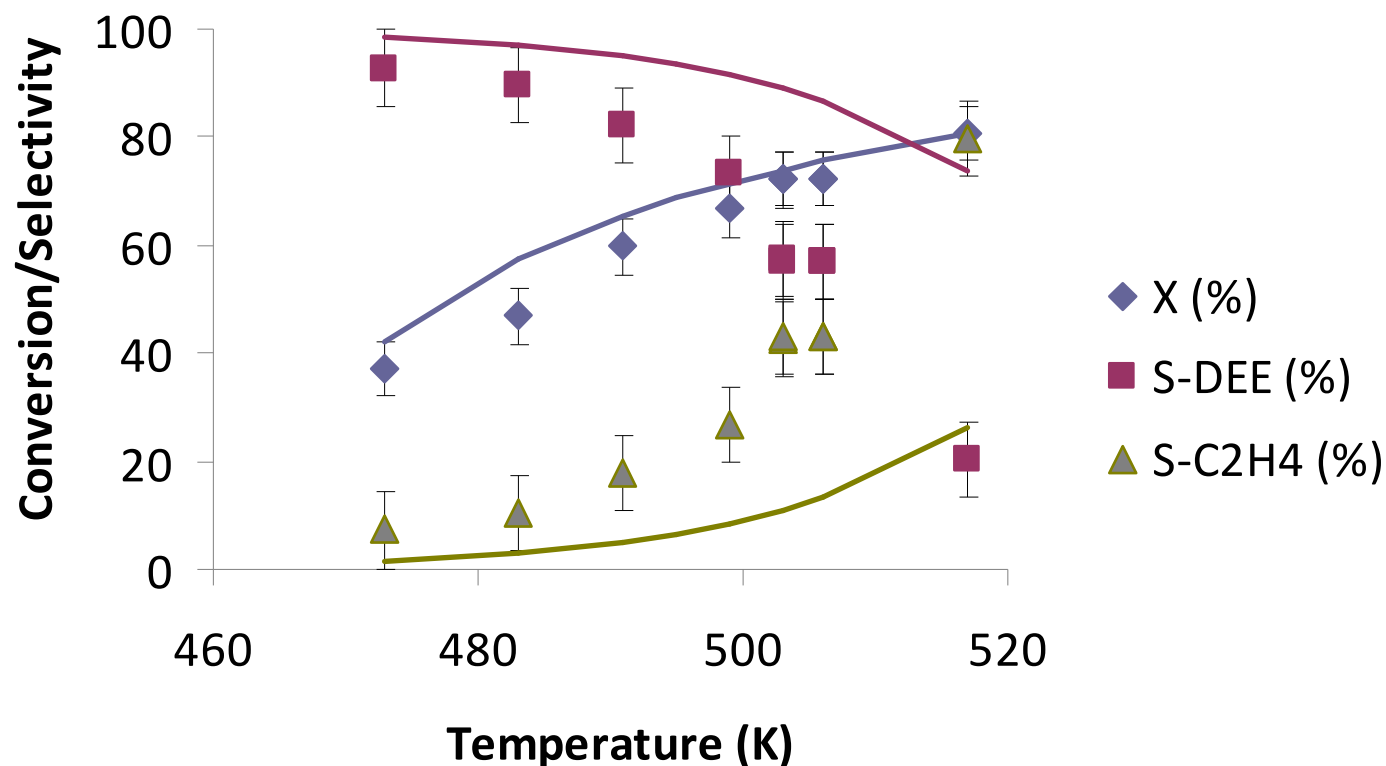
In agreement with experimental observations

