Analysis of diffusion limitation in the alkylation of benzene over H-ZSM-5 by combining quantum chemical calculations, molecular simulations and a continuum approach

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Motivation

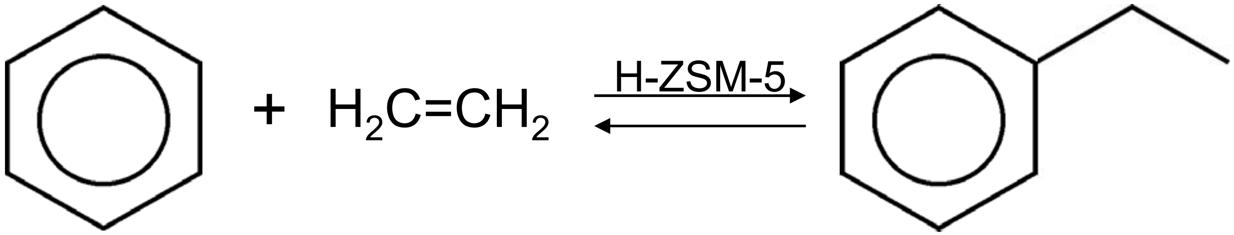
Methods based on statistical and quantum mechanics have reached a level of sophistication that they can now be used to describe elementary processes involved in heterogeneous catalysis almost quantitatively.

We should use these methods to reach long-standing goals of theoretical research in heterogeneous catalysis:

- Predict effects of catalyst composition and structure on reaction rates and product distribution
- What is the best zeolite structure for a given reaction?

Problem

Taking the example of the alkylation of benzene with ethene over H-ZSM-5,

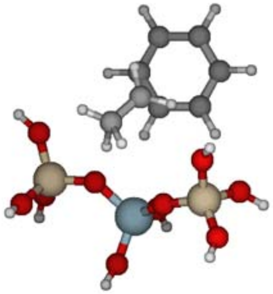


the following data should be computed fully based on molecular simulation techniques (Quantum mechanics, Molecular dynamics, Monte Carlo)

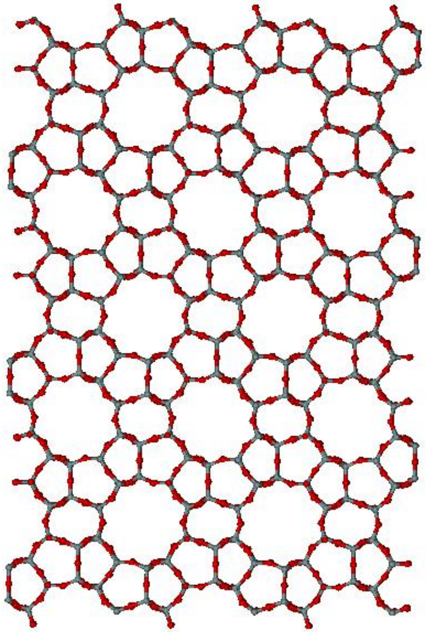
- reaction mechanism
- rate constants
- multicomponent diffusivities inside the pores

and used in a continuum model to calculate the overall activity of a catalyst particle

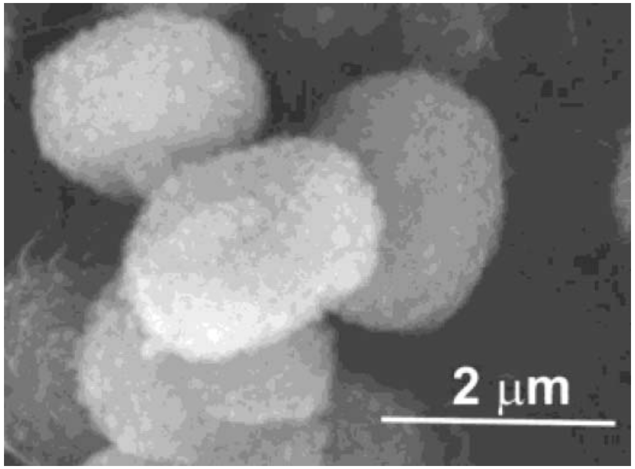
Modeling approach



Active site



Unit cell



Christensen et al.; JACS 125 (2003) 13370

Crystal

wanted:

- activation energies
- rate constants

methods:

- DFT / MP2
- TST

wanted:

- adsorption isotherms
- diffusivities

methods:

- Monte Carlo
- Molecular dynamics

wanted:

- concentration profiles
- overall rates of reaction

methods:

- Maxwell-Stefan eqns combined with IAST

Calculation procedure

molecular simulation

species loading inside pore [mol/kg]

molar flux [mol/m^{2}s]

reaction rate [mol/m^{3}s]

Zeolite density [kg/m^3]

$$\frac{\partial q_i}{\partial t} = -\frac{1}{\rho}\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2 \boxed{N_i}\right) + \frac{1}{\rho}\nu_i \boxed{r}; \quad i = 1,2,\ldots,n$$

radial coordinate [m]

M-S eqns

$$(N) = -\rho\underbrace{[\Delta][\Gamma]}\nabla(q)$$

Functions of diffusion path

$$\frac{r}{\rho} = k_f q_{E+B,H+} - k_b q_{EB,H+}$$

Amount of co-adsorbed C_2H_4 + C_6H_6 at the acid sites [mol/kg]

Amount of adsorbed C_8H_{10} at the acid sites [mol/kg]

Boundary conditions:

- symmetry condition in center of sphere
- constant loadings on exterior surface (adsorption equilibrium)

Maxwell-Stefan equations

- Method for prediction of multi-component diffusion based on information on pure component diffusion

$$-\rho\frac{\theta_i}{RT}\nabla\mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n}\frac{q_jN_i - q_iN_j}{q_{i,sat}\,q_{j,sat}\,\text{Đ}_{ij}} + \frac{N_i}{q_{i,sat}\,\text{Đ}_i};\; i=1,2,\ldots,n$$

from MD

$$\frac{q_i}{RT}\nabla\mu_i = \sum_{j=1}^{n}\Gamma_{ij}\nabla q_j;\quad \Gamma_{ij} = \frac{q_i}{f_i}\frac{\partial f_i}{\partial q_j};\quad i,j=1,..n$$

differentiation of mixture isotherm model e.g. IAST

$$q_{j,sat}\,\text{Đ}_{ij} = \left[q_{j,sat}\,\text{Đ}_{ii}\right]^{q_i/(q_i+q_j)}\left[q_{i,sat}\,\text{Đ}_{jj}\right]^{q_j/(q_i+q_j)} = q_{i,sat}\,\text{Đ}_{ji}$$

from MD

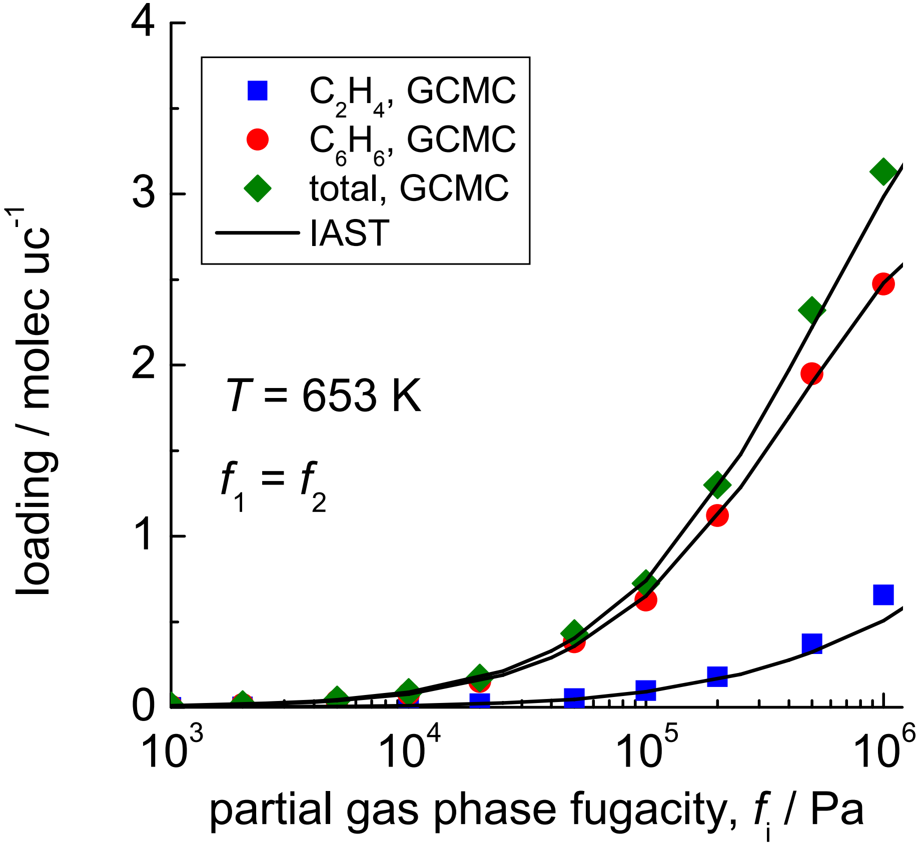
$$(N) = -\rho\underbrace{[\Delta][\Gamma]}_{\text{Functions of diffusion path}}\nabla(q)$$

