UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Ab initio based micro-kinetic modeling of benzene hydrogenation on Pd(111), as a function of hydrogen coverage

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ERIC

Catalytic hydrogenation of benzene

Industrial applications:

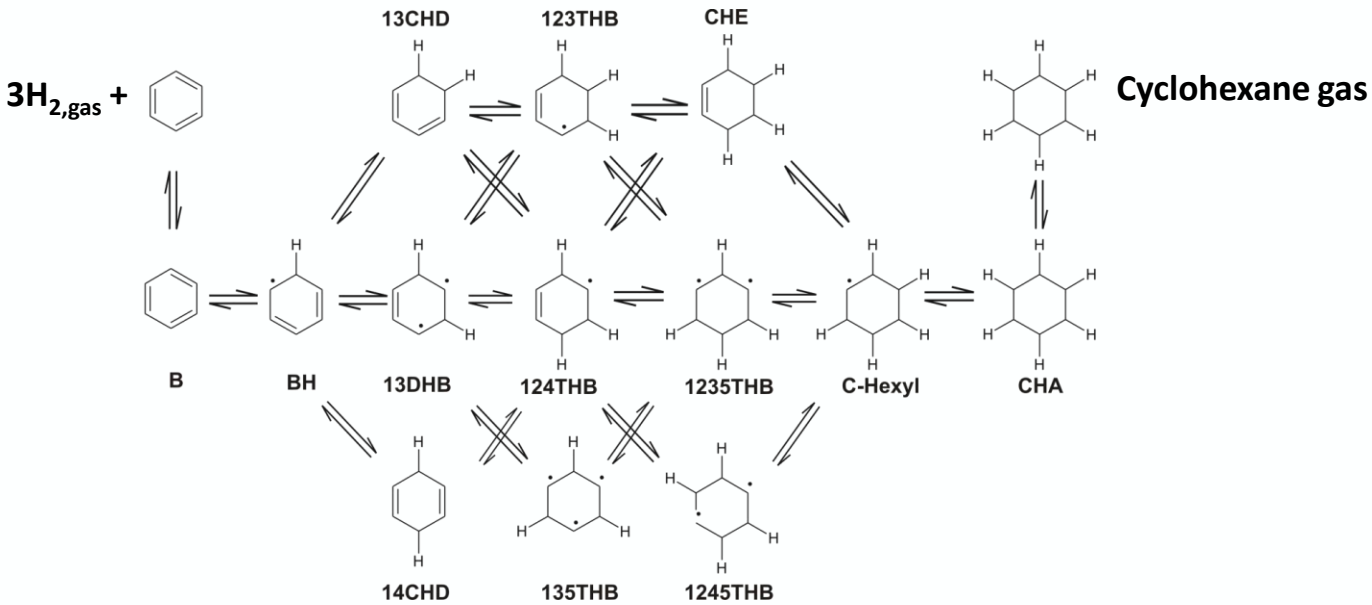
- Hydrotreating of fuels
- Petrochemical industry (nylon)

Environmental applications:

Production of clean fuels

(benzene is carcinogen type A)

- ❑ Complex catalytic reaction network, with multiple possible adsorption sites
- ❑ For one adsorption site → full network with13 intermediates
- ❑ Palladium is a widely used catalyst for hydrogenation reactions
- ❑ Pd(111) is the most abundant and stable surface

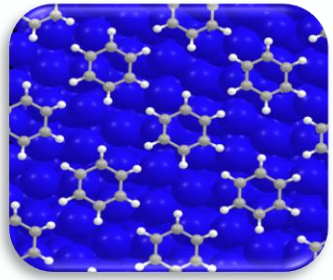


Integrating theoretical models into industry

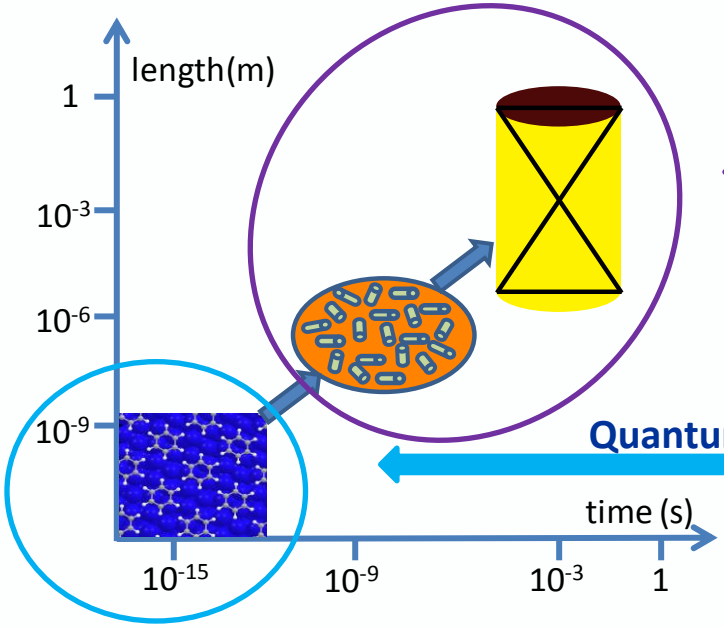
Important goal in industry:

developing new catalysts with novel catalytic properties

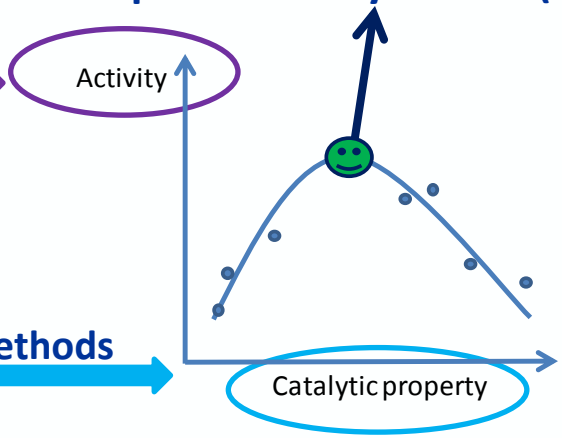
Ab initio based kinetics



Industrial models



Optimal catalyst as a f(conditions)



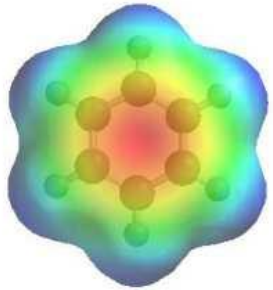
Quantum chemistry methods

Outline

- Introduction
- Methodology
- Results
- Conclusions

Density Functional Theory (DFT)

Idea of DFT: minimize energy with respect to the electron density



The energy is a functional of *ρ*:

E[ρ] → *ρ(r)* → *r(x,y,z)*

$$E[\rho] = \boxed{-\frac{1}{2}\sum_{i=1}^{n}\int \phi_i^*(r_i)\nabla^2\phi_i(r_i)dr_i} \boxed{-\sum_{x=1}^{N}\frac{Z_x}{r_{xi}}\rho(r_i)dr_i} \boxed{+\frac{1}{2}\int\int\frac{\rho(r_1)\rho(r_2)}{r_{12}}dr_1dr_2} \boxed{+E^{XC}[\rho]}$$

Kinetic energy

Nuclear-electron interactions

Coulombic repulsions

Exchange and correlation functional

Biggest challenge→ source of inaccuracy

Different approximations:

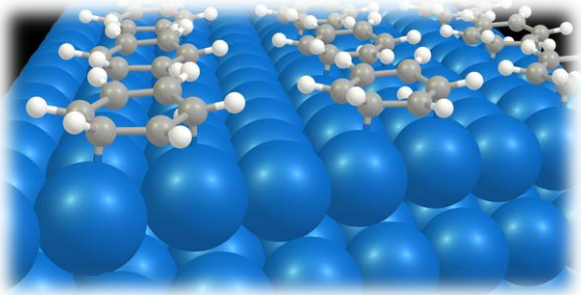
This work uses the Generalized gradient approximation (PW91)

