A Single-Event MicroKinetic Model for the Hydrogenation of Aromatic Components on a Pt catalyst

Tapan Bera, Joris W. Thybaut, Guy B. Marin

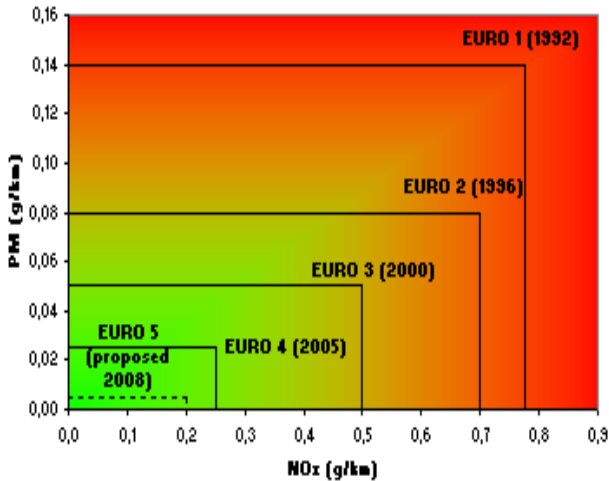*Laboratory for Chemical Technology, Ghent University*
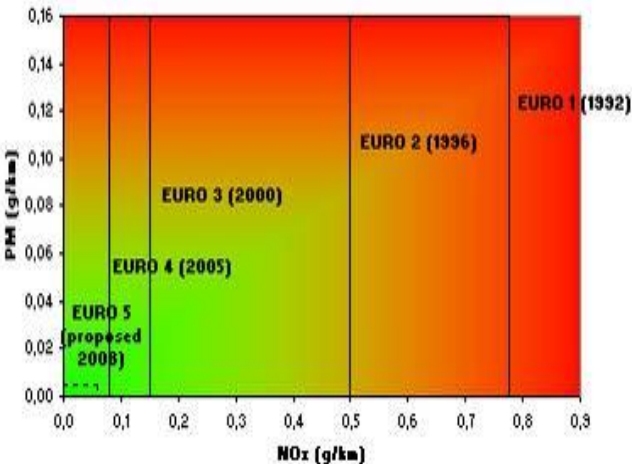
http://www.lct.UGent.be

Emission standard

Reduction of hazardous emissions: a global concern

NOx and PM emission standards for diesel cars

NOx and PM emission standards for petrol cars

Diesel fuel properties correlate emissions:

Emission of	Decreases as		
	Sulfur	**Total aromatics**	**Cetane number**
NOx	---	decreases	increases
HC	---	decreases	increases
CO	---	decreases	increases
SOx	decreases	---	---
Particles	decreases	decreases	increases

Fuels quality improvement

Reduction of particulate emission

Evolution diesel specifications

		EU Adopted 2000	EU Adopted 2005	WWFC[1]	
				Euro 1, 2	Euro 3, 4
Density at 15°C, kg/m^3	Max.	845	845	820-850	820-850
Sulfur, ppmw	Max.	350	50	300	30
Cetane number	Min.	51	51	53	55
Aromatics, vol %					
Total	Max.	---	---	25	15
PA's	Max.	11	11	5	2
95 % Boiling point, °C	Max.	360	360	355	350

[1] World-Wide Fuel Charter, 2002

Importance of aromatics hydrogenation

• Fuel quality: cetane number, smoke point

• Industrially: cyclohexane produced from benzene hydrogenation is base chemiical of nylon6,6

Cooper and Donnis **Appl. Catal. A Gen.** 1996
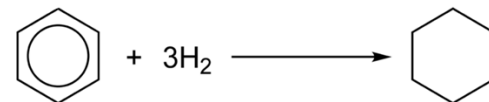
• Environmental: carcinogenic character

Single-Event MicroKinetics (SEMK)

- ## Conventional kinetic model
  - – power law model, LHHW model
  - – parameters depending on the feed, operating condition
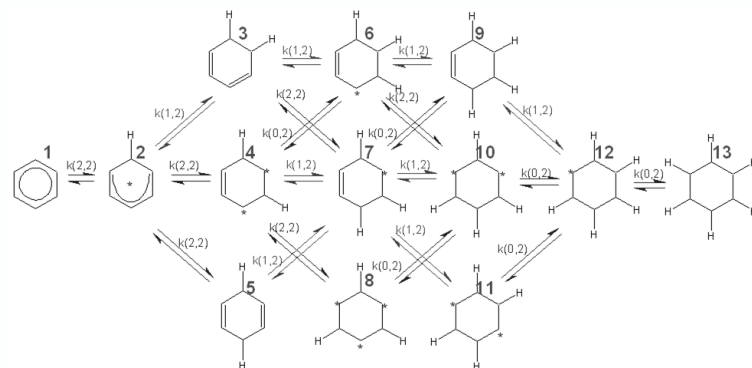
- ## Single-Event Micro-Kinetic (SEMK) model
  - – fundamental model
    based on elementary step
  - – consider all surface
    intermediate without
    rate determining step
  - – resulting more reliable extrapolation