Adsorption

Continuum model requires mixture adsorption isotherms at arbitrary bulk compositions and pressures

- pure component isotherms: MC simulations
- mixture adsorption isotherms: IAST using pure component isotherms as input
- Validation by selected mixture MC simulations

MC mixture simulation vs. IAST



Good agreement between MC mixture simulation and IAST for industrially relevant pressures

Diffusion

Continuum model requires diffusivities at arbitrary compositions of the adsorbed phase

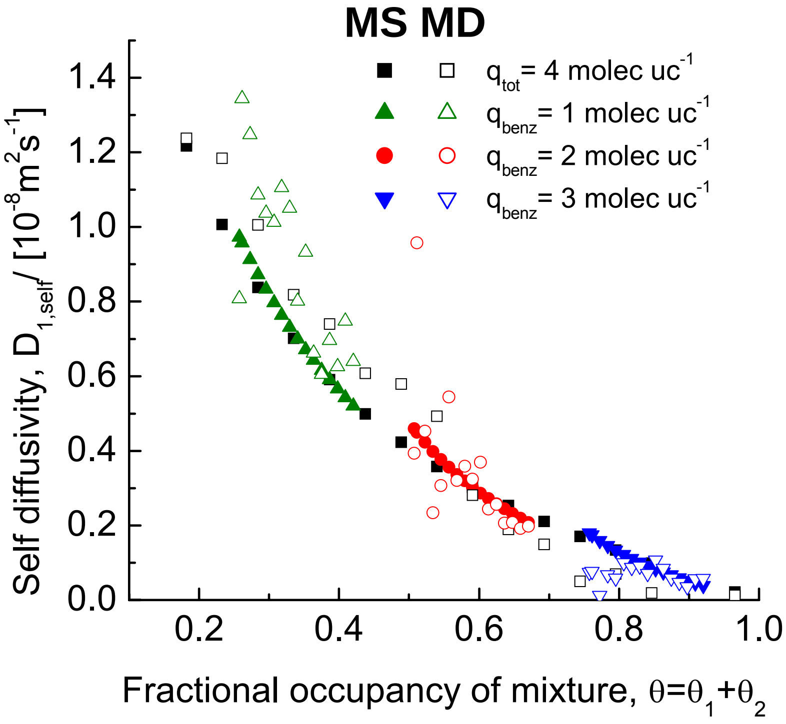
- multiple MD simulation campaigns for different loadings and temperatures
- usage of MD data to parameterize M-S equations:

$$D_{1,self} = 1 \Big/ \left(\frac{1}{\text{Đ}_1} + \frac{\theta_1}{\text{Đ}_{11}} + \frac{\theta_2}{\text{Đ}_{12}} \right)$$

$$q_{j,sat}\text{Đ}_{ij} = \left[q_{j,sat}\text{Đ}_{ii} \right]^{q_i/(q_i+q_j)} \left[q_{i,sat}\text{Đ}_{jj} \right]^{q_j/(q_i+q_j)}$$

$$\frac{\text{Đ}_{ii}}{\text{Đ}_i} = a_1 \exp\left(-a_2\theta_i\right) + a_3 \exp\left(-a_4\theta_i\right)$$

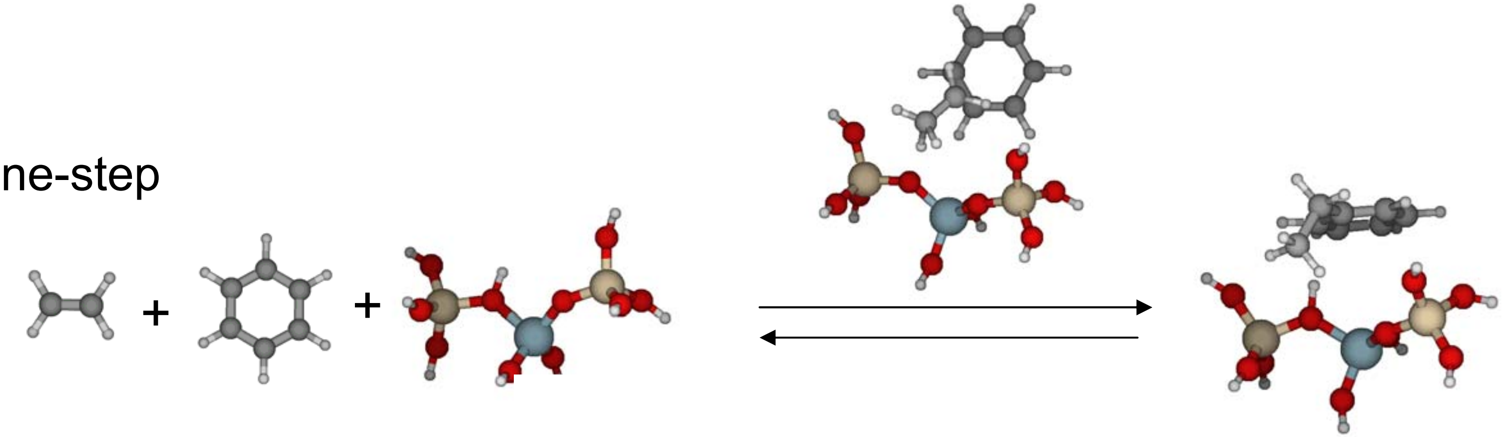
Self-diffusivity of ethene in ethene-benzene mixture



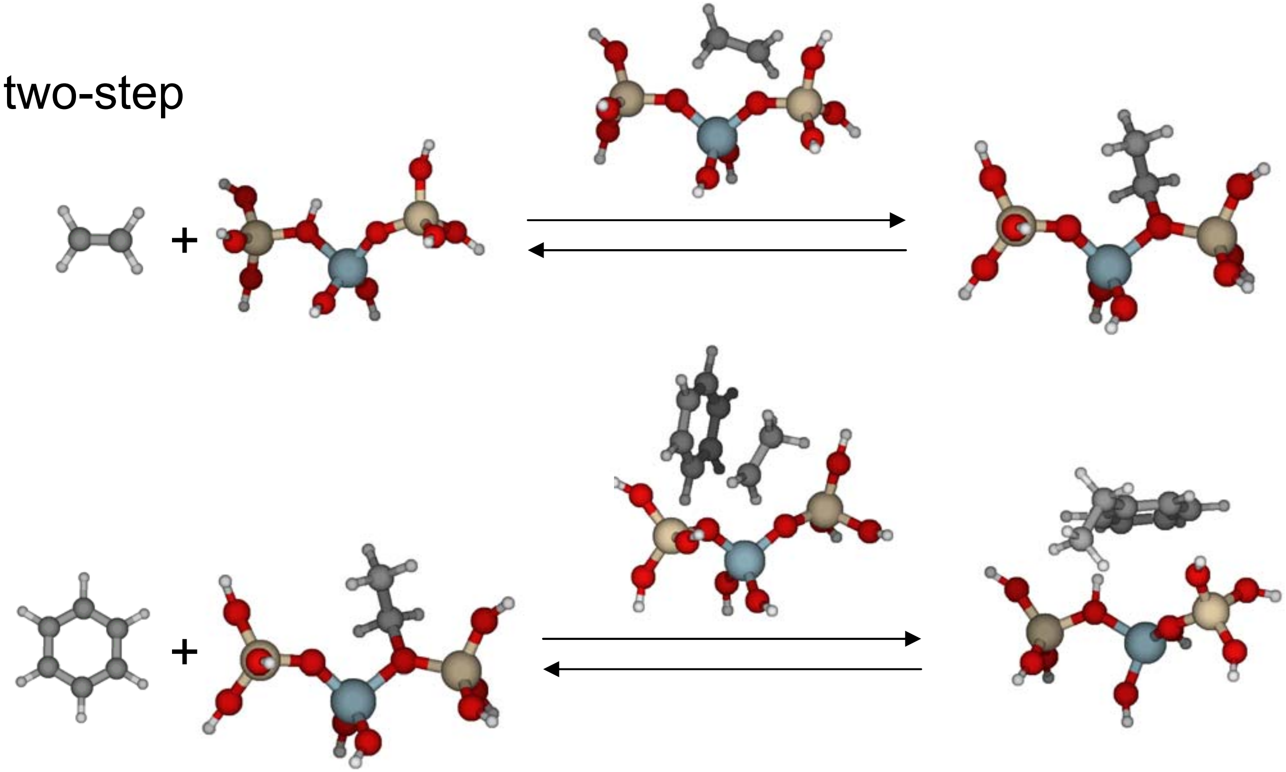
	$D_{i,self}$	Đ_i	Đ_{ii}	$a_1 - a_4$
C_2H_4	MD	MD	Eq. (1)	fitted to pure comp. MD data
C_6H_6	N/A	<---------------- fitted to binary mixture MD data -------------->		
C_8H_{10}	N/A	<---------------- fitted to binary mixture MD data -------------->		