Computational approach: catalyst model & DFT

Periodic DFT calculations

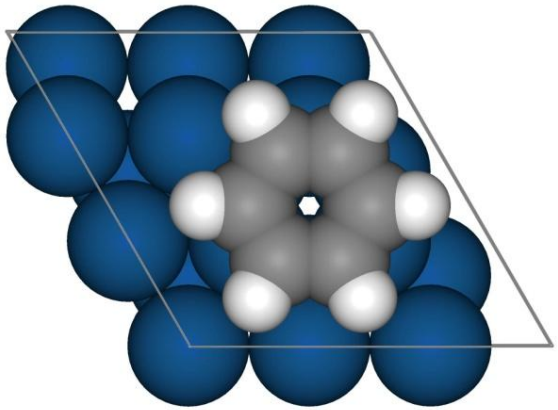
b-initio VASP ackage ienna imulation

fcc Pd(111)



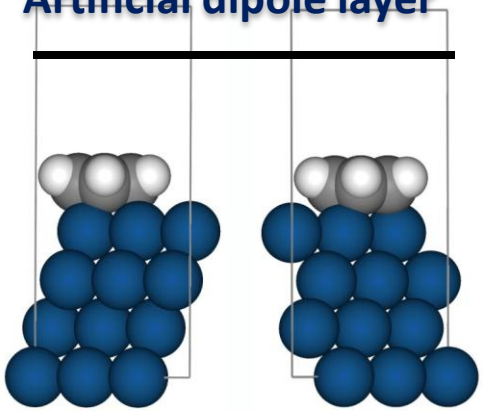
- **Computational details:**
  - **PAW (Encut=400 eV)**
  - **5 5 1 K-points**
  - **Methfessel Paxton, σ=0.3 eV**
  - **Non-spin polarized systems**

Unit cell:



Top view

Artificial dipole layer



Vacuum layer 11 Å

Relax 2 upper layers

Fix 2 bottom layers

Side view

Statistical thermodynamics

- DFT calculations provide:
  - Electronic energy at 0 K from geometry optimization (E_{el})
  - Vibrational frequencies from harmonic oscillator frequency analysis (ν)

Use of **statistical thermodynamics** to link between microscopic and macroscopic properties. Calculates the thermodynamic parameters as a function of T with the **partition function, *q*(*V,T*)**

$$q(V,T) = q_{elec}(T)\,q_{trans}(V,T)\,q_{rot}(T)\,q_{vib}(T) \qquad q_{vib}(T) = \prod_{i=1}^{3N-6}\left(\frac{1}{1-e^{-h\omega_i/k_B T}}\right)$$

Are the species **mobile** on the catalytic surface?

no

Immobile surface species

$q_{rot}(T) = q_{trans}(V,T) = 1$

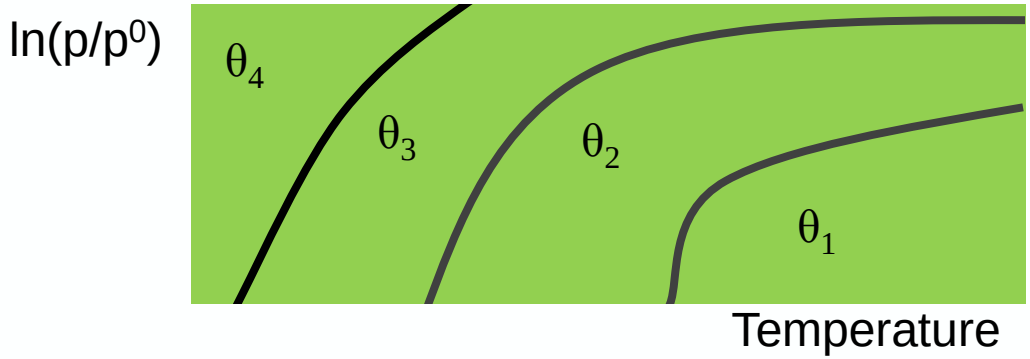
yes

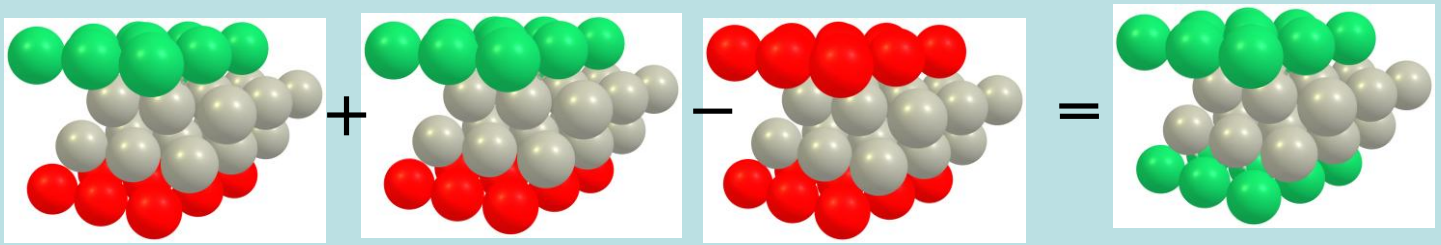
Mobile surface species

- Free rotation $q_{rot} = \frac{8\pi^2 IkT}{h^2\sigma}$
- Free translation $q_{trans} = \left(\frac{2\pi MkT}{h^2}\right)V$

$$q_{mobile} = \frac{q_{immobile}^{vibr}}{q_{nD}^{vibr}} \times q_{nD}^{trans/\,rot}$$

Thermodynamic diagrams





Optimized surface Non-optimized surface

$$\Gamma_{0K,relaxed} = 2 \cdot \Gamma_{0K,opt} - \Gamma_{0K,non-opt} =$$

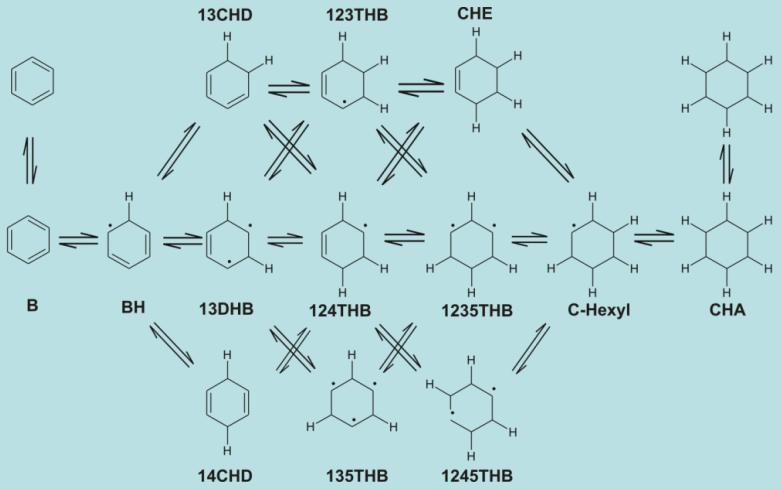
$$= 2 \times \left(\frac{E_{slab,opt} - n_{Pd,\mathrm{supercell}} \times E_{bulk,opt} - \sum_i E_{i(g)} \times n_i}{2 \cdot A_{opt}} \right) - \left(\frac{E_{slab,non-opt} - n_{Pd,\mathrm{supercell}} \times E_{bulk,non-opt}}{2 \cdot A_{non-opt}} \right)$$

$$\Gamma_{(T,P_i)} = \Gamma_{0K,relaxed} + \sum_i \frac{n_i}{N_a \times A} \times \left[T \cdot S^0_{i(T)} - H^0_{i(T)} + H^0_{i(0K)} - R \cdot T \cdot \ln \frac{P_i}{P^0} \right]$$

Microkinetic modeling

Full reaction network:

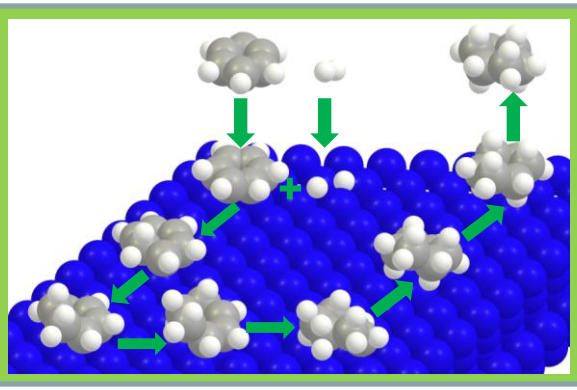
$B_g + * \leftrightarrow B^*$	K_B
$H_{2,g} + 2* \leftrightarrow 2H^*$	K_{H2}
$B^* + H^* \leftrightarrow BH^* + *$	K_1
$BH^* + H^* \leftrightarrow 13CHD^* + *$	K_{2a}
$BH^* + H^* \leftrightarrow 13DHB^* + *$	K_{2b}
$BH^* + H^* \leftrightarrow 14CHD^* + *$	K_{2c}
$13CHD^* + H^* \leftrightarrow 123THB^* + *$	K_{3a}
$13CHD^* + H^* \leftrightarrow 124THB^* + *$	K_{3b}
$13DHB^* + H^* \leftrightarrow 123THB^* + *$	K_{3c}
$13DHB^* + H^* \leftrightarrow 124THB^* + *$	K_{3d}
$13DHB^* + H^* \leftrightarrow 135THB^* + *$	K_{3e}
$14CHD^* + H^* \leftrightarrow 124THB^* + *$	K_{3f}
$123THB^* + H^* \leftrightarrow CHE^* + *$	K_{4a}
$123THB^* + H^* \leftrightarrow 1235THB^* + *$	K_{4b}
$124THB^* + H^* \leftrightarrow CHE^* + *$	K_{4c}
$124THB^* + H^* \leftrightarrow 1235THB^* + *$	K_{4d}
$124THB^* + H^* \leftrightarrow 1245THB^* + *$	K_{4e}
$135THB^* + H^* \leftrightarrow 1235THB^* + *$	K_{4f}
$CHE^* + H^* \leftrightarrow c\text{-}hexyl^* + *$	K_{5a}
$1235THB^* + H^* \leftrightarrow c\text{-}hexyl^* + *$	K_{5b}
$1245THB^* + H^* \leftrightarrow c\text{-}hexyl^* + *$	K_{5c}
$c\text{-}hexyl^* + H^* \leftrightarrow CHA^* + *$	K_6
$CHA_g + * \leftrightarrow CHA^*$	K_{CHA}



$$r = c_t \cdot (k_{des,CHA} \cdot \theta_{CHA} - k_{ads,CHA} \cdot p_{CHA} \cdot \theta_{CHA})$$

Dominant path with rate determining step

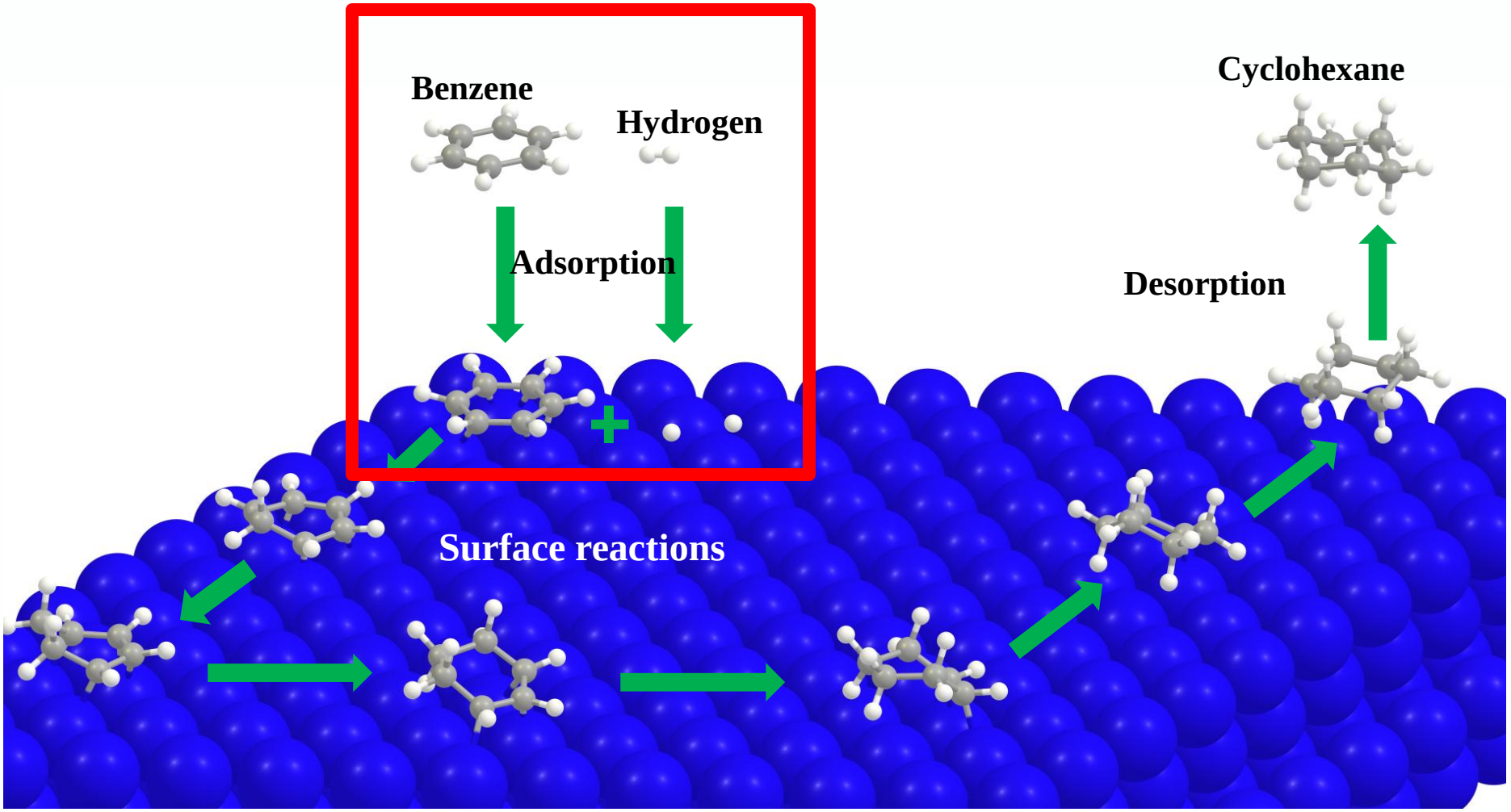
$$r = \frac{c_t \cdot k_{j(RDS)} \cdot (\prod_{i=1}^{i=j-1} K_i) \cdot K_B \cdot p_B \cdot K_{H2}^{j} \cdot p_{H2}^{\frac{j}{2}}}{(1 + K_B \cdot p_B + (K_{H2} \cdot p_{H2})^{\frac{1}{2}})^2}$$