- Introduction
- Reaction network
  - reaction family definition
  - automated reaction network generation
  - rate equations
- Parameter calculation and estimation
  - experimental data
  - regression results
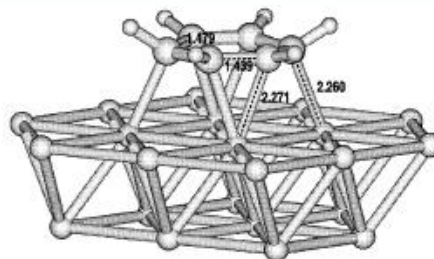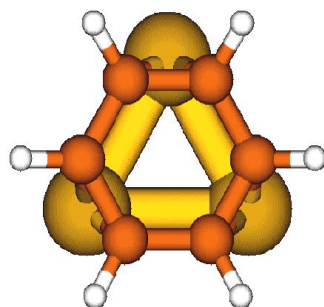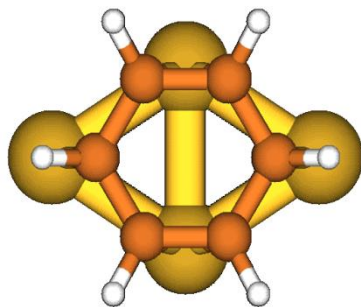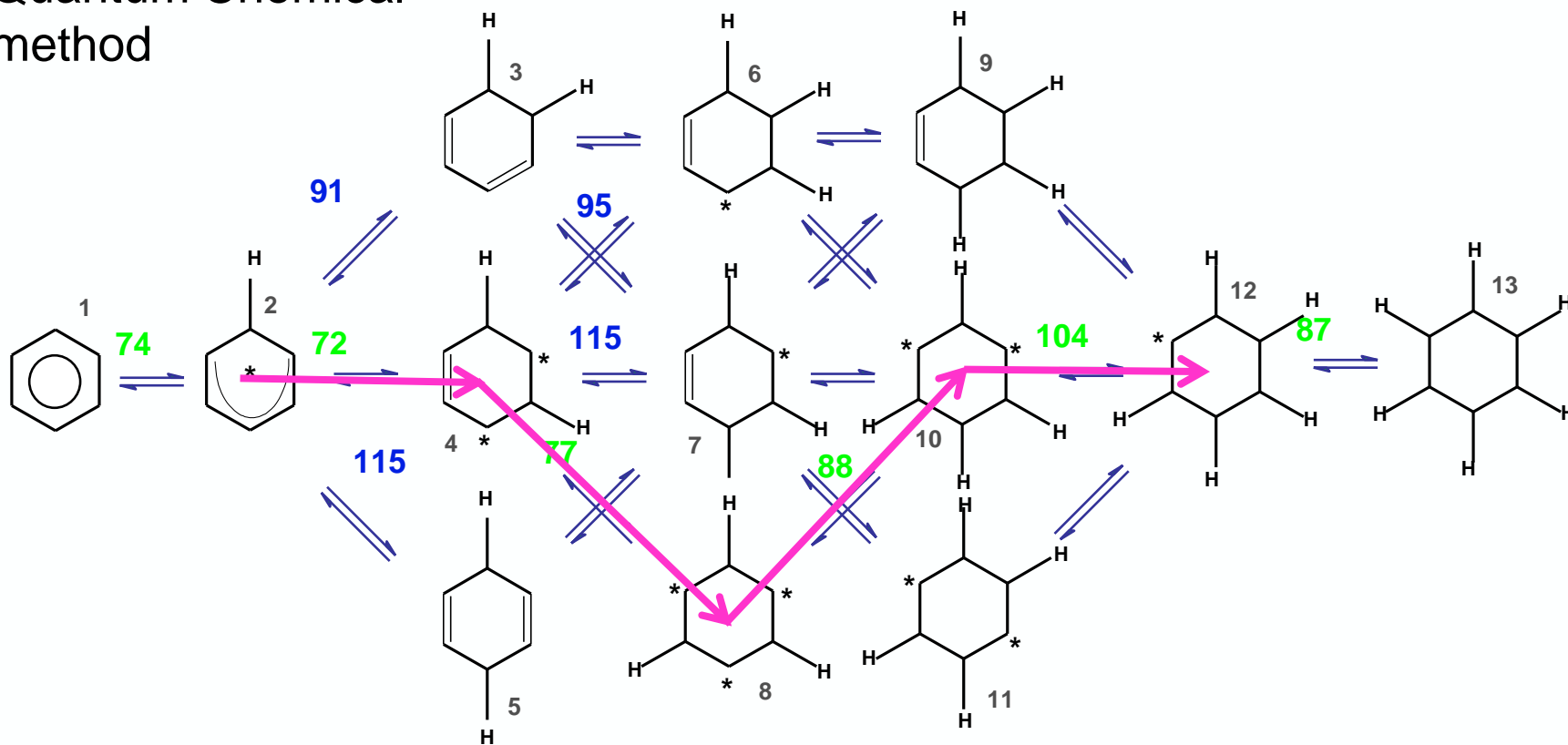- Conclusions

Hydrogenation: elementary steps

- **Horiuti-Polanyi mechanism**

$$H_2(g) + 2\,* \rightleftharpoons 2\,H* \qquad K_{H2}$$

$$A(g) + * \rightleftharpoons A* \qquad K_A$$

$$AH_i* + H* \rightleftharpoons AH_{i+1}* + * \qquad K_{i+1} \quad (i=0,..5)$$

$$AH_6* \rightleftharpoons AH_6(g) + * \qquad K_{AH6}$$

- **Adsorption steps quasi-equilibrated**

- Activation energy assessment through ab initio calculations

Benzene hydrogenation network
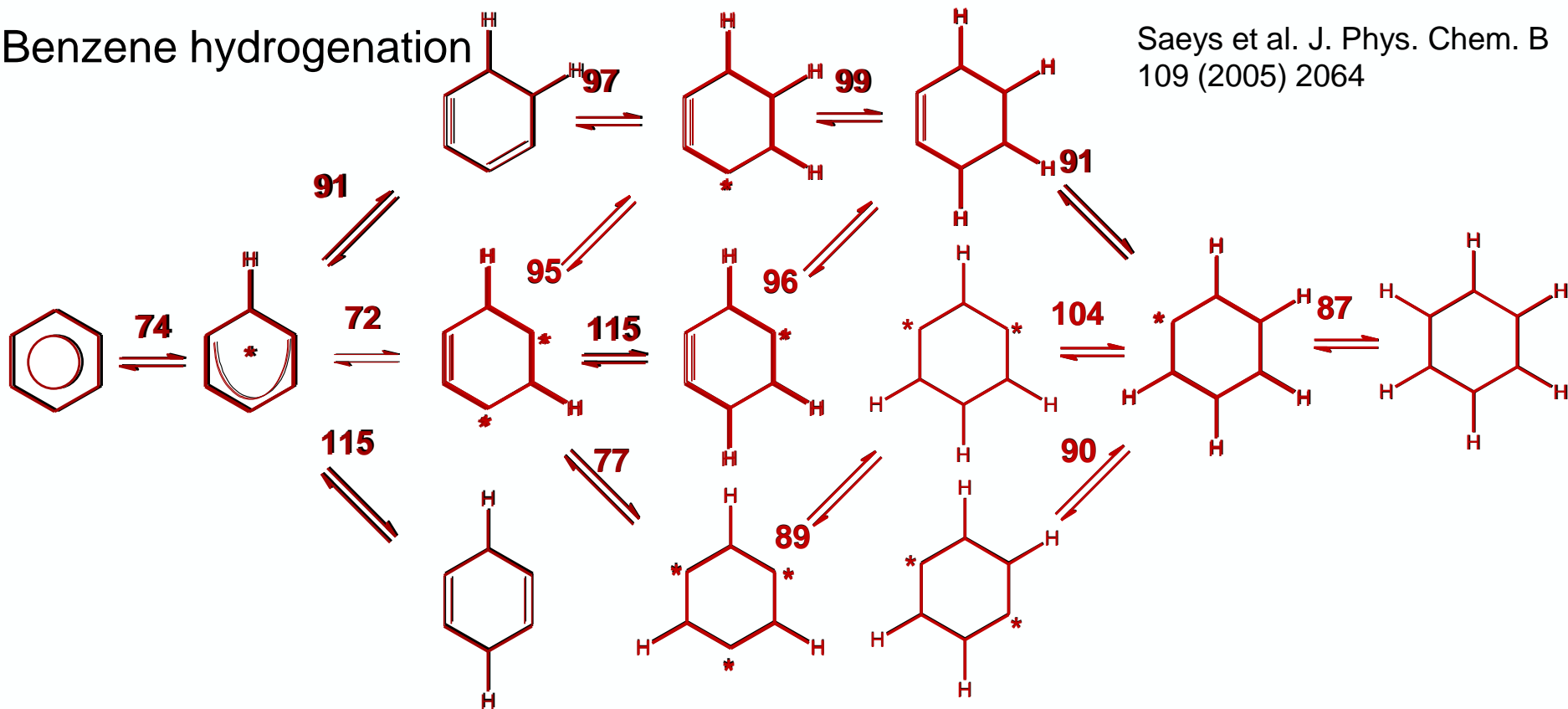
Quantum Chemical method