Validation of ab initio SEMK : H-ZSM-5

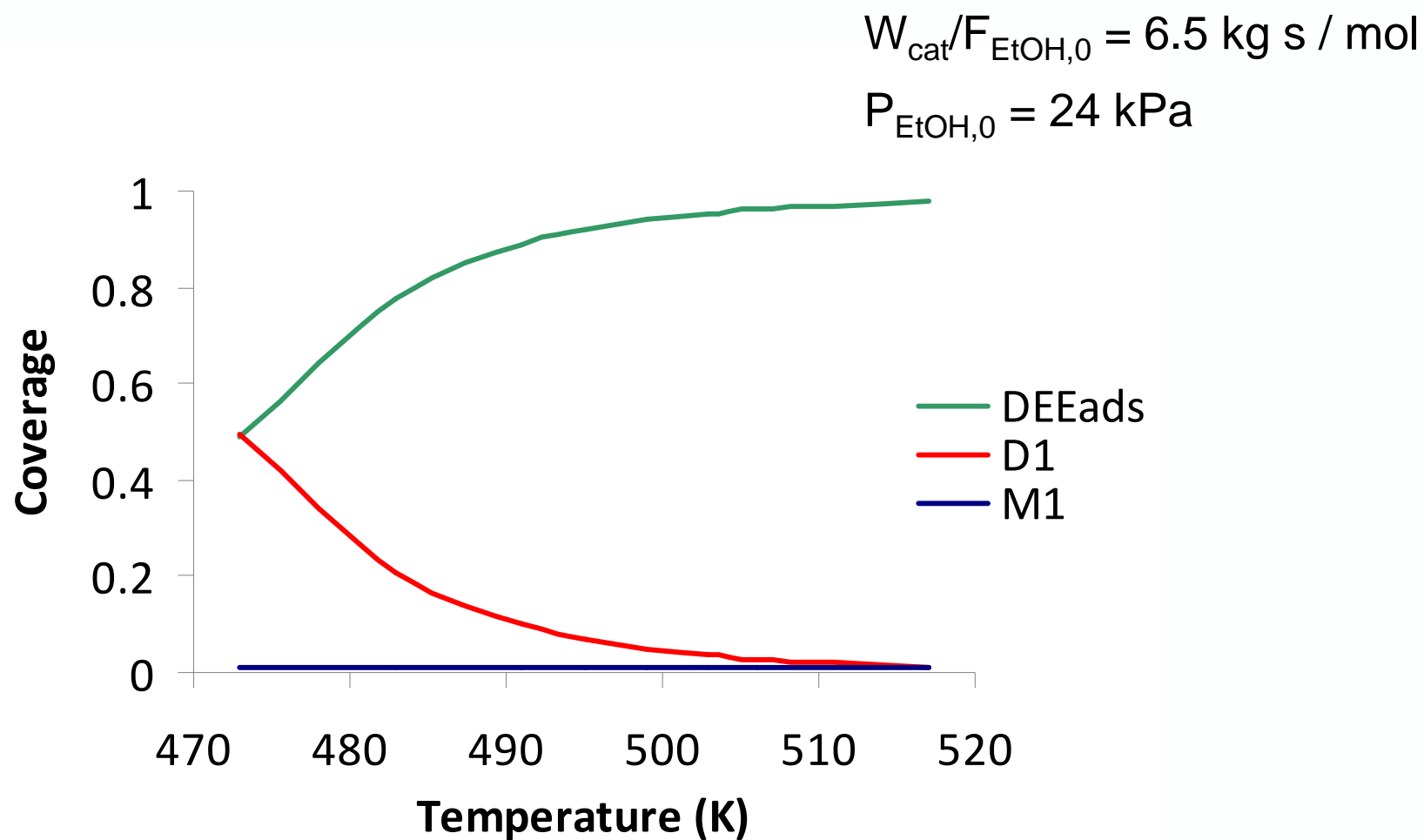


$$W_{\text{cat}}/F_{\text{EtOH},0} = 6.5 \text{ kg s / mol}$$