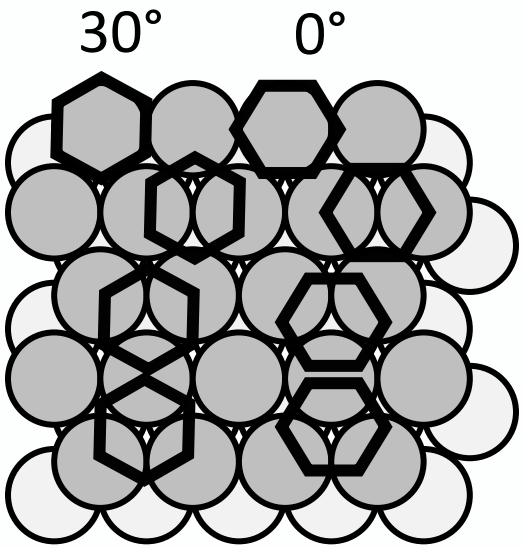
Outline

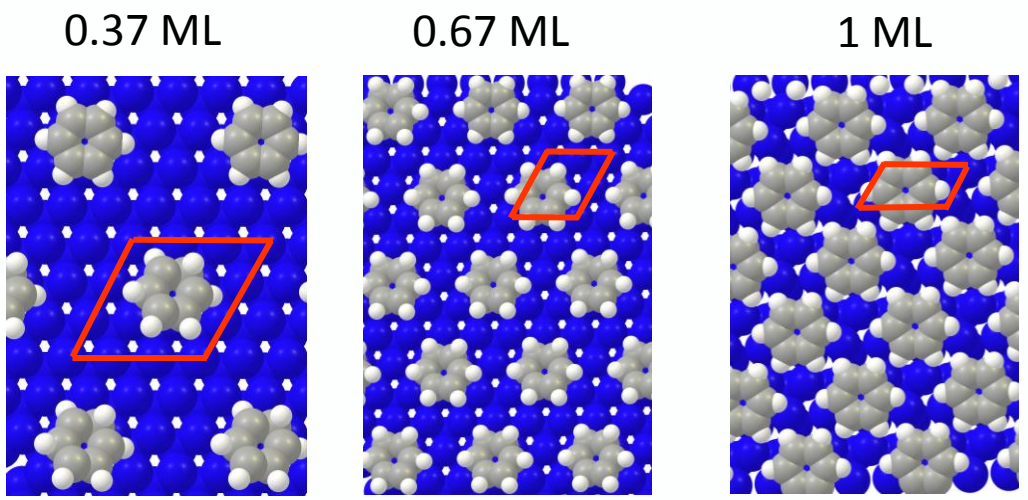
- Introduction
- Methodology
- **Results**
- Conclusions

Results for the adsorption

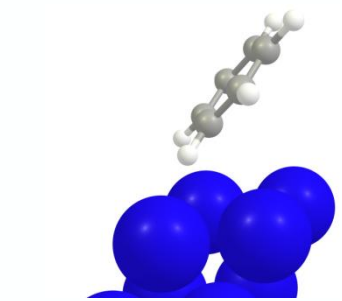


Benzene adsorption



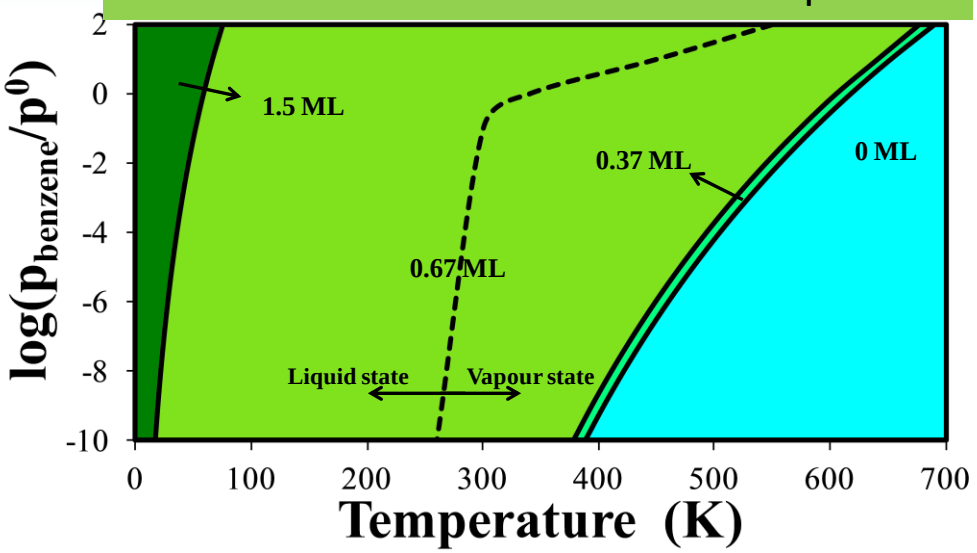


θ ≤1 ML: bridge30 and hollow-hcp0
θ >1 ML: tilted configuration



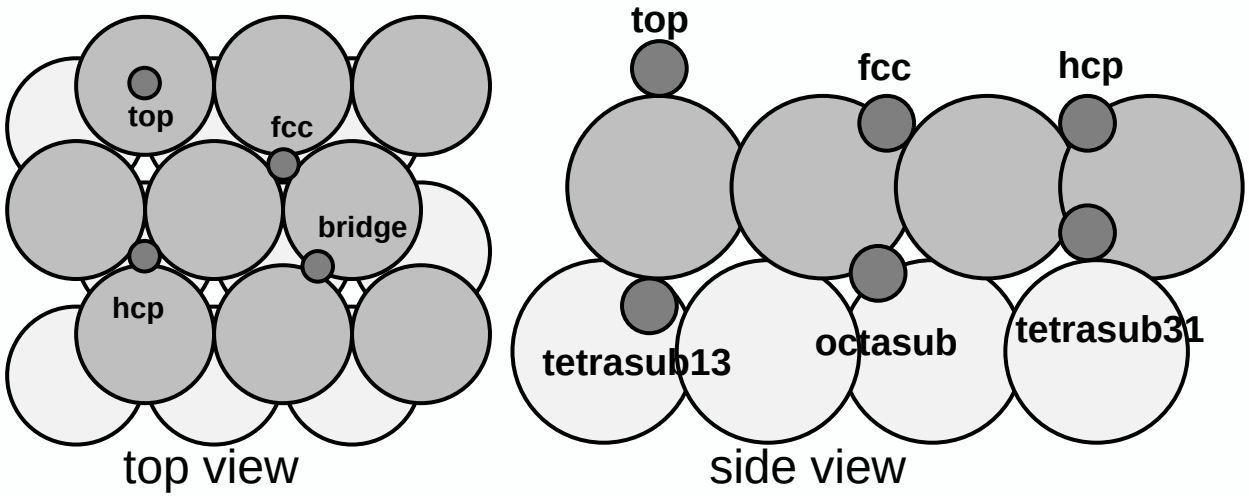
tilted geometry

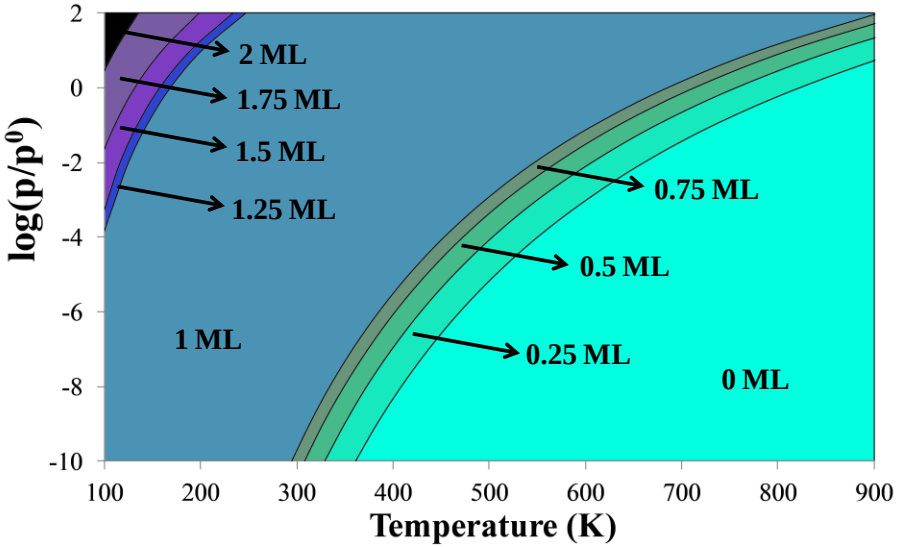
Reaction conditions:θ ~ 0.67 ML expected