Reaction

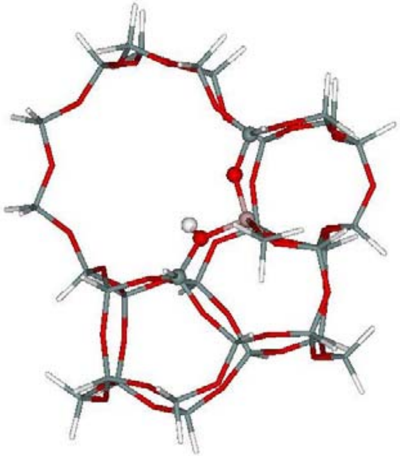
one-step



two-step



T33 cluster



Details: Hansen et al., J. Phys. Chem. C 112 (2008) 15402

Reaction

$$E_{\mathrm{a,corr}} = E^{\mathrm{DFT}}_{\mathrm{a,T33}} + \left(E^{\mathrm{MP2}}_{\mathrm{a,T5}\leftarrow\mathrm{T33}} - E^{\mathrm{DFT}}_{\mathrm{a,T5}\leftarrow\mathrm{T33}}\right)$$

DFT-barrier,
T33-cluster

MP2-barrier
T5-cluster, cut out from DFT-converged T33-cluster

$E_{\mathrm{a,corr}}$, kJ/mol

1-step	2-step	
120.5	99.2	110.5

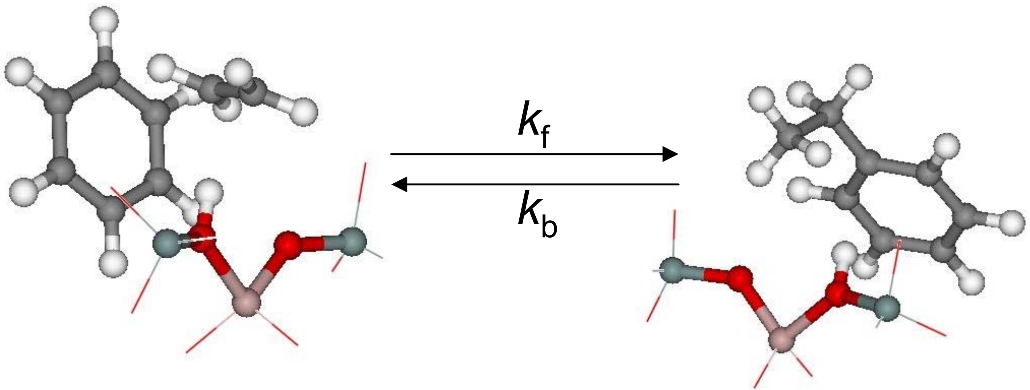
rate coefficients at 650 K, s^{-1}

1-step	k_1	4.97×10^{0}
	k_{-1}	9.75×10^{-4}
2-step	k_1	1.14×10^{3}
	k_{-1}	1.12×10^{2}
	k_2	1.84×10^{3}
	k_{-2}	6.98×10^{0}

Details: Hansen et al., J. Phys. Chem. C 112 (2008) 15402

Rate expression for 1-step scheme

- QM + TST provides rate coefficients for elementary turnovers:



$$\frac{\text{mol of co-adsorbed } C_2H_4 + C_6H_6}{\text{mol } H^+ \times \text{time}}$$

Continuum model requires rates at arbitrary compositions of the adsorbed phase

- Rate of reaction:

$$\frac{r}{\rho} = k_f q_{E+B,H+} - k_b q_{EB,H+}$$

Amount of co-adsorbed $C_2H_4 + C_6H_6$ at the acid sites [mol/kg]

Amount of adsorbed C_8H_{10} at the acid sites [mol/kg]

How do we know $q_{E+B,H+}$?

⇨ we express $q_{E+B,H+}$ as function of q_E, q_B, q_{EB}

Conventional LH-expression

$$r = k_1\theta_A\theta_B - k_2\theta_C$$

Problems

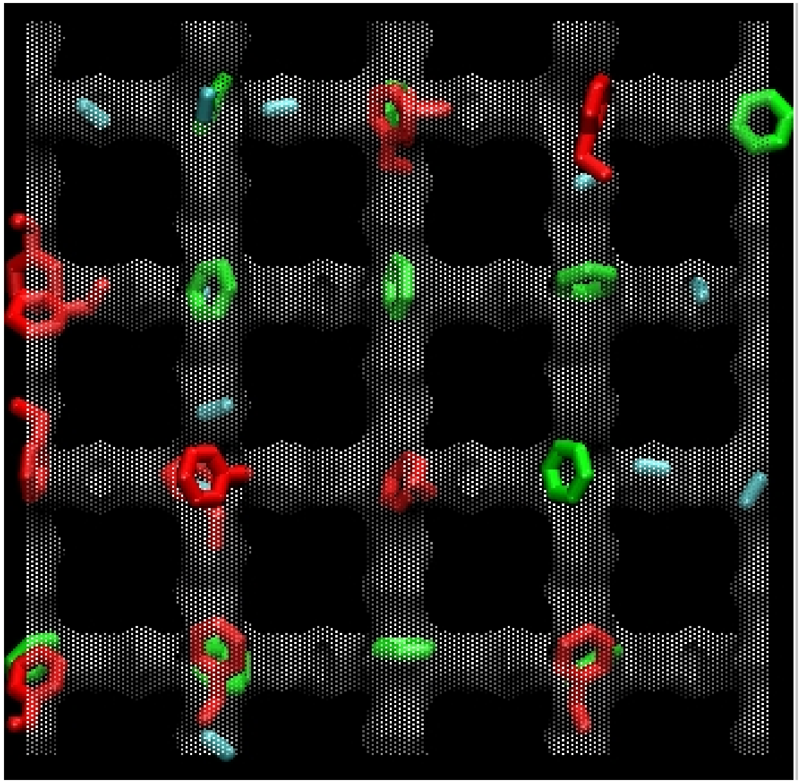
- Reactants not equally distributed
- Different saturation capacities of reactants

Rate expression for 1-step scheme

- Rate expression has to reflect pore architecture of the zeolite

⇨ Tailor made for a given guest-host system

MD Snapshot



Mechanistic model

Factor to account for active site blocking by ethylbenzene

$$q_{E+B,H+} = \frac{q_B}{22-3.25q_B-3.5q_{EB}} \cdot q_E \cdot \frac{q_B}{q_B+q_{EB}} \cdot \frac{\gamma}{4}$$