$$P_{\text{EtOH},0} = 24 \text{ kPa}$$



Surface coverages H-ZSM-5

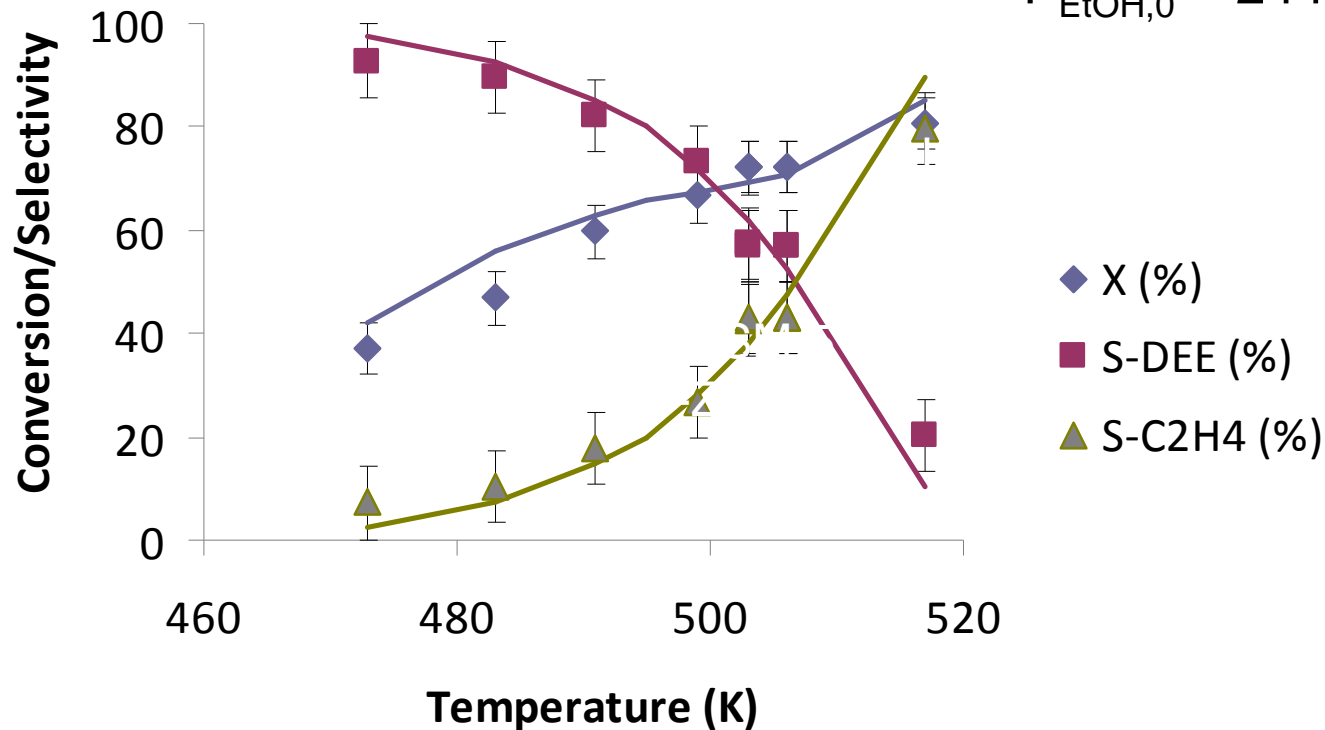


Path for ethene formation from DEE

H-ZSM-5

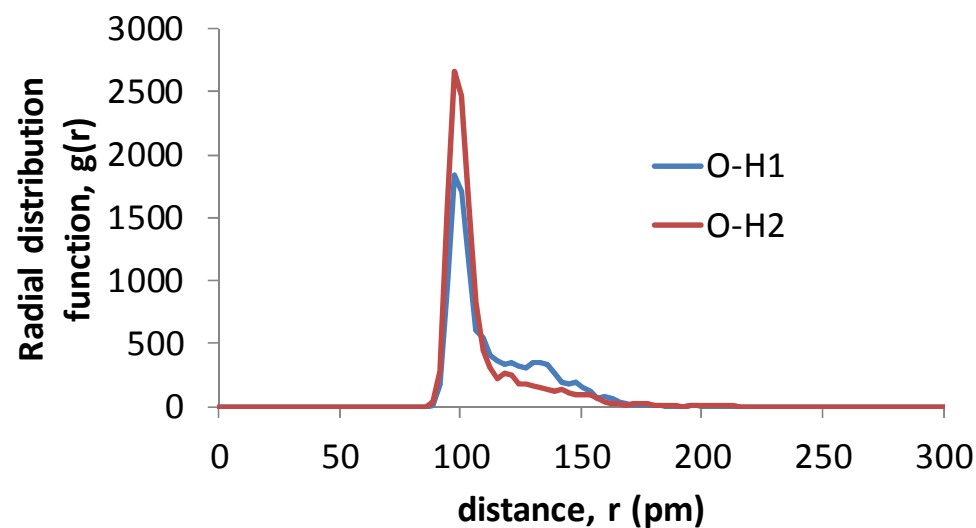