Hydrogen adsorption

$\theta_H \leq 1ML \rightarrow$ Surface hollow sites
$1ML < \theta_H \leq 2ML \rightarrow$ Surf+Subsurface

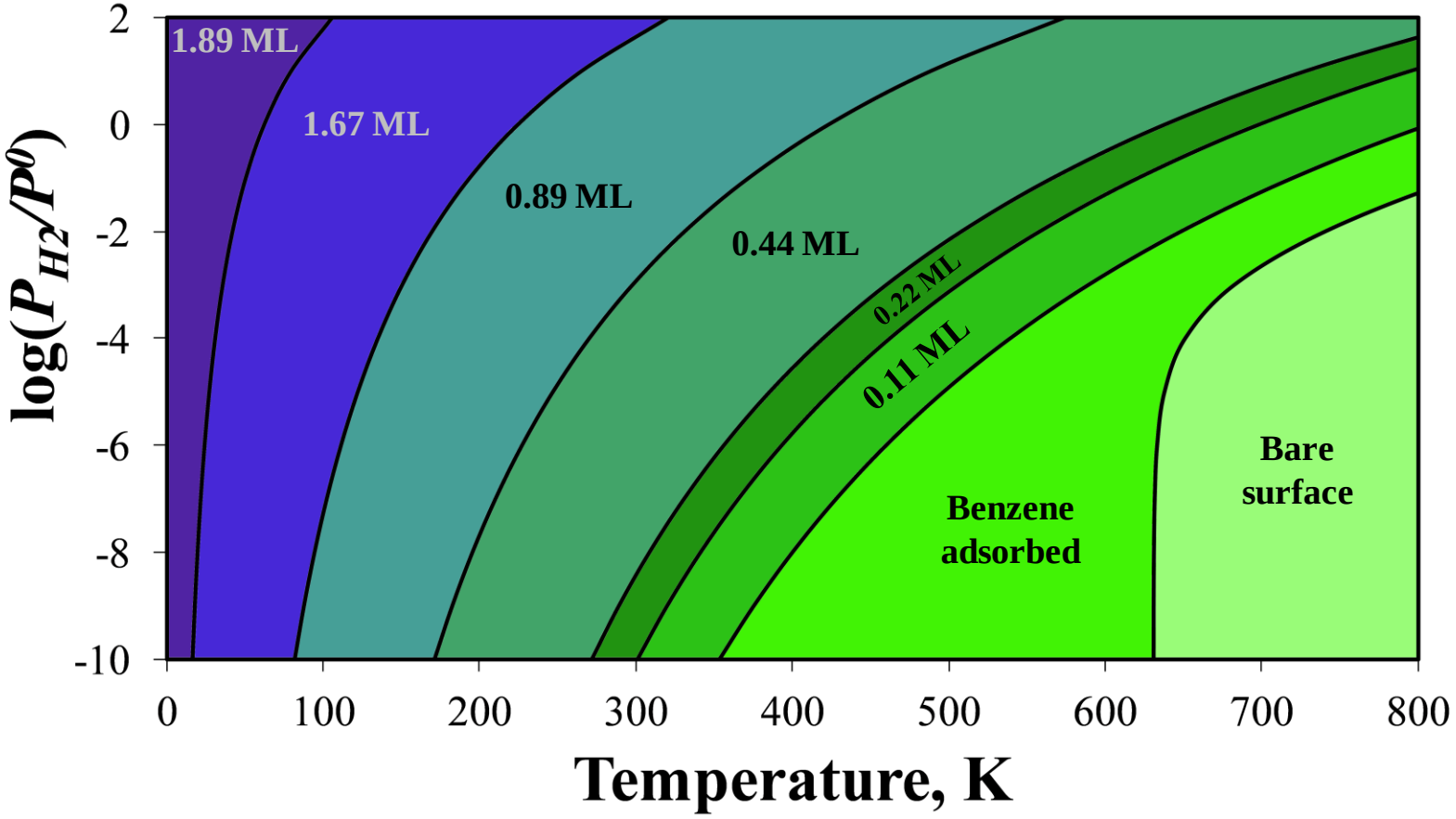




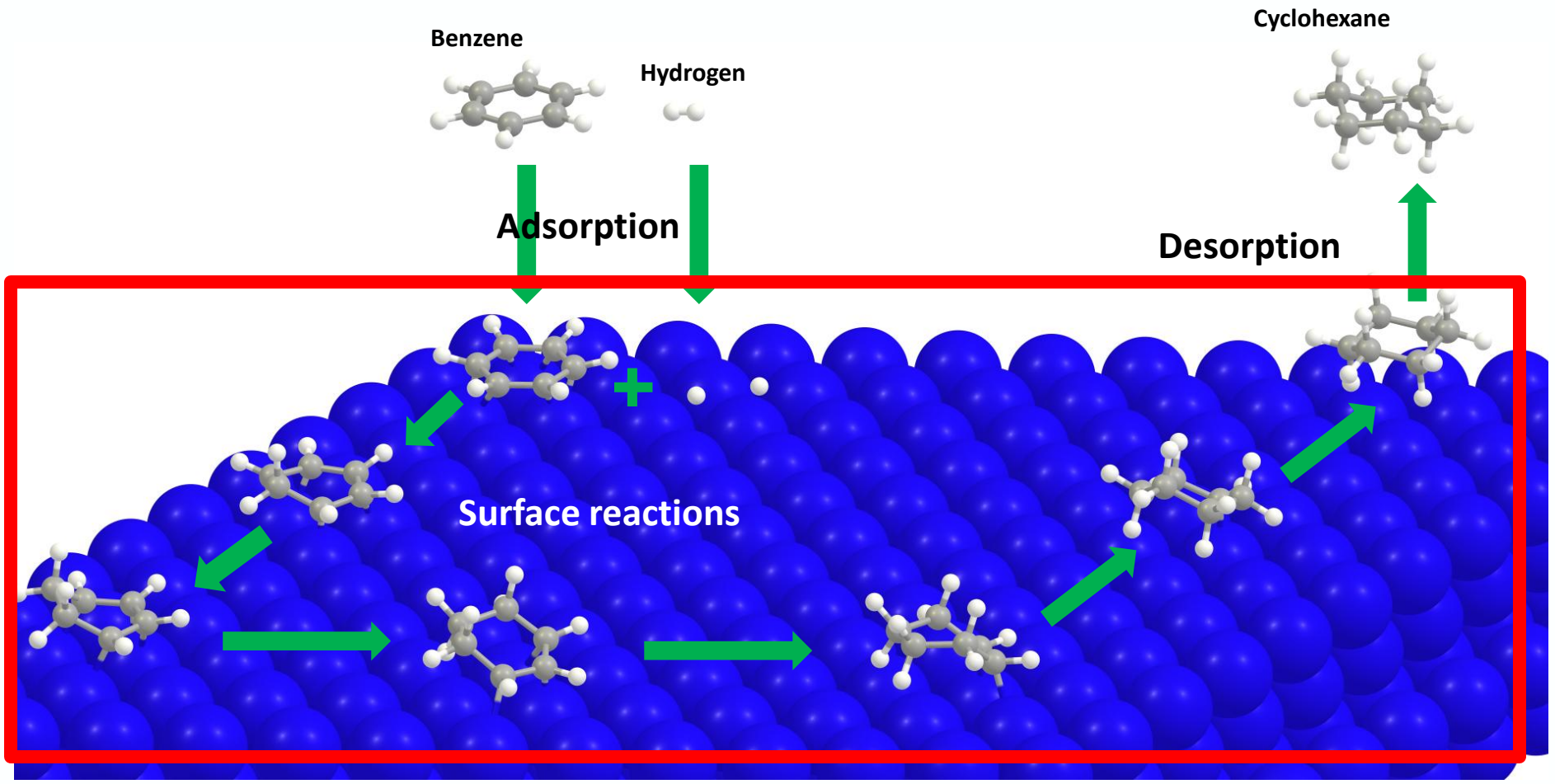
Hydrogenation conditions (450 K, >1 bar):
θ_H~1ML of surface hollow hydrogen