Saeys M, Reyniers MF, Thybaut JW, Neurock M, Marin GB, **J.Cat.** 2005

8

Ab initio calculation

Benzene hydrogenation

Saeys et al. J. Phys. Chem. B 109 (2005) 2064

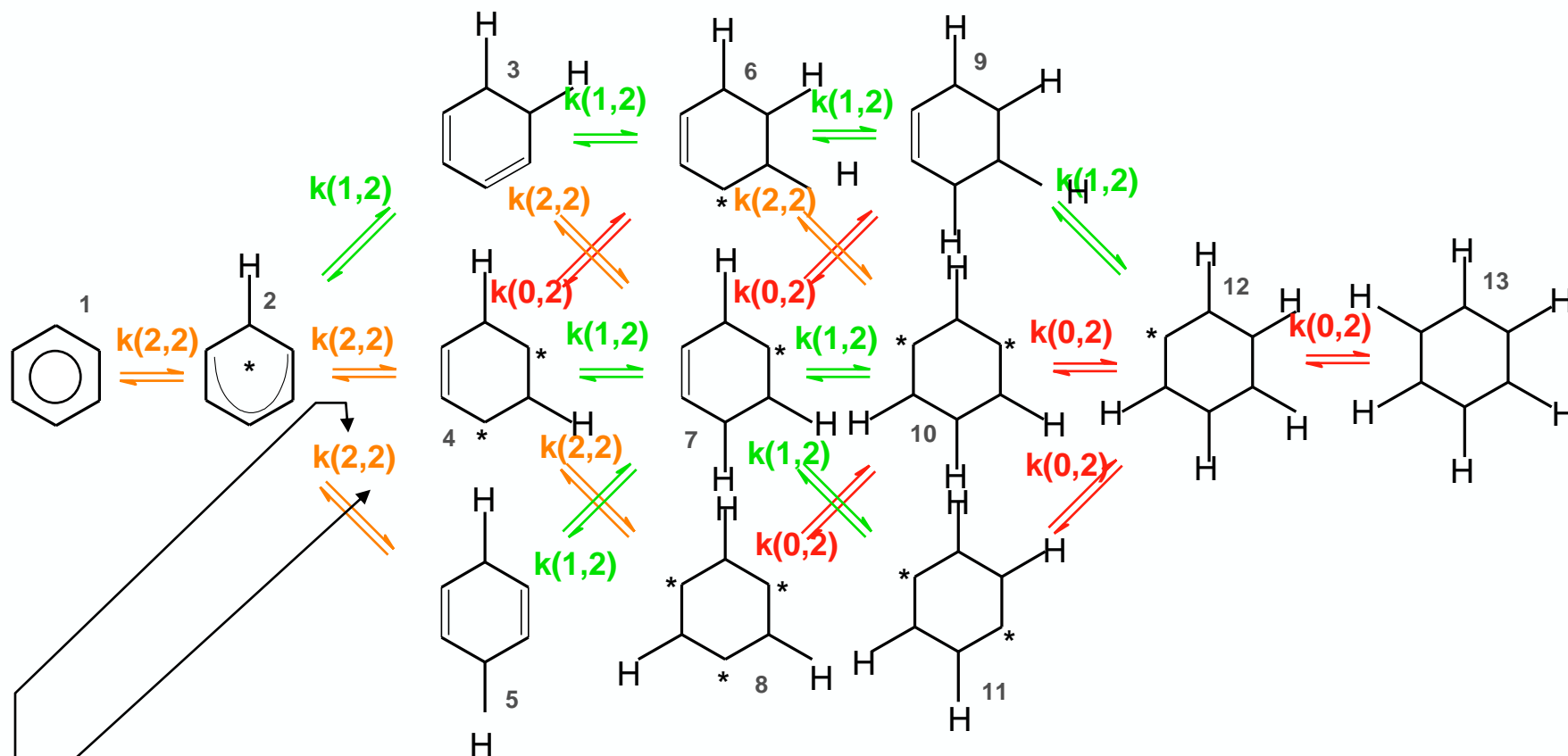**Distinctive feature:**-Saturation of the 1st neighbors

-Branching degree of the Carbon atom

SEMK of Aromatics

- Large number of species
- Large number of elementary steps
- Limited number of reaction families defined based on
  - Saturation state of nearest neighbor ($m=0,1,2$)

  - Degree of branching of reacing C-atom ($n=2,3$)