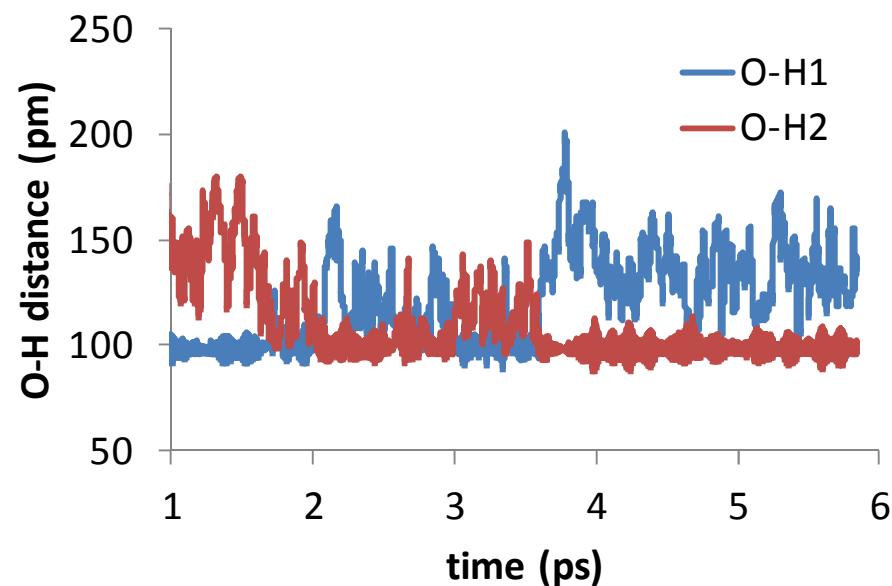
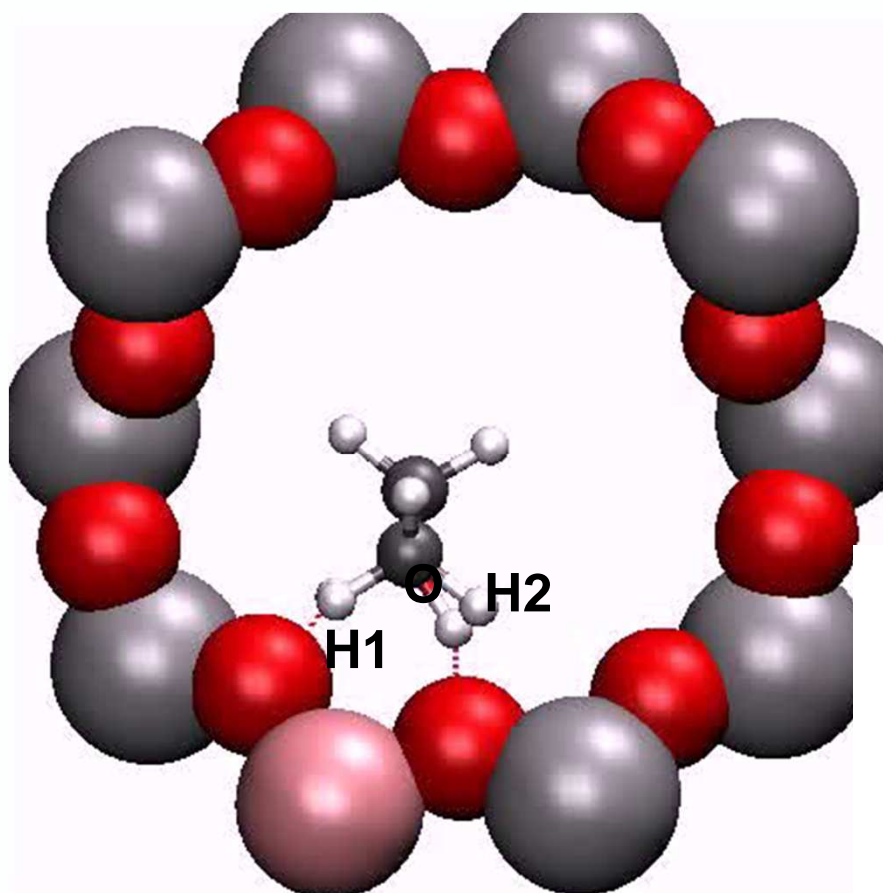
$W_{\text{cat}}/F_{\text{EtOH},0} = 6.5 \text{ kg s / mol}$