Benzene and hydrogen co-adsorption

Hydrogenation conditions (450 K, >1 bar):
0.44ML < θ_H < 0.89 ML surface hydrogen

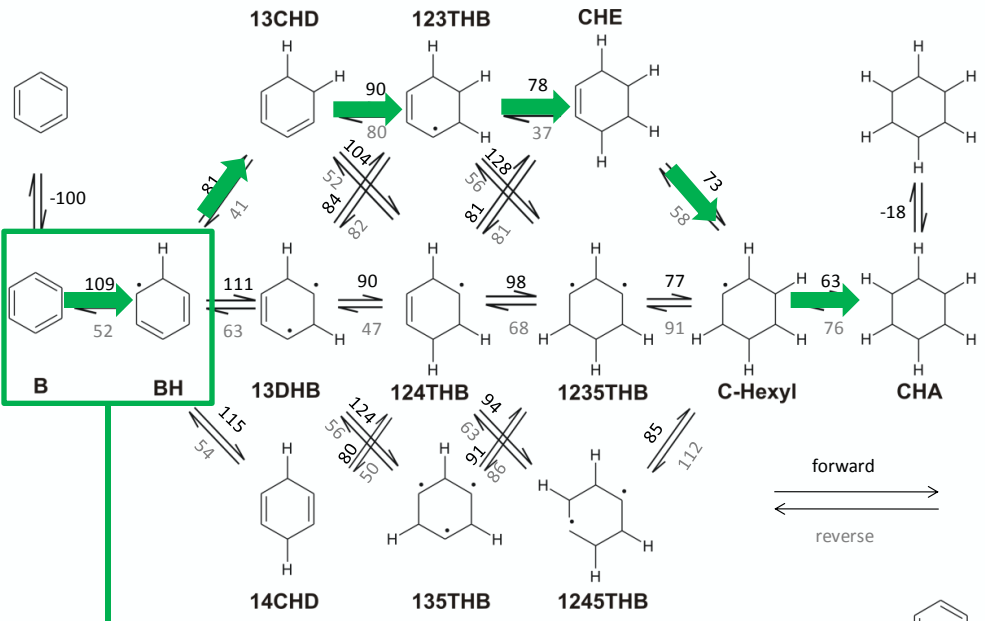


Results for the surface reactions



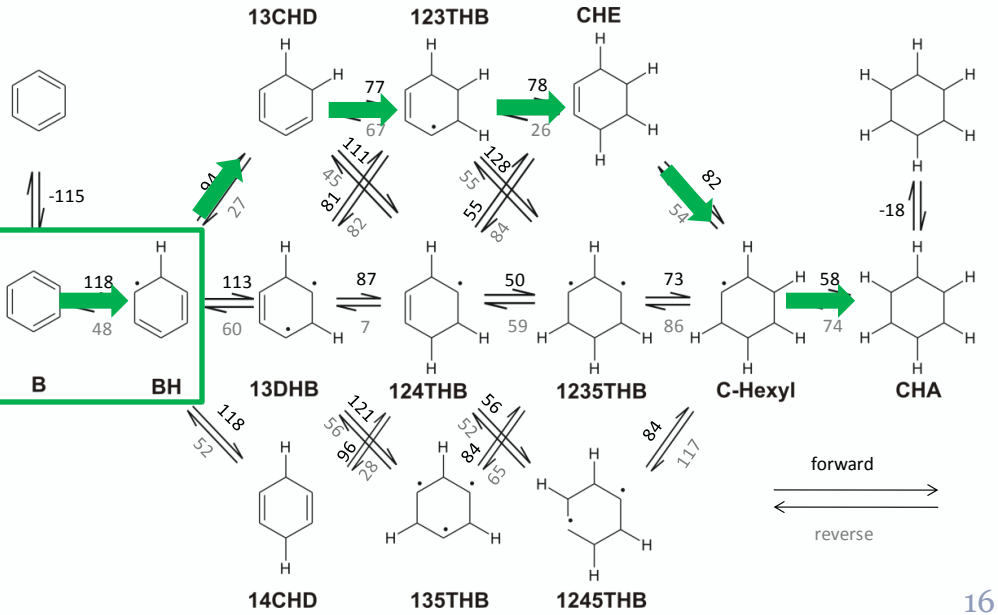
Electronic barriers for surface reactions