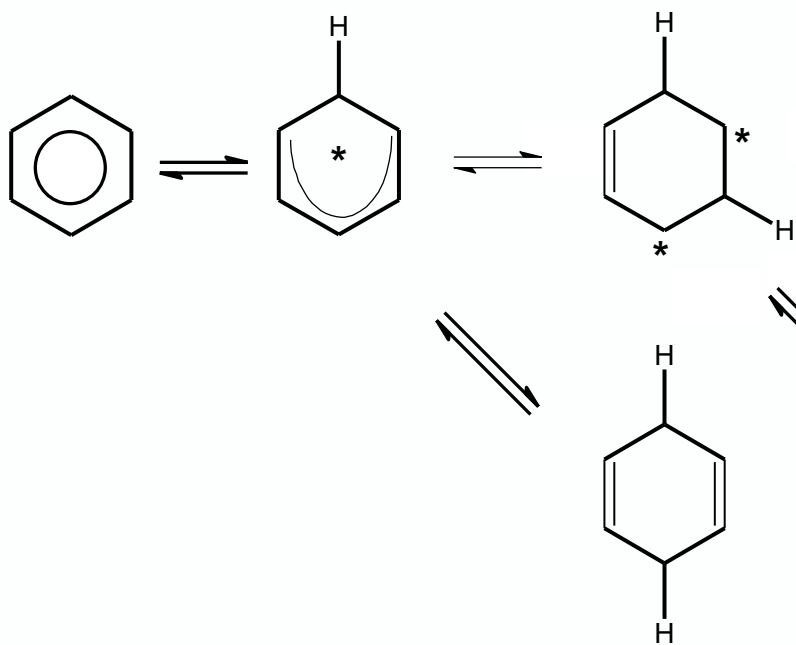energy / enthalpy considerations

- Accounting for symmetry effects (entropy)

- Branching degree
- Number of unsaturated nearest neighbors

Single-Event concept

symmetry effects within a reaction family

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

$$S = S_{trans} + S_{rot} + S_{vib}$$

$$S_{rot} = \tilde{S}_{rot} - R \ln \sigma$$

$$\sigma_{glob} = \frac{\sigma_{ext} \sigma_{int}}{2^n}$$

$$k(m,n) = \frac{\sigma_{global}^{reactant}}{\sigma_{global}^{\#}} \frac{k_b T}{h} \exp\left(\frac{\Delta \tilde{S}^{0,\#}}{R}\right) \exp\left(-\frac{\Delta H^{0,\#}}{RT}\right)$$

$$k(m,n) = n_e \tilde{k}(m;n)$$

Reaction network generation

- aromatics
- cyclodienyl
- cyclodienes
- cycloalkenyl
- cycloalkenes
- cycloalkyl
- cycloalkanes

previously existing species

newly defined species

metal chemisorbed cyclic hydrocarbons

network size:

	# species	#reactions
benzene	13	20
toluene	40	104
O-xylene	36	96

Label

0

2 2 2 2 2 2

20 20 20 20 20 21

→ Unsaturated naphthenic carbon

H
6
1
*

Boolean matrix

	1	2	3	4	5	6	
1	0	1	0	0	0	1	1
2	1	0	1	0	0	0	1
3	0	1	0	1	0	0	1
4	0	0	1	0	1	0	1
5	0	0	0	1	0	1	1
6	1	0	0	0	1	0	0

Unsaturated naphthenic carbon

Saturated naphthenic carbon

Network size:

	# Species	#Reactions
Benzene	13	20
Toluene	40	104
O-xylene	36	96

Rate equations

$$R_j \quad = \quad \sum_i r_{i \to j}^{hyd/deh} - r_{j \to i}^{deh/hyd}$$

i,j: metal chemisorbed cyclic hydrocarbons

$$R_j \quad = \quad \sum_i \left(\begin{array}{l} n_{e,i \to j} \left[\tilde{k}_{hyd}(m_i, n_i) C_{H^*} + \tilde{k}_{deh}(m_i, n_i) C_* \right] C_i \\ -n_{e,j \to i} \left[\tilde{k}_{hyd}(m_i, n_i) C_{H^*} + \tilde{k}_{deh}(m_i, n_i) C_* \right] C_j \end{array} \right)$$
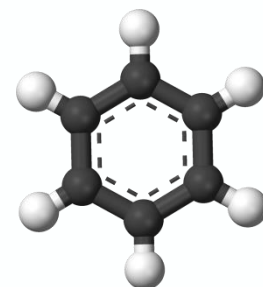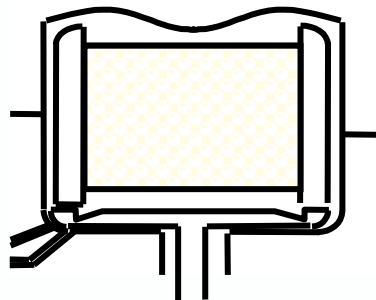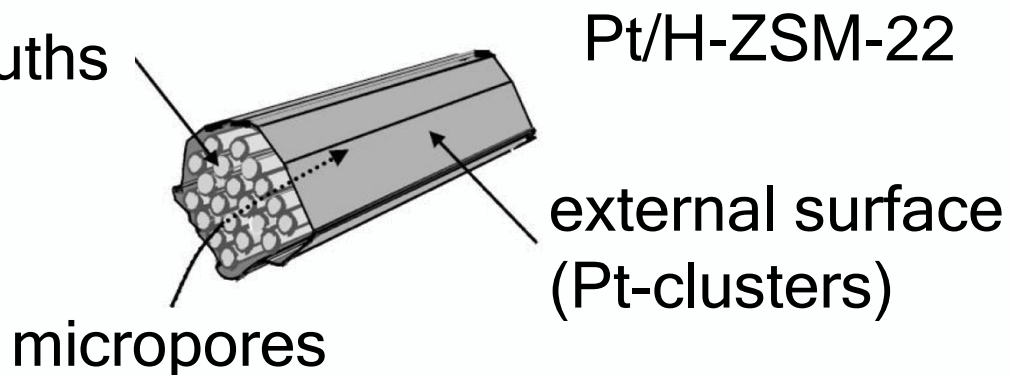
C_i, C_{H^*} and C_* obtained from:

• chemisorption equilibria for aromatic, hydrogen and cyclohexane

• pseudo steady state approximation for all other metal chemisorbed cyclic hydrocarbons