$P_{\text{EtOH},0} = 24 \text{ kPa}$



→ **Better** agreement between theory (full lines) and experiment (points),
if the rate coefficient for ethylene formation from DEE is increased (x 10)

Molecular Dynamics simulation at 500K



Conclusions: molecular modeling

- Detailed **reaction network** can be constructed with limited a priori 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**
- Deviation between simulated and experimental yields over range of conditions allow to **identify important steps** that are either missing from the network and/or need to be found/calculated more accurately by e.g. **molecular dynamics**

Overview

- Introduction
- Bottom-up approach: alkylation of benzene
- Top-down approach: catalytic cracking
- Molecular modeling:
 - Adsorption of alkanes and alkenes
 - Conversion of alcohols
- Conclusions

Conclusions

- Combine bottom-up and top-down
- Experimental data
 - Hypothesis verification
 - Model validation
- Models
 - First principles
 - Limited number of adjustable parameters
 - Catalyst descriptors

Experimental and theoretical methods in kinetic studies

Reyniers MF and Marin GB

Annual review of chemical and biomolecular engineering vol. 5, 2014

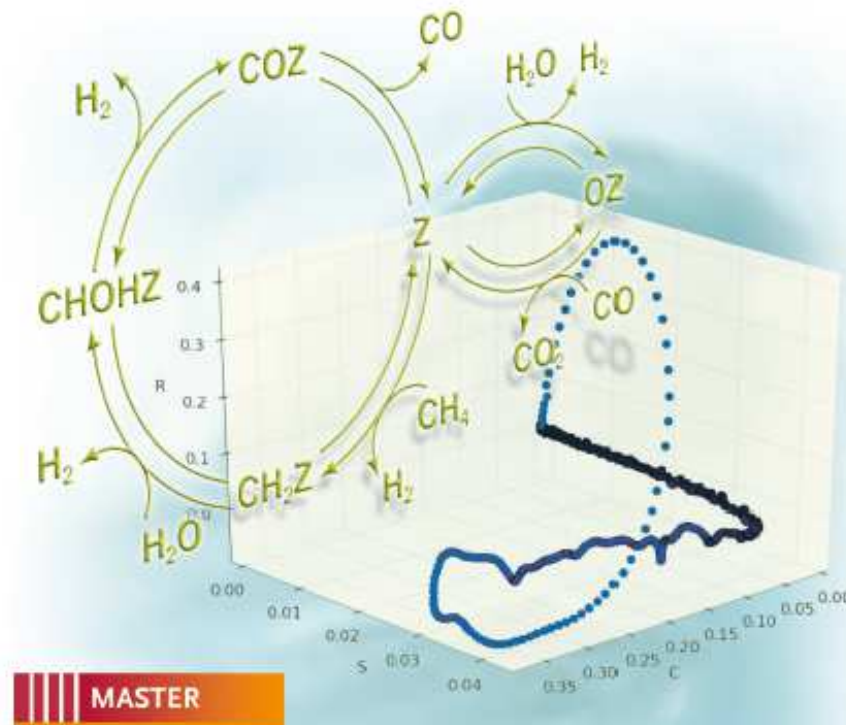
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- PhD student Kristof Van der Borgh