***Hollow* species**

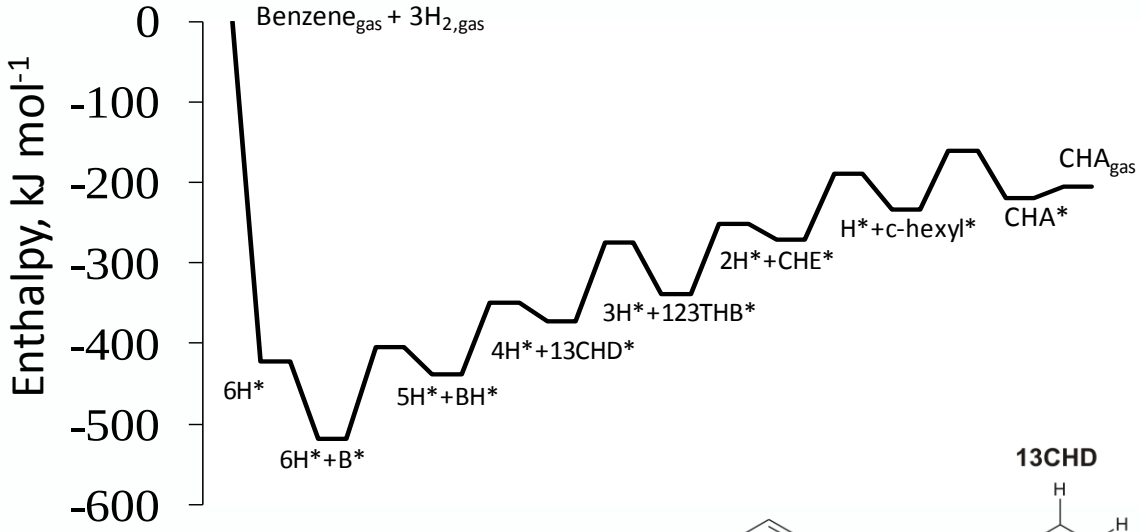


Potential rate determining step
k_{RDS} strongly influences *r*

***Bridge* species**



Thermodynamics & kinetics

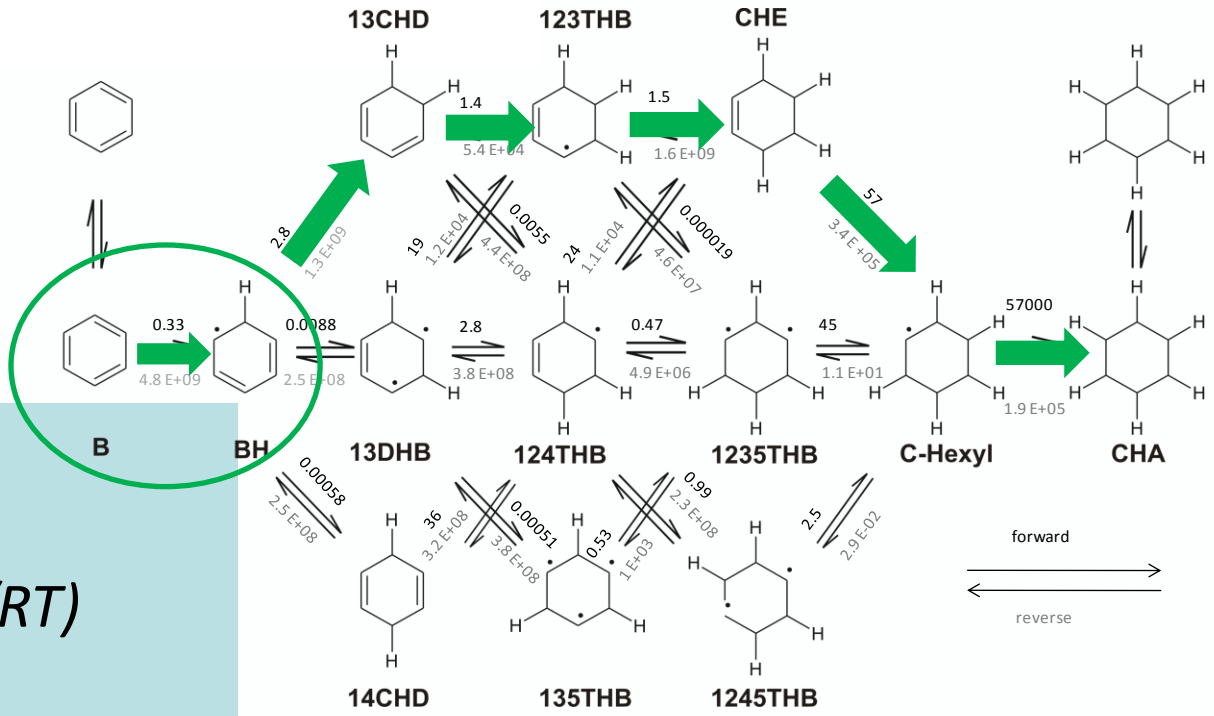


Dominant path
T=450K
Hydrogen with free translation
CHA free translation & rotation
Cyclohexyl with free rotation

E_{el}, ν

q
U
H
S
…

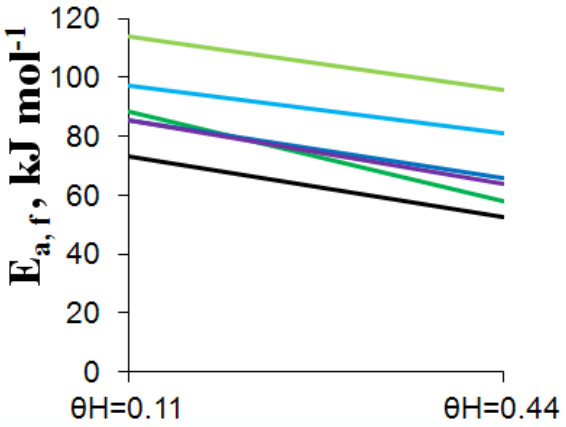
$A = f(S,T)$
$E_a = f(H,T)$
$k = A\ exp(-E_a/RT)$
$K=k_f/k_r$

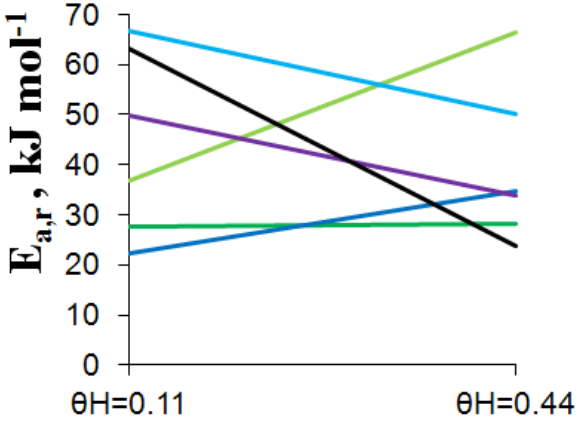


Coverage dependent kinetics

Dominant path evolution of kinetics with coverage, 0.11 ML≤ θ≤0. 44 ML

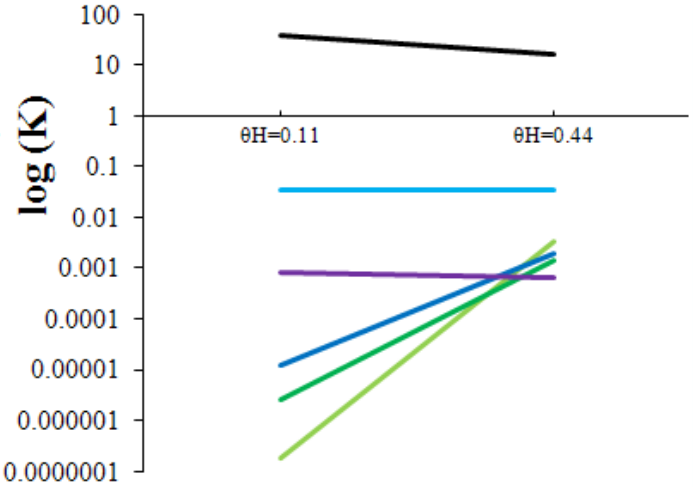
Activation energy



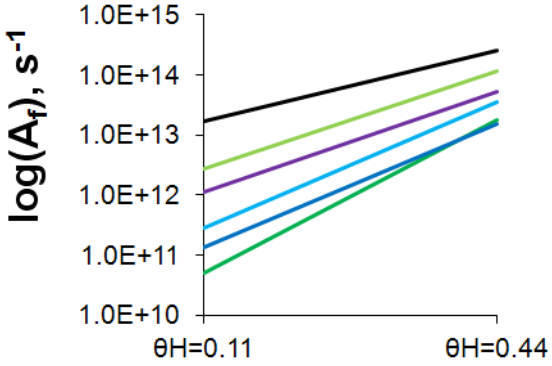


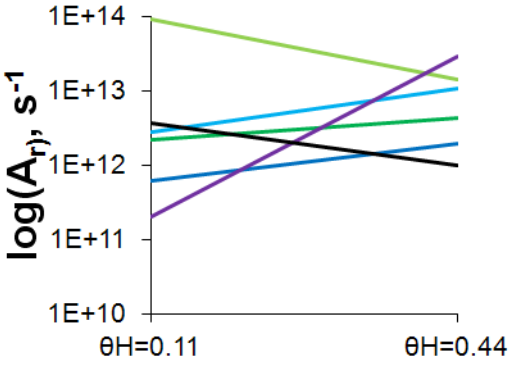
1st step 4th step
2nd step 5th step
3rd step 6th step

Equilibrium coefficient



Pre-exponential factor





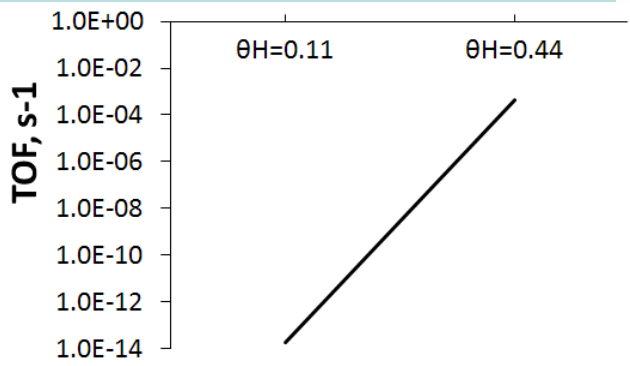
Large increase in K_{eq} for 1st, 2nd and 4th reactions