• site balance

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Experimental methods

pore mouths

Pt/H-ZSM-22

external surface
(Pt-clusters)

micropores

Berty-reactor:

- gas phase
- perfectly mixed
- continuous flow

benzene:

- ab initio reaction path analysis available
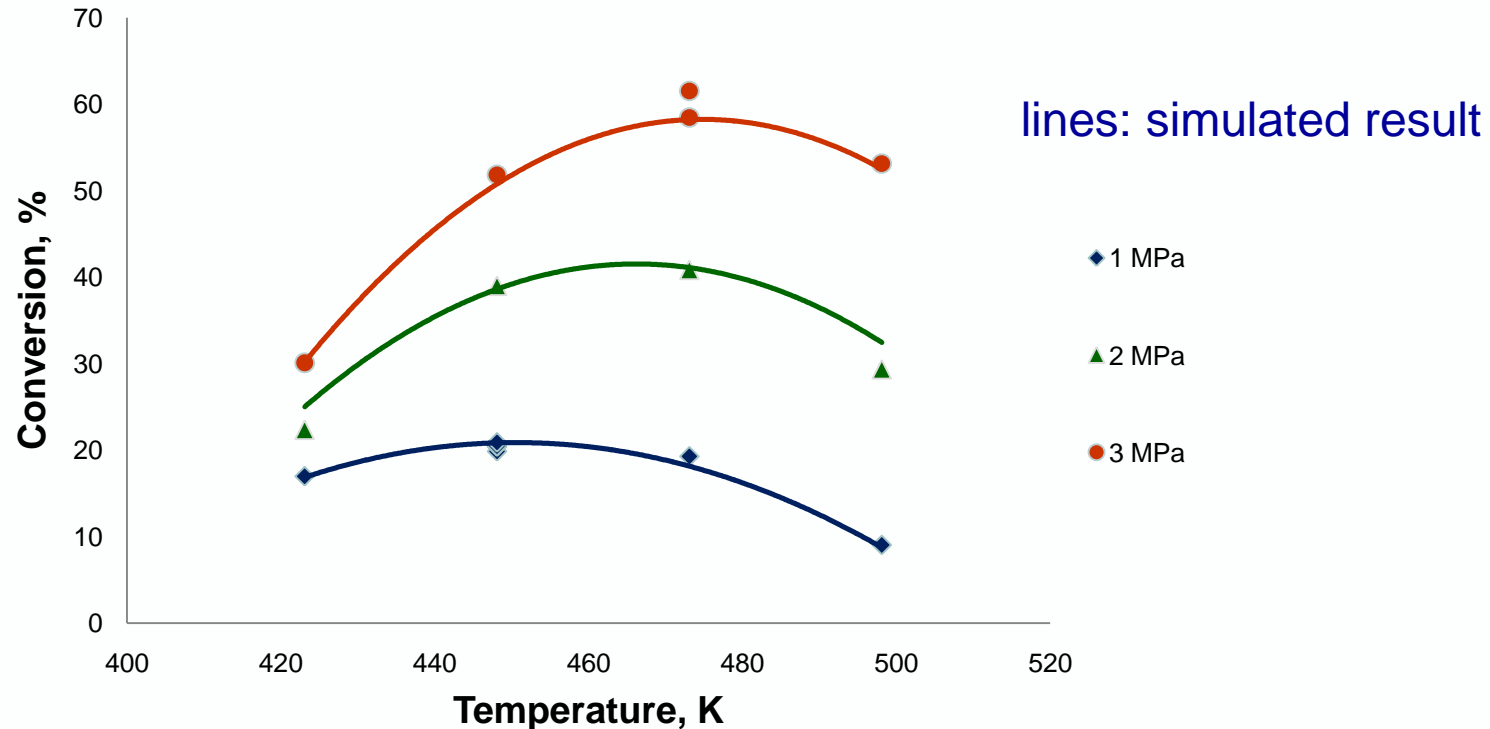- a single secondary reaction

Operating conditions

T (K)	p_{tot} (MPa)	$p_{benzene}$ (kPa)	$p_{hydrogen}$ (kPa)
423 – 498	1 – 3	10 – 60	100 – 600