Kinetics of Chemical Reactions

Decoding Complexity

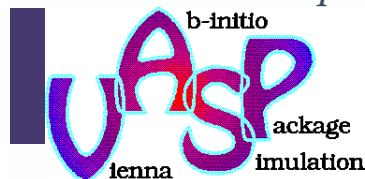


Glossary

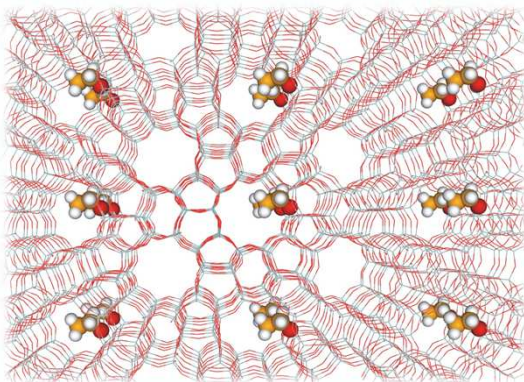
- activation enthalpy: for an elementary step, it is the difference in enthalpy between transition state and reactants
- elementary step: the irreducible act of reaction in which reactants are transformed into products directly, i.e., without passing through an intermediate that is susceptible of isolation
- mechanism: a vague term, related to Latin "machina," used loosely to describe a reaction network, or a reaction sequence, or the stereochemistry of an elementary step. Sometimes called a "model". If based on kinetic arguments, it is occasionally called a "kinetic mechanism".

Glossary

- rate-determining step: if, in a reaction sequence, consisting of n steps, $(n - 1)$ steps are reversible and if the rate of each one is very much larger in either direction than the rate of the n th step, the latter is said to be rate-determining
- transition state: the configuration of highest potential energy along the path of lowest energy between reactants and products. Synonymous with activated complex.



Dispersion – corrected pbc[DFT-D]



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

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

- **Vasp.4.6.disp.gamma.mpi4.0**
- **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:**
 $E_{cutoff} = 600 \text{ eV}, \Delta E_{SCF} = 10^{-6} \text{ eV}, \text{Max force} = 0.02 \text{ eV/\AA}$
- **NEB-CI** 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. 113 (2000) 9978