Fraction of ethene co-adsorbed with benzene in intersection

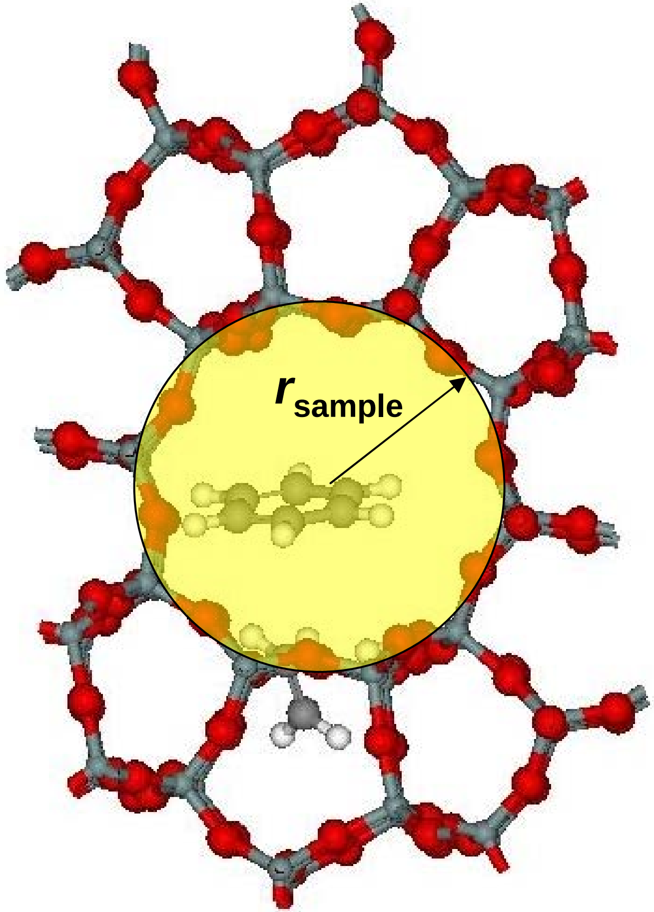
Number of active sites per uc

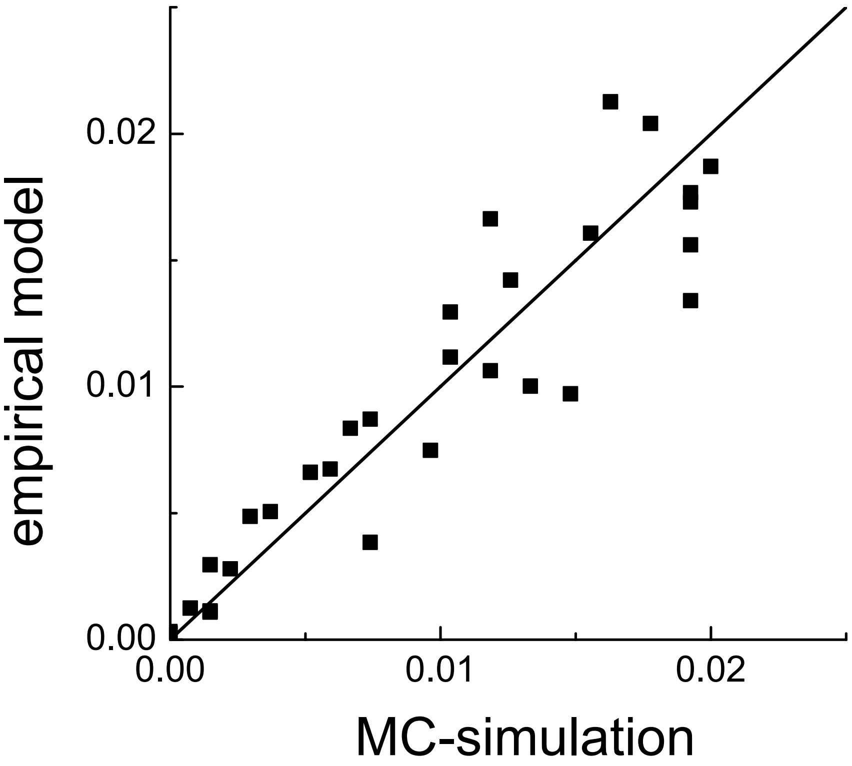
$$q_{EB,H+} = q_{EB}\frac{q_{EB}}{q_B+q_{EB}} \cdot \frac{\gamma}{4}$$

Hansen et al., J. Phys. Chem. C 113 (2009) 235

Rate expression vs. MC simulation

- MC simulations of ethene-benzene mixture at different loadings inside zeolite
- Sampling amount of co-adsorbed E+B



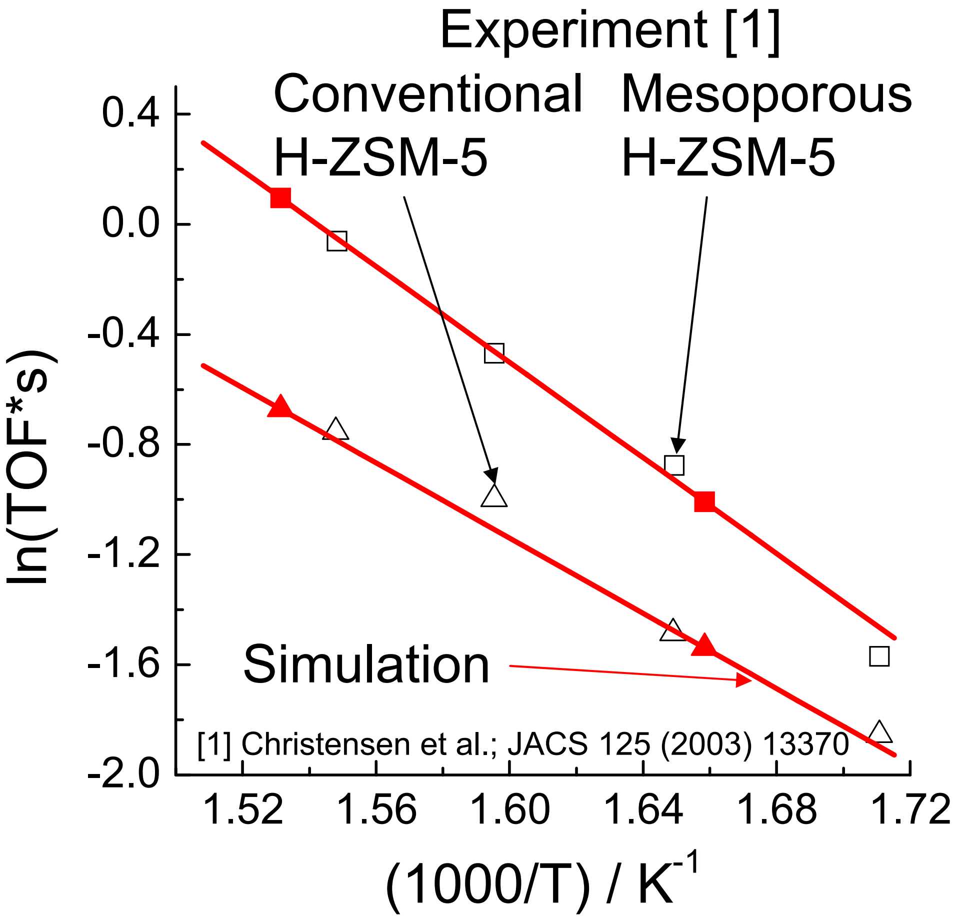


Model and simulation are in good agreement

Re-adjustment

Problem: no quantitative agreement between simulation and experiment

- 1-step scheme: too low activity; 2-step scheme: too high activity
- Extracted *Đ*s of aromatics likely too high: Problem with conventional MD and slow diffusing species



[1] Christensen et al.; JACS 125 (2003) 13370

Solution

Independent adjustment of preexponential factor *A* and order of magnitude of *Đ*:

Fit *A* to □

- Data hardly affected by transport limitations

Fit *Đ* to △

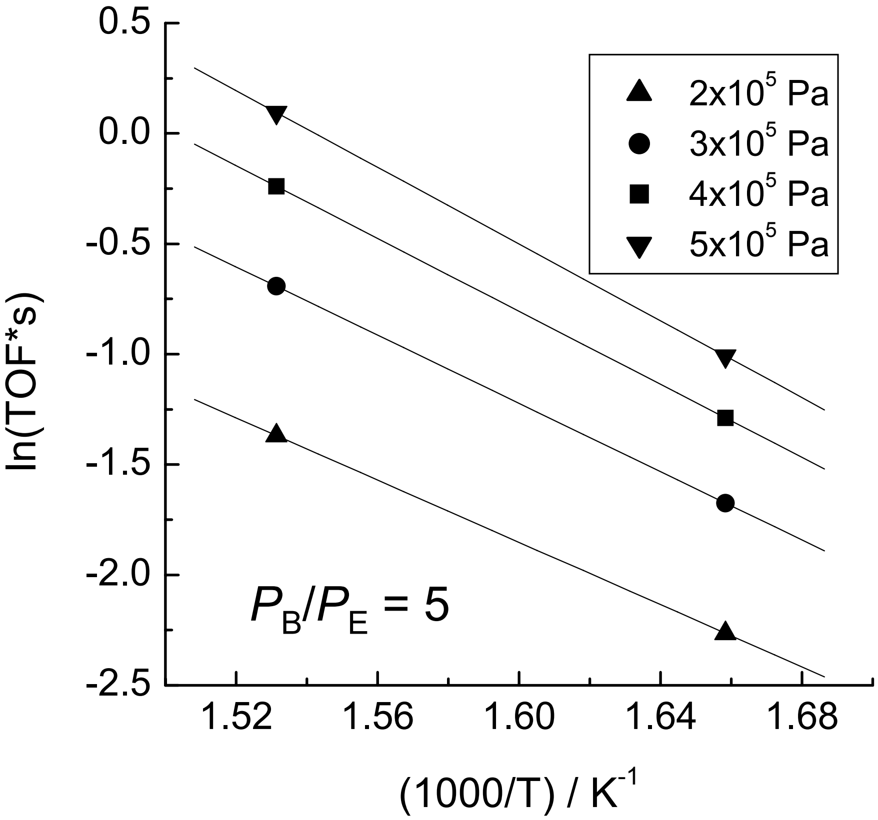
- Data strongly affected by transport limitations

Results

	fitted	unfitted
A =	3.2×10^{12} s^{-1}	2.6×10^{10} s^{-1}
Đ ≈	10^{-13} m^{2} s^{-1}	10^{-10} m^{2} s^{-1}