- W/F$_0$:20 – 70 kg$_{cat}$ s mol^{-1}
- Data set of 43 experiments

Experimental results

Temperature effect: adsorption effects
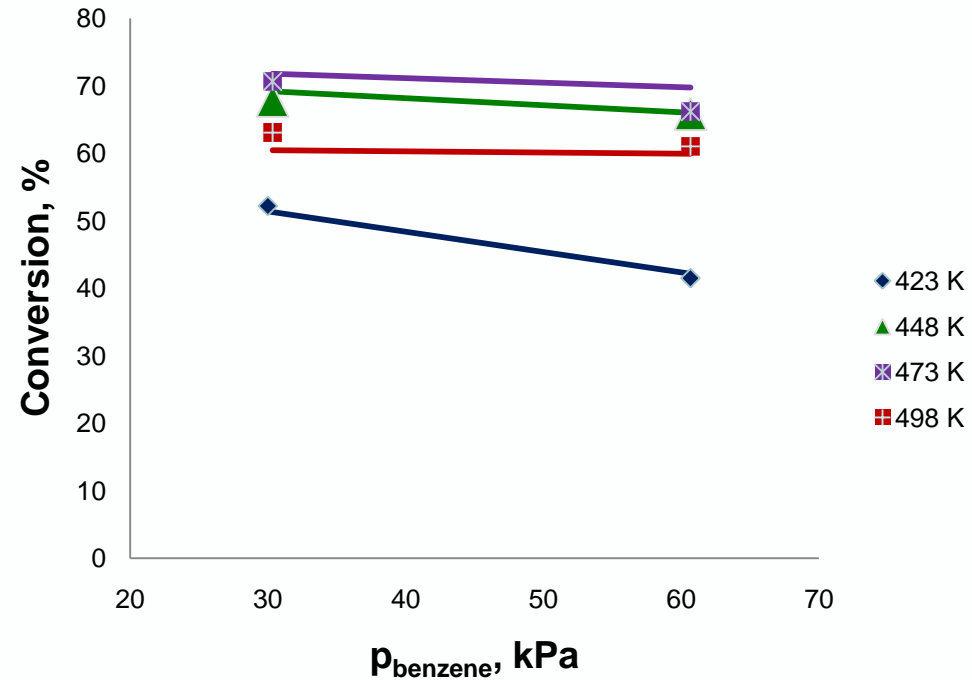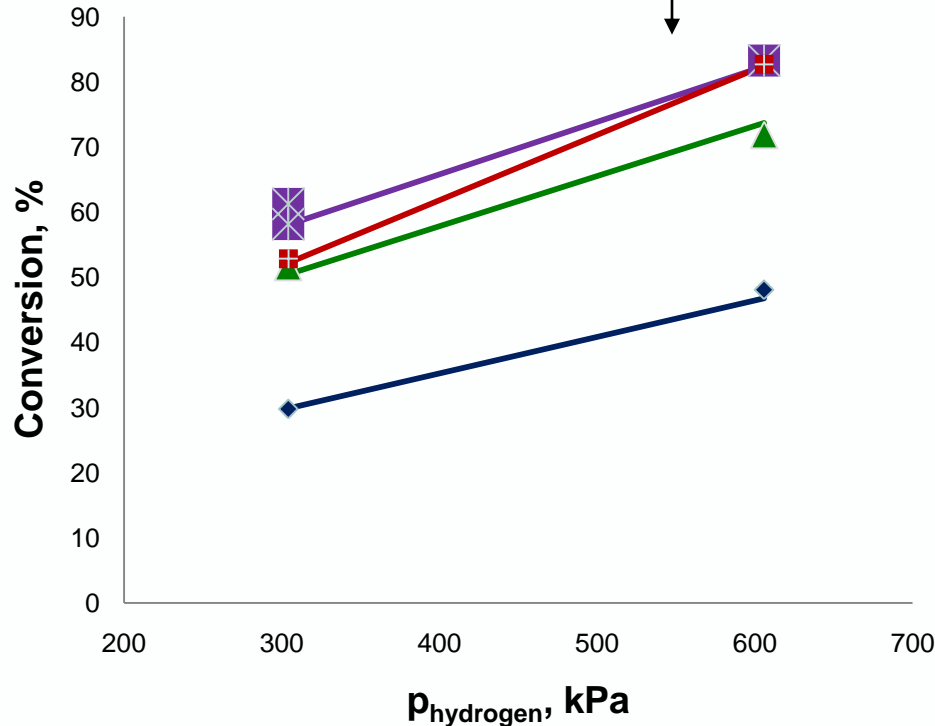

lines: simulated result

positive at lower T/negative at higher T

maximum shifts to higher T with increasing p_t

Experimental results

Inlet partial pressure effects:

- no or inhibiting effect by benzene $\longrightarrow$

- positive effect by hydrogen

Conversion, % (vs **p_benzene, kPa**)

- ◆ 423 K
- ▲ 448 K
- ✖ 473 K
- ⊞ 498 K

Conversion, % (vs **p_hydrogen, kPa**)

- ◆ 423 K
- ▲ 448 K
- ✖ 473 K
- ⊞ 498 K

lines: simulated result

Model parameters of benzene

- 3 reaction families
  - rate coefficient
  - equilibrium coefficient

- H_2, benzene, cyclohexane
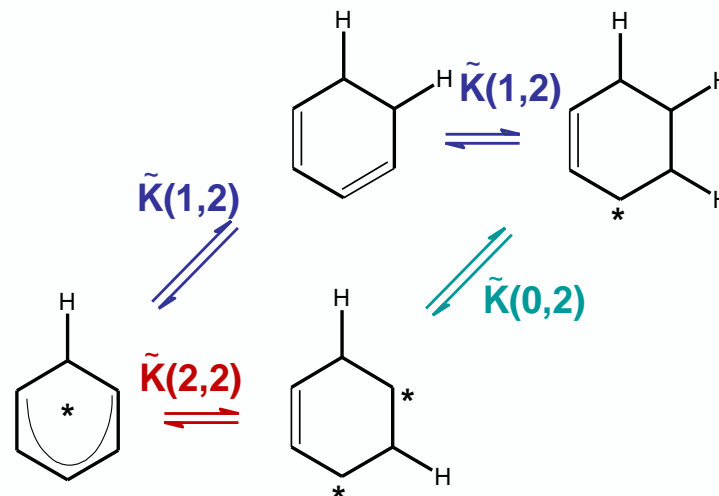 - chemisorption coefficient

  9 coefficients

  18 parameters

Values obtained from

- thermodynamic consistency (4 parameters)

- statistical thermodynamics (7 preexponential factors)

- Regression :

  7 parameters

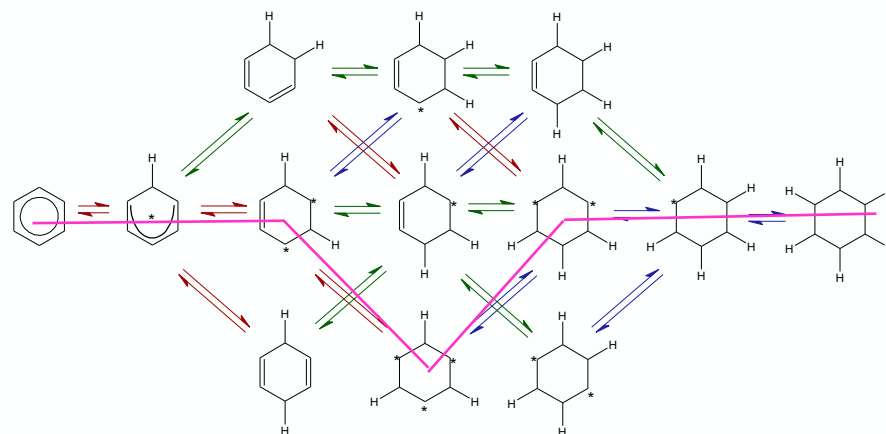 (3 activation energies,4 reaction & adsorption enthalpies)