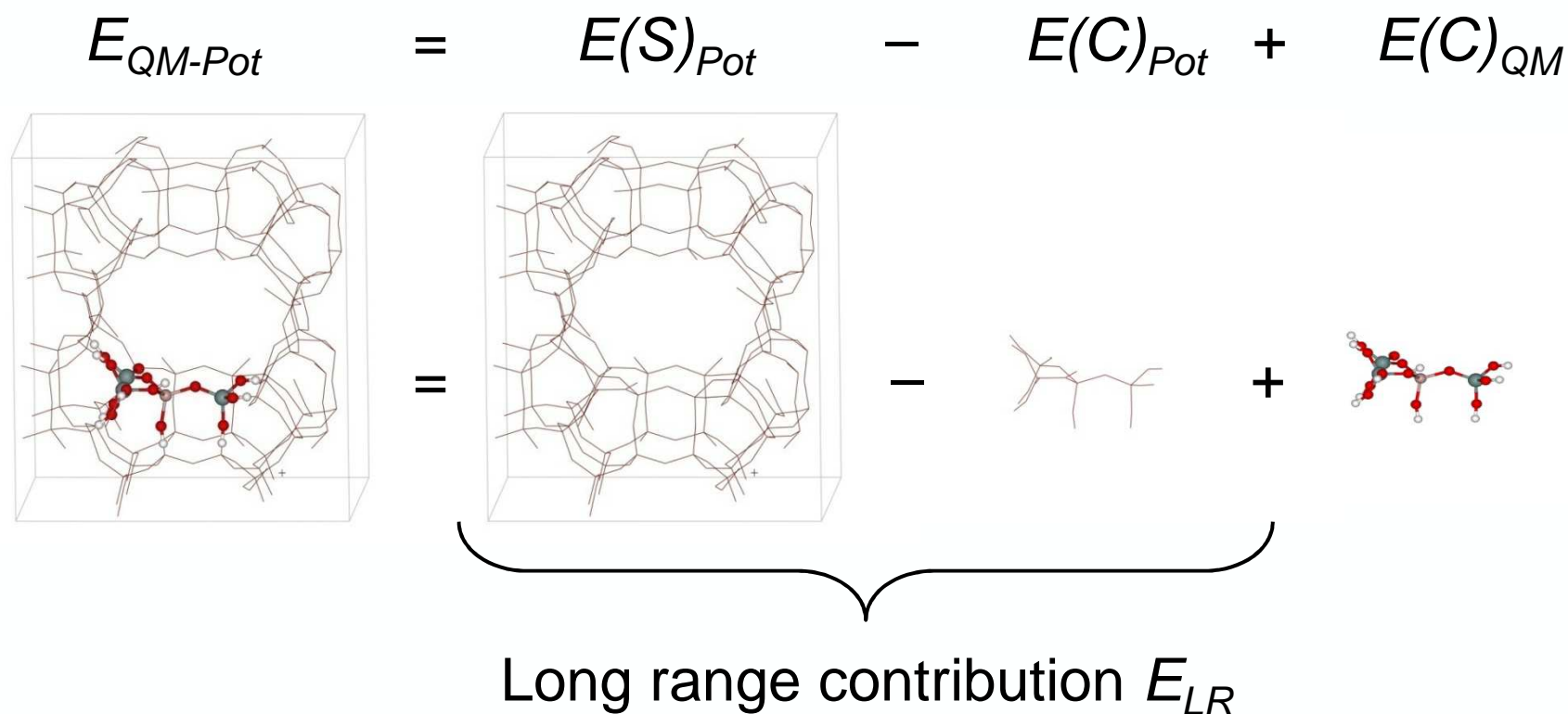
[4] De Moor et al. J. Chem. Theory Comput. 7 (2011) 1090

Hybrid QM-MM: QM-Pot (MP2//B3LYP)

Pot: core/shell zeolite force field extended with C_b-O_b, C-C, C-H

QM: embedded 3T/4T cluster optimized at B3LYP/T(O)DZP;

single point energy MP2/TZVP



Statistical thermodynamics

Partition function $\rightarrow Q = \frac{q^N}{N!} = \frac{(q^{tran} q^{vib} q^{rot} q^{elec})^N}{N!}$

$$U = E_{QM-Pot} + E_{ZPE} + k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$S = k_B \ln Q + k_B \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \quad \begin{aligned} H &= U + PV \\ G &= H - TS \end{aligned}$$

$$\Delta H(T) = \Delta E_{elec} + \Delta E_{ZPVE} + \Delta E_{0 \rightarrow T}$$

Standard state (300 K & 1 atm): ΔH^0 , ΔS^0 and ΔG^0