Results

Apparent Arrhenius parameters



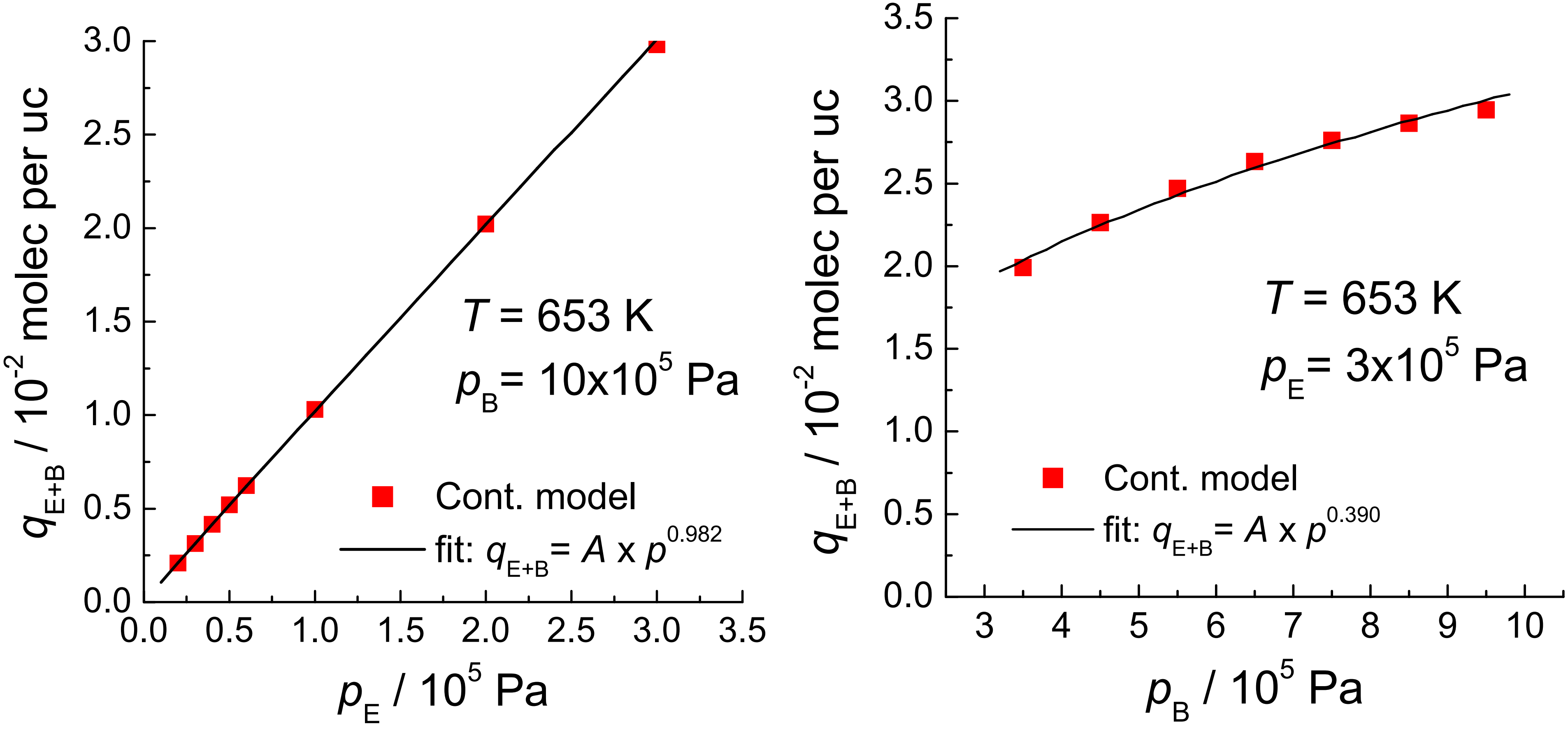
p [10^5 Pa]	E_{app} [kJ mol^{-1}]	A_{app} [s^{-1}]
2.0	58.7	1.25E+04
3.0	64.3	6.95E+04
4.0	68.7	2.46E+05
5.0	72.3	6.63E+05

⇨ Function of pressure and composition

Hansen et al., J. Phys. Chem. C 113 (2009) 235

Results

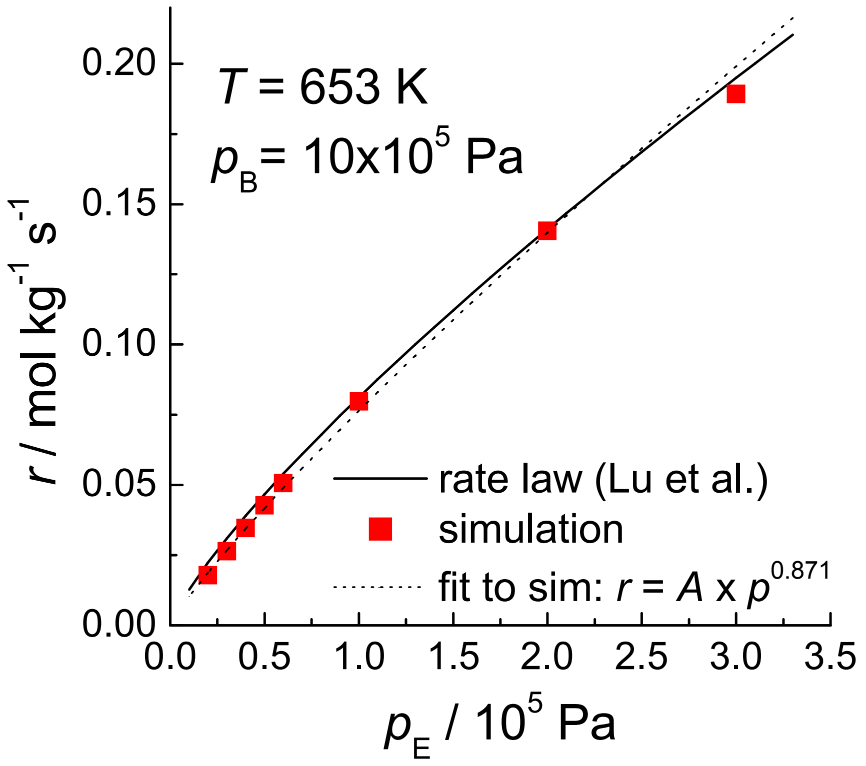
How does the co-adsorbed amount of C_2H_4 + C_6H_6 depend on the partial pressures?

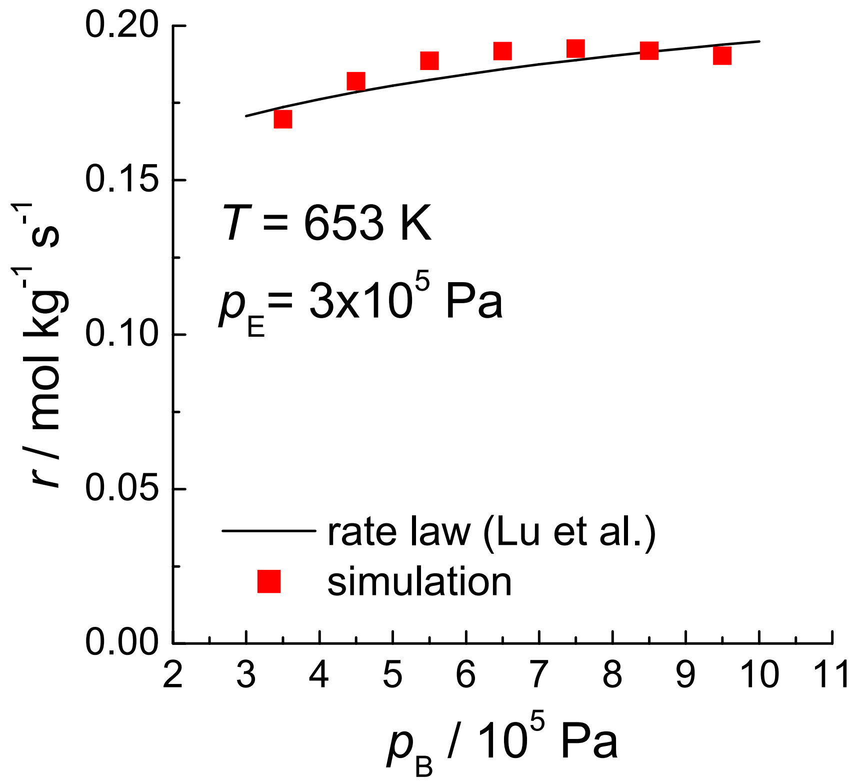


⇨ In absence of diffusion limitation: 1st order in p_E; 0.4 order in p_B

Results

How does diffusion limitation influence the macroscopic rate orders?





- exponent with respect to p_E: 0.87 Exp. ≈ 0.8 [1]
- exponent with respect to p_B: around 0 Exp. ≈ 0.1

⇨ Good agreement with experimental observations

[1] Lu et al.; Petrochemical Technol. (China) 30 (2001) 182.