Thermodynamic consistency

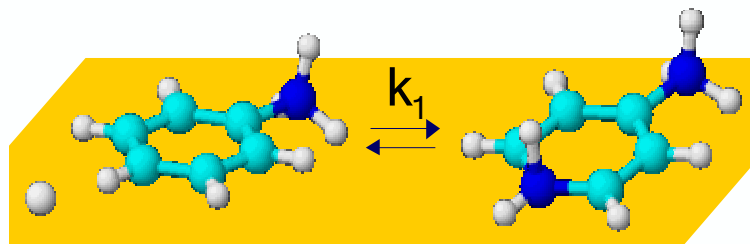$$\tilde{K}(1,2) \cdot \tilde{K}(1,2) = \tilde{K}(2,2) \cdot \tilde{K}(0,2)$$

Both for enthalpy and entropy

$$K = \frac{K_{chem,B} K_{chem,H_2}^3 K_{r(2,2)}^3 K_{r(0,2)}^3}{K_{chem,CH}}$$

Pre-exponential factors

Calculation of preexponential factors:

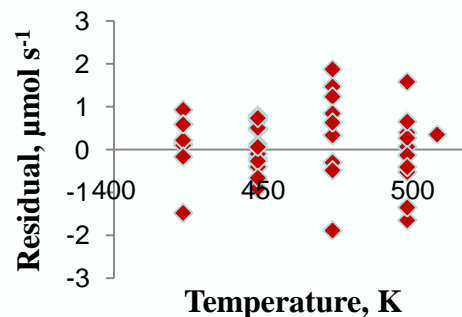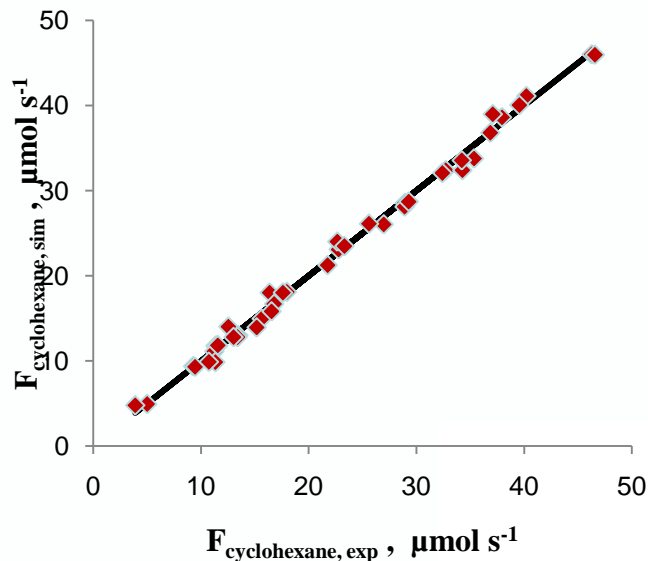$$k_1 = \frac{k_B T}{h} \frac{Q''_{A-H^{\neq}}}{Q''_A Q''_H} \exp\left(-\frac{E^{0,\neq}}{k_B T}\right)$$

$$\underbrace{}_{k_1^0} \quad \text{with} \quad Q''_A = q''_{A,trans}\, q_{A,rot}\, q_{A,vib}$$

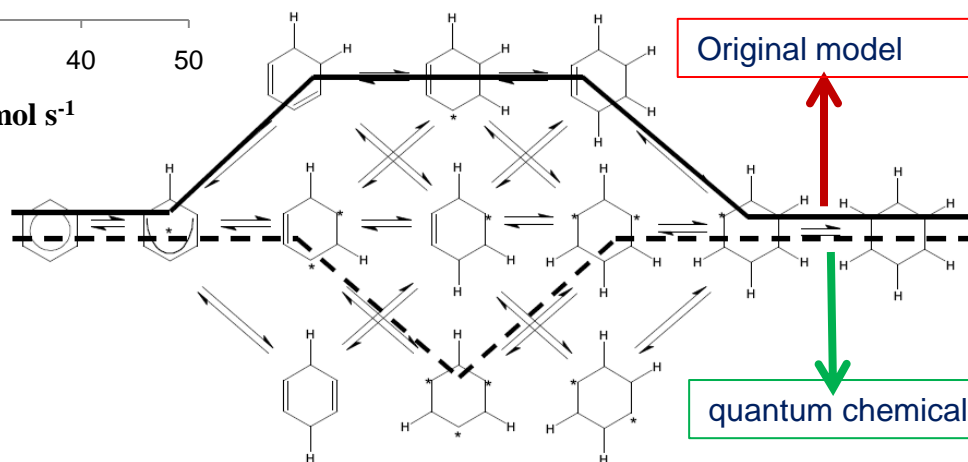|	Value adopted
K_A^0, Pa^{-1}	10^{-12}
$K_{H_2}^0$, ,Pa^{-1}	10^{-11}
k_{surf}^0, , s^{-1}	10^{16}
K_{surf}^0	1

- $k_{surf}^0 \approx 10^8$ to 10^{16} s^{-1}
- $K_{surf}^0 \approx 1$ to 10^{-5}
- $K_A^0 \approx 10^{-10}$ to 10^{-13} Pa^{-1}
- $K_{H_2}^0 \approx 10^{-8}$ to 10^{-13} Pa^{-1}

Regression results: original model

– **Unconstrained regression** [the activation energies $E_a(m,n)$ are assessed separately]

Parameter values (kJ mol^{-1})		
$E_a(0,2)$	$E_a(1,2)$,	$E_a(2,2)$
61.9 ± 2.1	50.9 ± 15.1	66.5 ± 0.6
$\Delta H(0,2)$	$\Delta H(1,2)$	$\Delta H(2,2)$
$2.2 \pm 1,3$	$4.3*$	6.5 ± 0.5
$\Delta H_{Benzene}$	$\Delta H_{cyclohexane}$	$\Delta H_{Hydrogen}$
$-64.5 \pm {<}0.5$	$-4.8*$	$-59.6 \pm {<}0.5$

F value: 4763

Original model

quantum chemical pathway

*: calculated from thermodynamic consistency

Regression results: simplified model

constrained regression: : Ea(1,2) > [Ea(0,2) = Ea(2,2)]

Parameter (kJ mol^{-1})	Original model: unconstrained regression	Simplified model Ea(2,2) = Ea(0,2) < Ea(1,2)
$E_a(0,2)$	61.9 ± 2.0	57.5 ± 0.5
$E_a(1,2)$	50.9 ± 15.1	65.1 ± 1.9
$E_a(2,2)$	66.5 ± 0.6	57.5 ± 0.5
$\Delta H(0,2)$	2.2 ± 1.2	7.9 ± 0.4
$\Delta H(1,2)$ *	4.3	4.5
$\Delta H(2,2)$	6.5 ± 0.5	1.2 ± 0.3
ΔH_B	-64.5 ± <0.5	-56.0 ± <0.5
ΔH_{H2}	-59.6 ± <0.5	-59.4 ± <0.5
ΔH_{CHA} *	-4.8	5.3
Number of parameters	7	6
F value	4763	4150