Coverage dependent kinetics

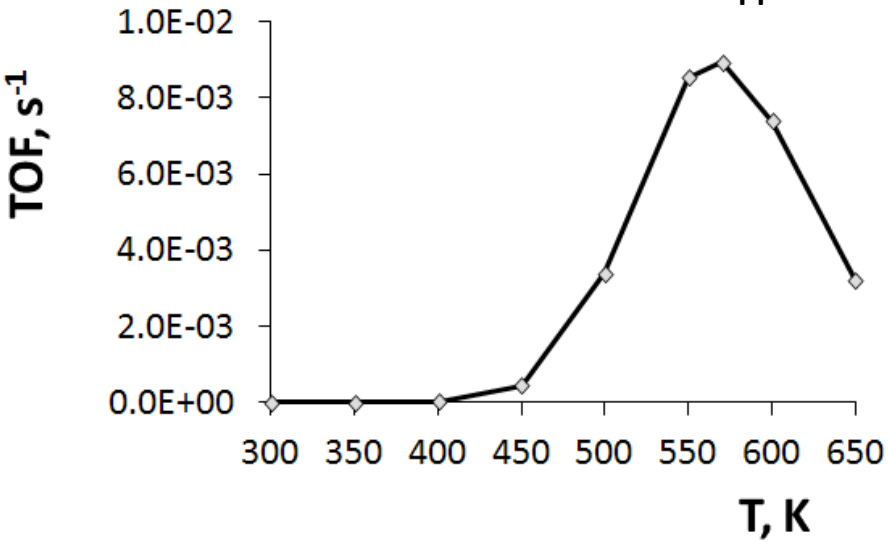
Higher hydrogen coverage:

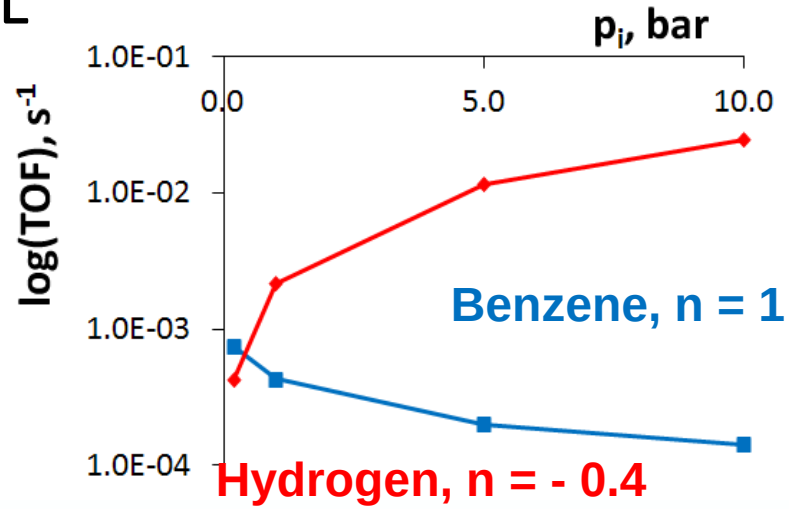
- Decrease of E_a
- Increase of A
- Decrease of hydrogen mobility

Simulation of the microkinetics: Large increase in TOF at high coverage



θ_H=0.44 ML





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Conclusions

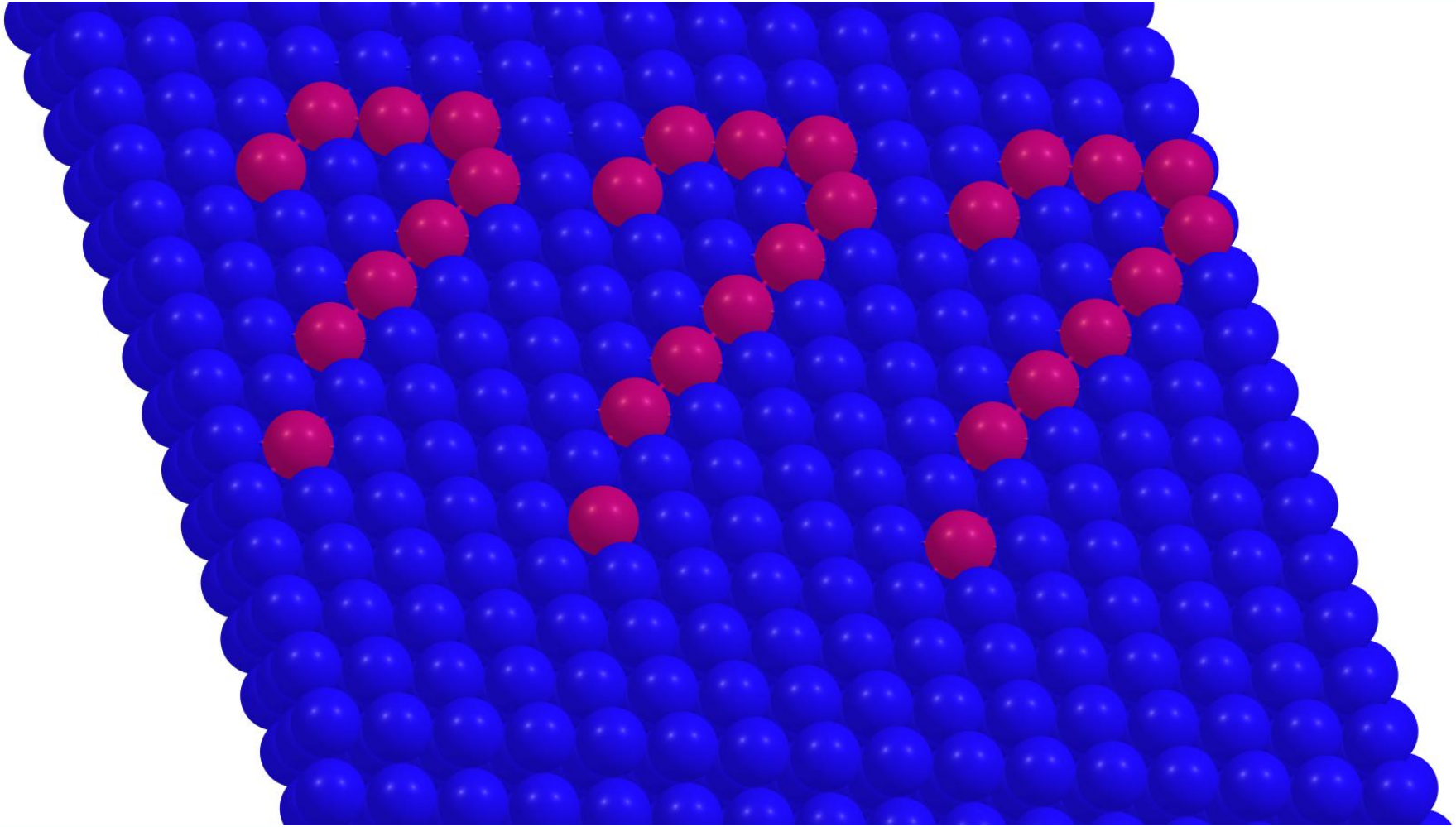
Benzene adsorption on Pd(111):
- Flat up to 1 ML
- Tilted above 1 ML
- 0.67 ML preferred at reaction conditions

Hydrogen adsorption on Pd(111):
- Surface hollow sites up to ML
- Combination with subsurface above 1 ML
- 1 ML preferred at reaction conditions

Co-adsorption on Pd(111):
$0.44\text{ML} < \theta_H < 0.89$ ML surface hydrogen at reaction conditions, with 0.67 ML of benzene

Ab initio based micro-kinetics:
- Potential dominant path and rate determining step (upper path and first reaction resp.)
- Inclusion of coverage effects:
  - Decrease activation energies
  - Increase pre-exponential factor
  - Affect the mobility of hydrogen, which also impact on the kinetics
- Simulation of micro-kinetics shows much higher activities at high coverage
- Inclusion of hydrogen coverage effects improve the description of the reaction network

Thank you for your attention



Glossary

Catalyst descriptor: Characteristic for a given catalyst that can be correlated with kinetic and thermodynamic properties

DFT: Density Functional Theory

Dimer method: force-based transition state search algorithm

GGA: generalized gradient approximation (within DFT theory)

MEP: Minimum Energy Path

NEB: Nudged Elastic Band method for the calculation of MEPs

PAW: Plane Augmented Waves (periodic calculation technique)

PES: Potential energy surface

PW91: Perdew-Wang type of DFT functional

VASP: Vienna Ab initio Simulation Package

ZPE: Zero point energy