Work in progress

improved estimation of rate coefficients:

- replace cluster calculations by periodic DFT
- Systematically account for BSSE and basis set incompleteness
- Account systematically for van-der-Waals interactions

Applications

- **Test of phenomenological rate laws**
- **Alkylation of benzene with ethane**

Test of phenomenological rate laws

Common rate laws in heterogeneous catalysis:

Langmuir Hinshelwood (LH): $$r_B = \frac{k_1 p_B p_E - k_{-1} p_{EB}}{\left(1 + K_B p_B + K_E p_E + K_{EB} p_{EB}\right)^2}$$

Power law (PL): $$r_B = k_1 p_E^{n_E} p_B^{n_B} - k_2 p_{EB}^{n_{EB}}$$

⇨ Parameter estimation: fitting to rate data from differential reactor

Here: fitting to data from computer experiments

Advantage: All kinetic data are known exactly

⇨ Discrepancies are due to intrinsic shortcomings of LH and PL models

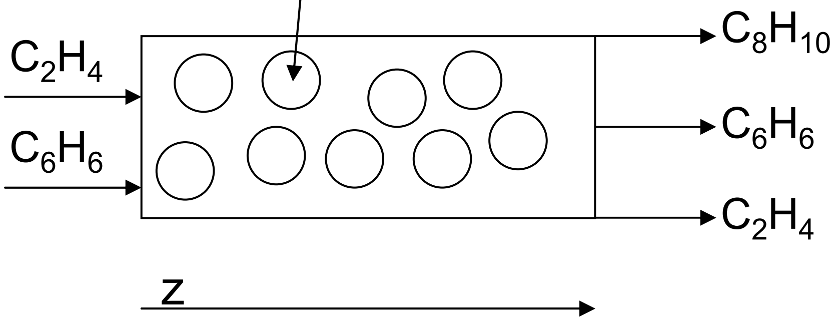
Fitting procedure

- Fixed bed reactor
- Plug flow
- small conversions < 2%

$$\frac{dF_i}{dz} + \frac{\tau}{L}\dot{m}\frac{1}{\rho}\frac{3}{R}n_i(z) = 0$$

Full continuum model for catalyst particle

$$r_B = \frac{F_{in}y_{B,in} - F_{out}y_{B,out}}{m_{cat}}$$

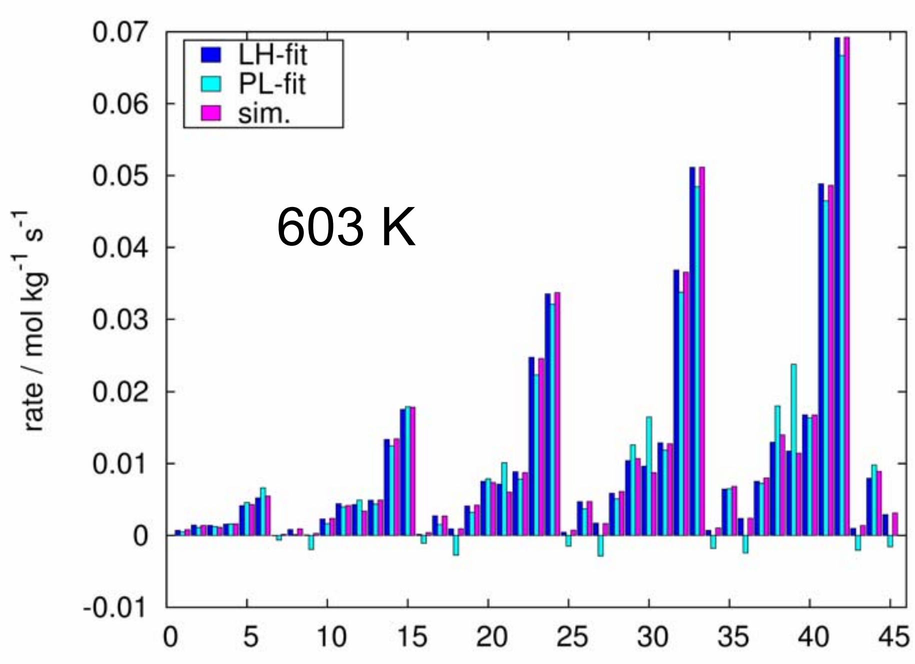


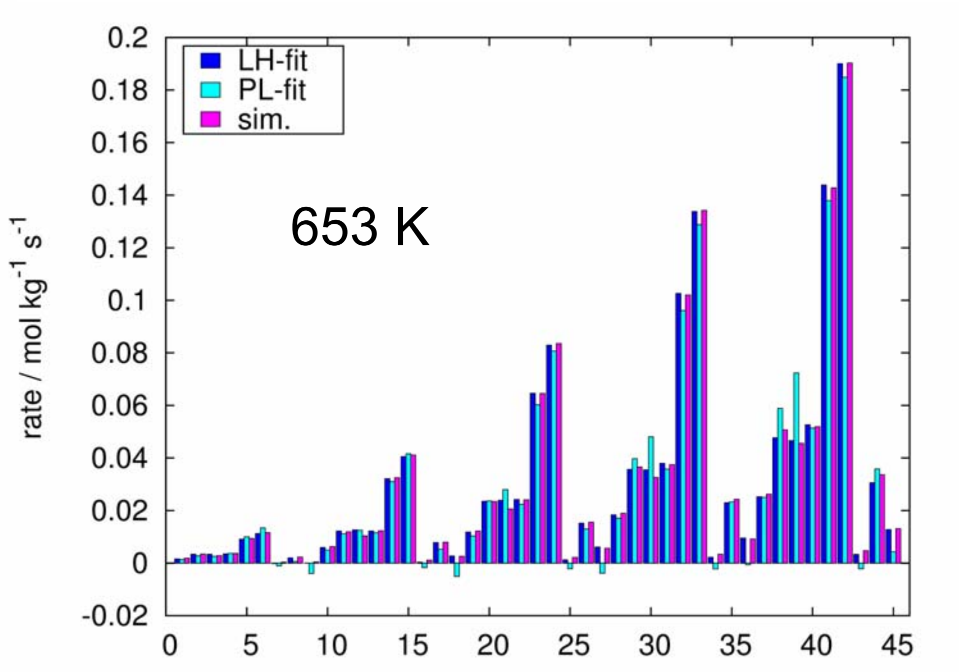
Least square minimization:

$$\min F = \sum_{i=1}^{m}\left[r_{B,i}(LH) - r_{B,i}(CM)\right]^2$$

Least square results

- 45 data points
- *P*=1–5 bar
- y_B= 0.5–0.9, y_E= 0.01–0.49, y_{EB}= 0.01–0.39





⇨ Agreement of LH better than of PL

Least square results

Activation energies: $k_1 = k_0 \exp\left(-\frac{E_a}{RT}\right)$

LH: 44.2 kJ/mol

PL: 67.3 kJ/mol

Intrinsic E_a: 120.5 kJ/mol

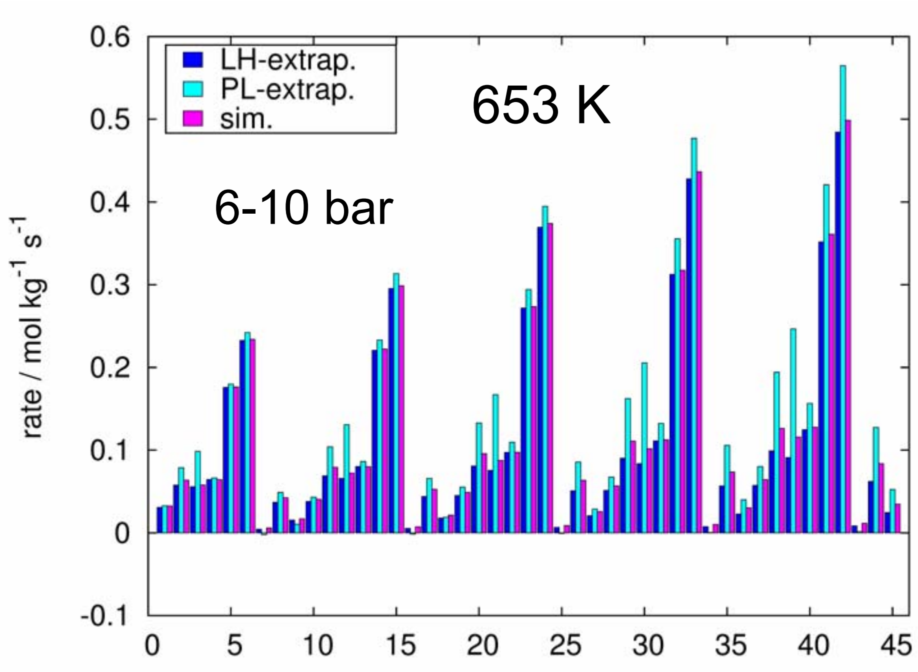
Apparent:

p [10^5 Pa]	E_{app} [kJ mol^{-1}]	A_{app} [s^{-1}]
2.0	58.7	1.25E+04
3.0	64.3	6.95E+04
4.0	68.7	2.46E+05
5.0	72.3	6.63E+05

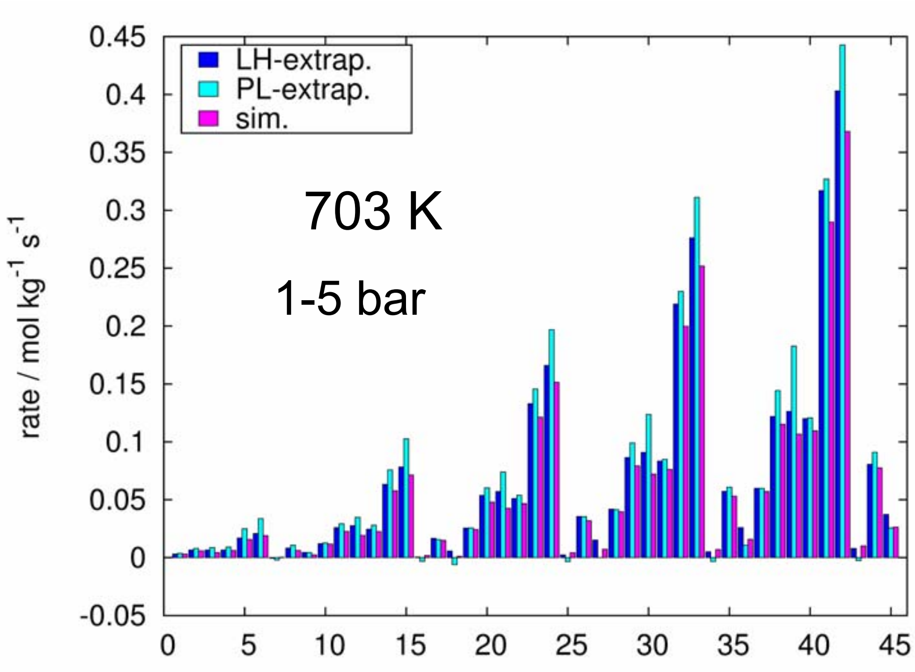
Energy parameter in empirical rate laws lacks any physical significance

Extrapolation…

…to higher pressure



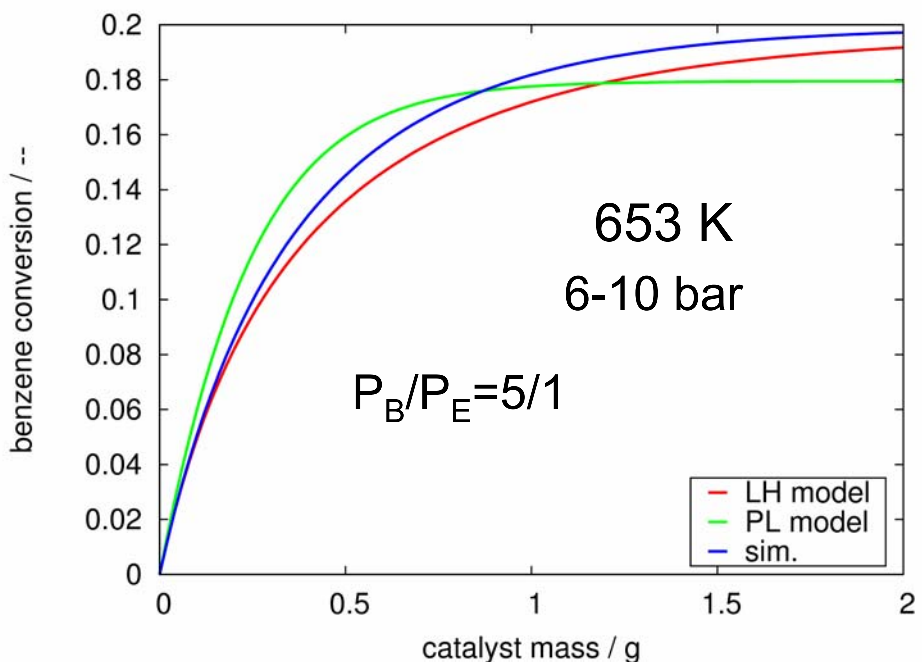
…to higher temperature



Extrapolation quality of LH model much better than of PL

Reactor simulations

Extrapolation to higher pressure:

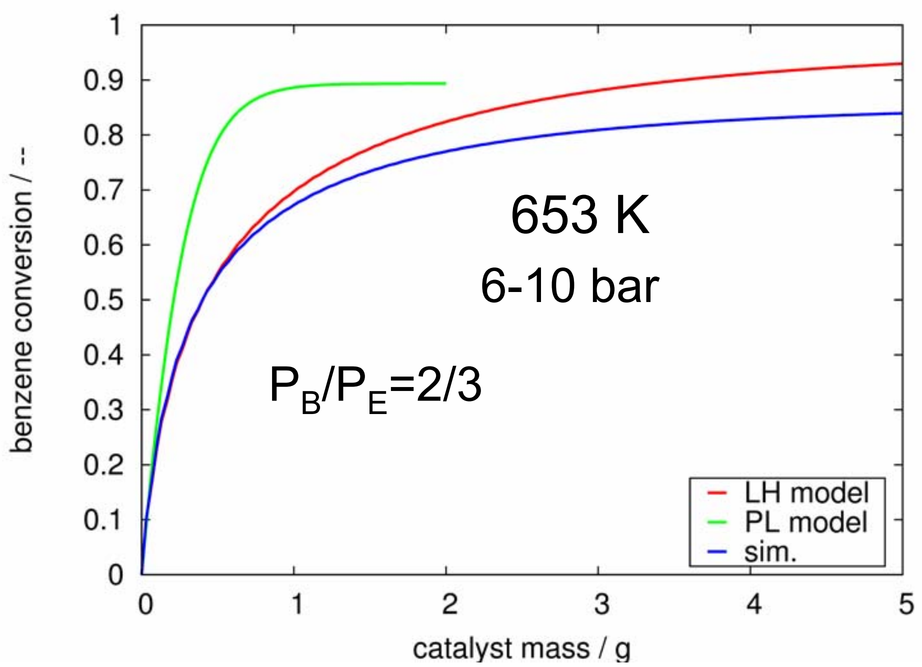


653 K

6-10 bar

$P_B/P_E=5/1$

Extrapolation to higher pressure and other composition:



653 K

6-10 bar

$P_B/P_E=2/3$

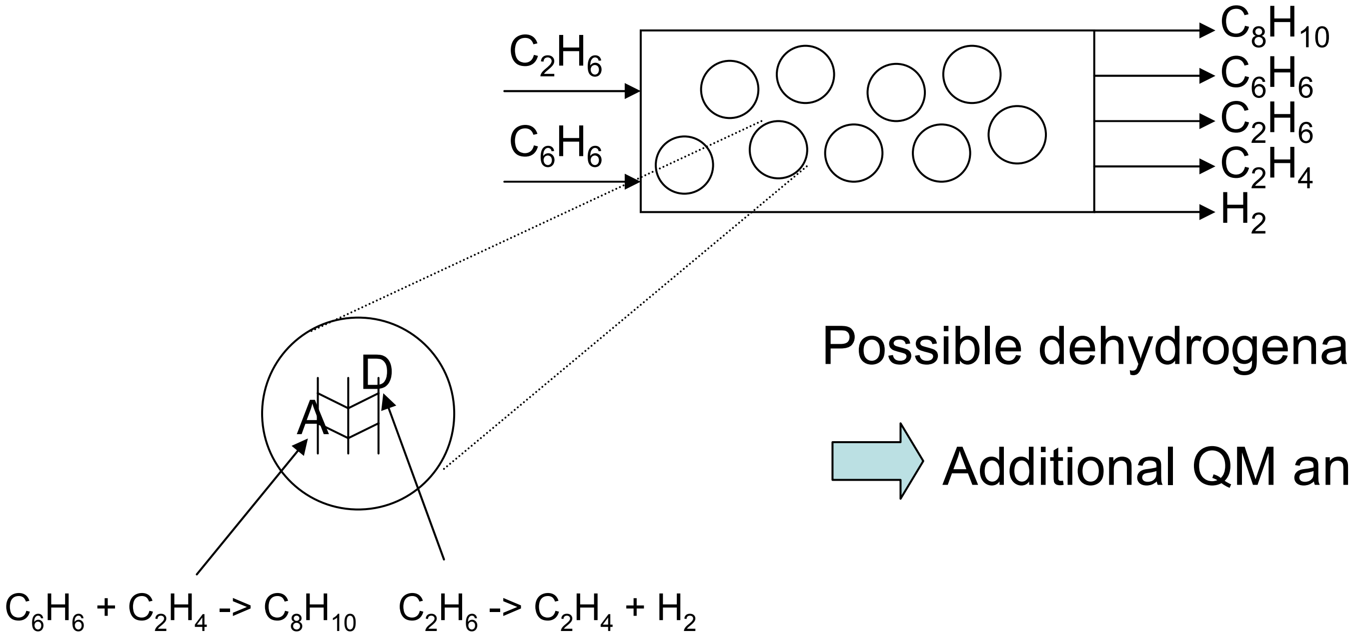
Significant deviations at higher conversion

Coupling of alkylation with dehydrogenation of ethane

Background:

- Ethene production is energy intensive
- Ethane is a much cheaper raw material

⇨ Bifunctional catalyst with dehydrogenation function

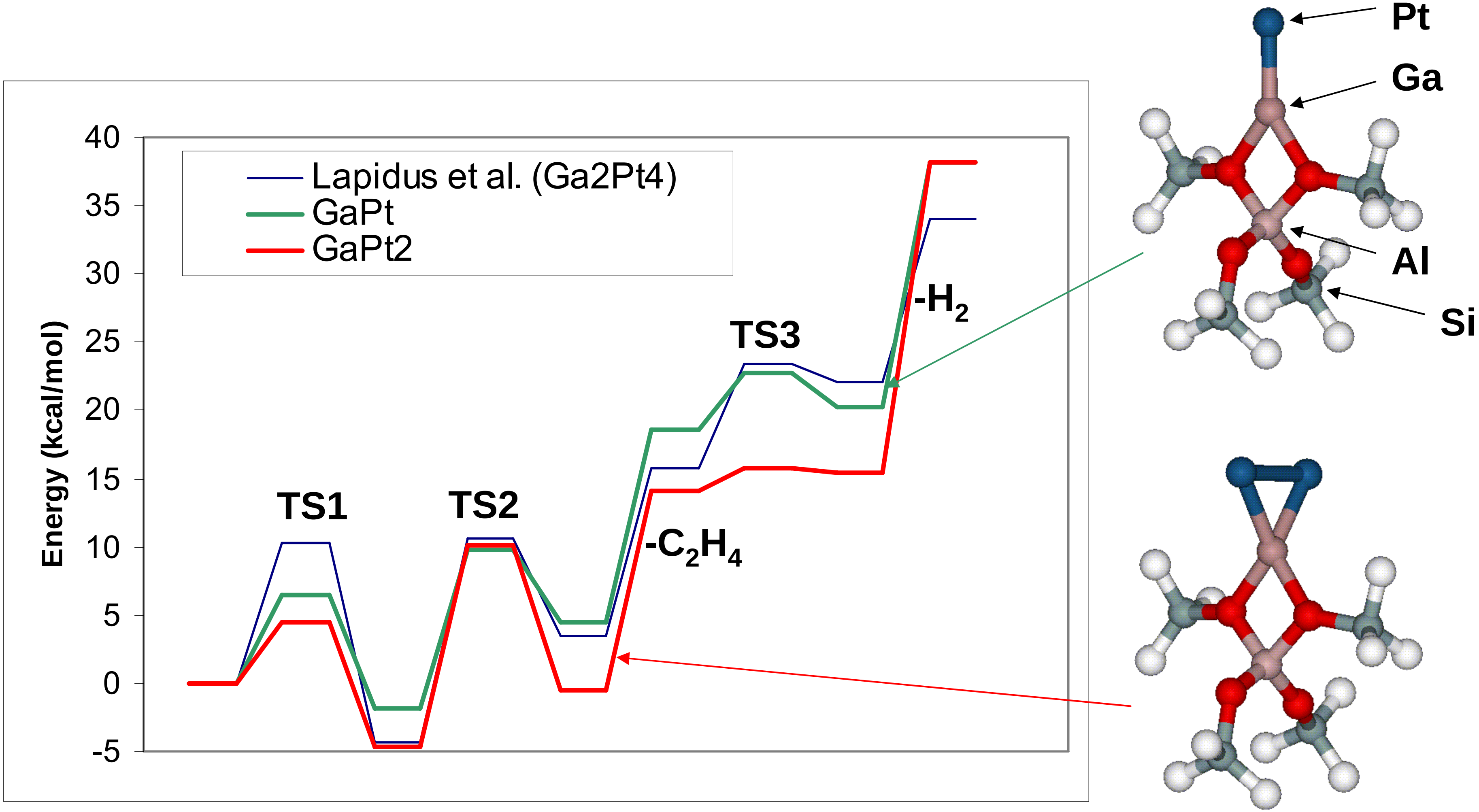


$C_6H_6 + C_2H_4$ -> C_8H_{10} C_2H_6 -> $C_2H_4 + H_2$

Possible dehydrogenation sites: Ga_xPt_y

⇨ Additional QM and MD simulations

QM-calculations



Kinetics

- dehydrogenation can be described as 5-step mechanism
- rate coefficients are much higher than for alkylation

Simplified description of dehydrogenation:

$$r_{deh} = k_1 q_{C2H6} - k_{-1} q_{C2H4} q_{H2}$$

effective rate constants

Problem: ratio k_1/k_{-1} has to ensure the correct equilibrium composition:

Implementation:

$$r_{deh} = k_1 \left(q_{C2H6} - \frac{1}{K_q} q_{C2H4} q_{H2} \right) \qquad K_q = \frac{\tilde{q}_{H2} \tilde{q}_{C2H4}}{\tilde{q}_{C2H6}}$$

Thermodynamics

- Conversion between K_a and K_q

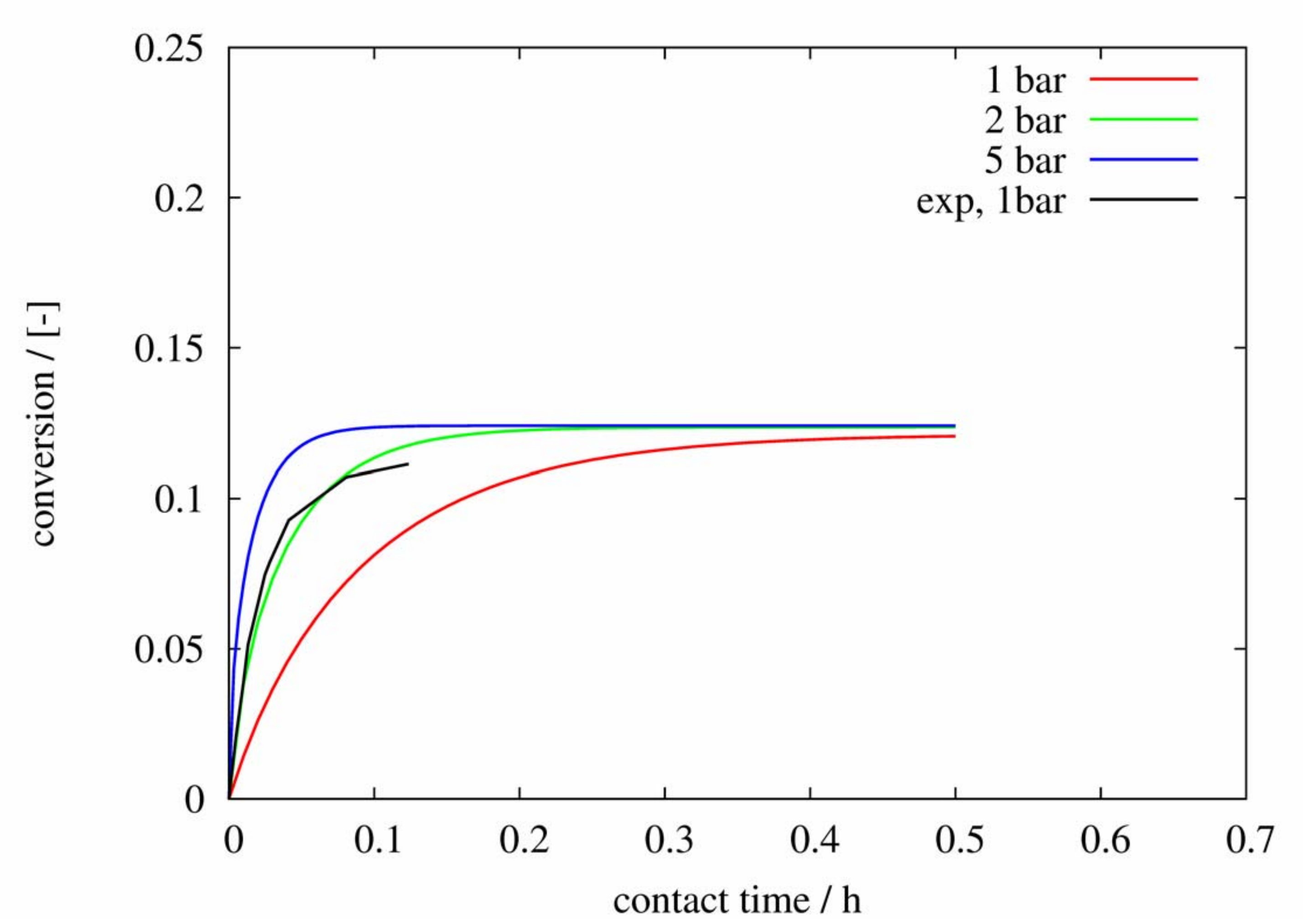
Thermodynamic equilibrium: $p_i^o x_i = p_{tot} y_i$ IAST

Chemical equilibrium: $K_a = \exp\left(\frac{-\Delta G_R^o}{RT}\right)$

$$\boxed{K_q = \frac{q_{H2}^{eq} q_{C2H4}^{eq}}{q_{C2H6}^{eq}} = K_a (1\text{bar}) q_{tot}^{eq} \frac{P_{C2H6}^o}{P_{H2}^o P_{C2H4}^o}}$$

⇨ Equilibrium composition depends on adsorption strengths of all species

Results



Exp.: Lukyanov, Vazhnova, J. Catal. 257 (2008) 382

Conclusions

- Model for simulation of overall activity of zeolitic catalyst particle is proposed
- All model parameters are determined from theoretical approaches describing the elementary processes adsorption, diffusion, reaction
- Clear separation between intrinsic kinetics and Adsorption / transport
- Apparent rate parameters were shown to be complex functions of zeolite structure, particle size, and reaction conditions

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