Working catalyst surface

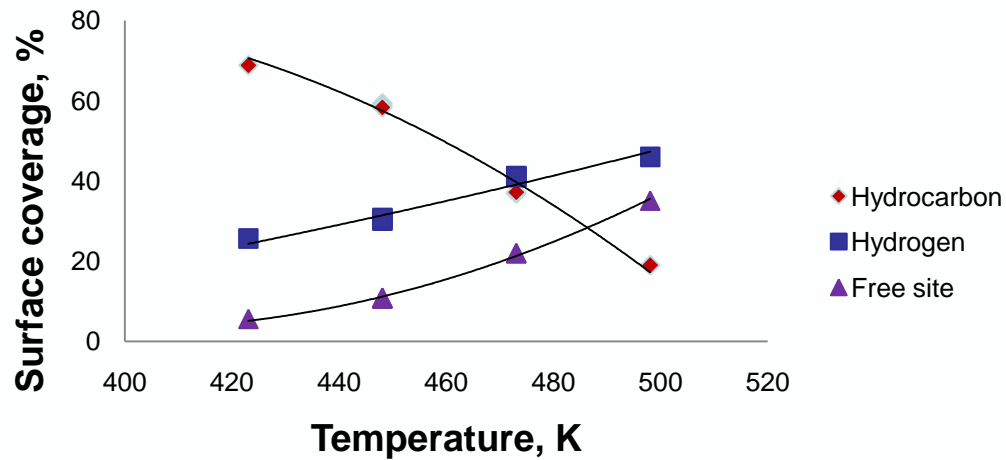| Parameter values (kJ mol⁻¹)		
$E_a(0,2)$	$E_a(1,2)$,	$E_a(2,2)$
61.9 ± 2.1	50.9 ± 15.1	66.5 ± 0.6
$\Delta H(0,2)$	$\Delta H(1,2)$	$\Delta H(2,2)$
2.2 ± 1,3	4.3*	6.5 ± 0.5
$\Delta H_{Benzene}$	$\Delta H_{cyclohexane}$	$\Delta H_{Hydrogen}$
-64.5 ± <0.5	-4.8*	-59.6 ± <0.5

Surface concentrations

- 60 % hydrocarbons
- 30 % hydrogen
- 10 % free

1	9.8
2	15.0
3	13.0
4	7.2
5	3.6
6	11.2
7	12.7
8	1.2
9	9.7
10	5.6
11	2.8
12	8.3
13	<<

Original model

Modeling results
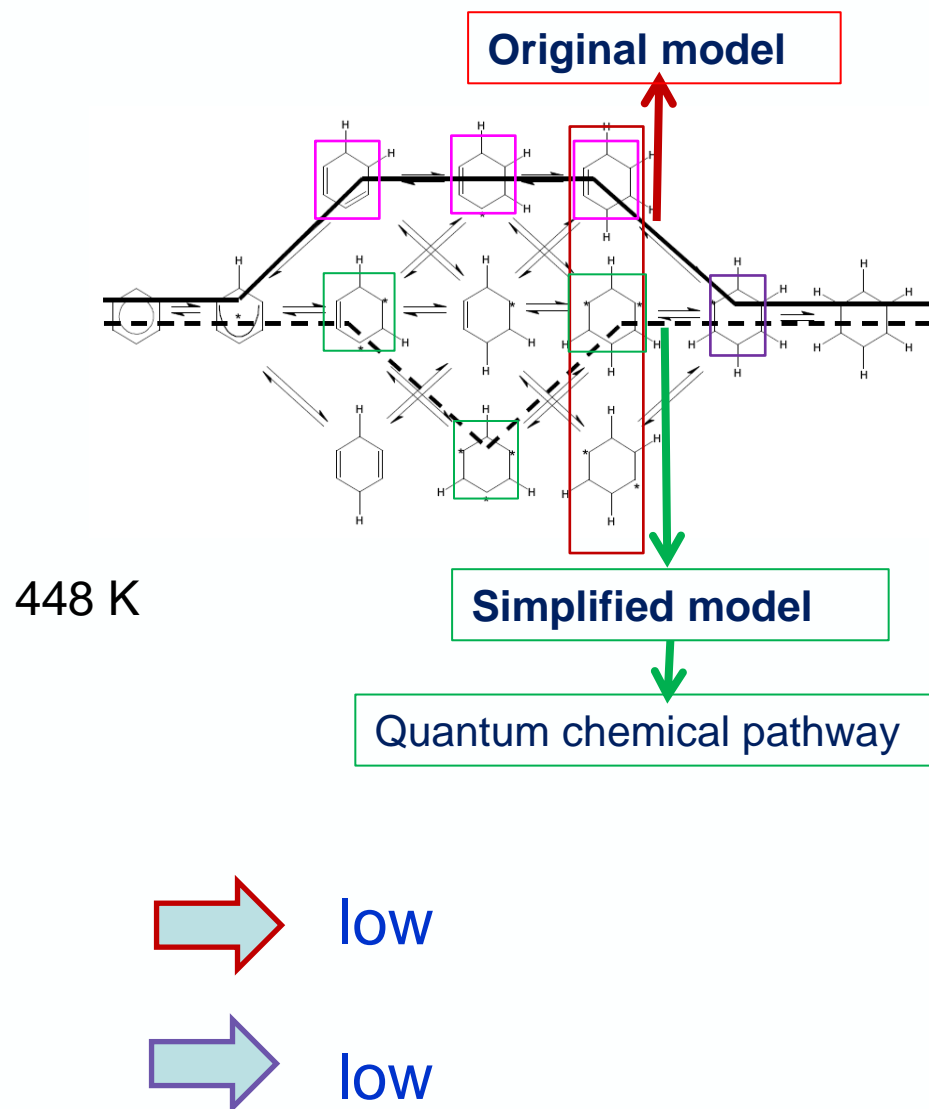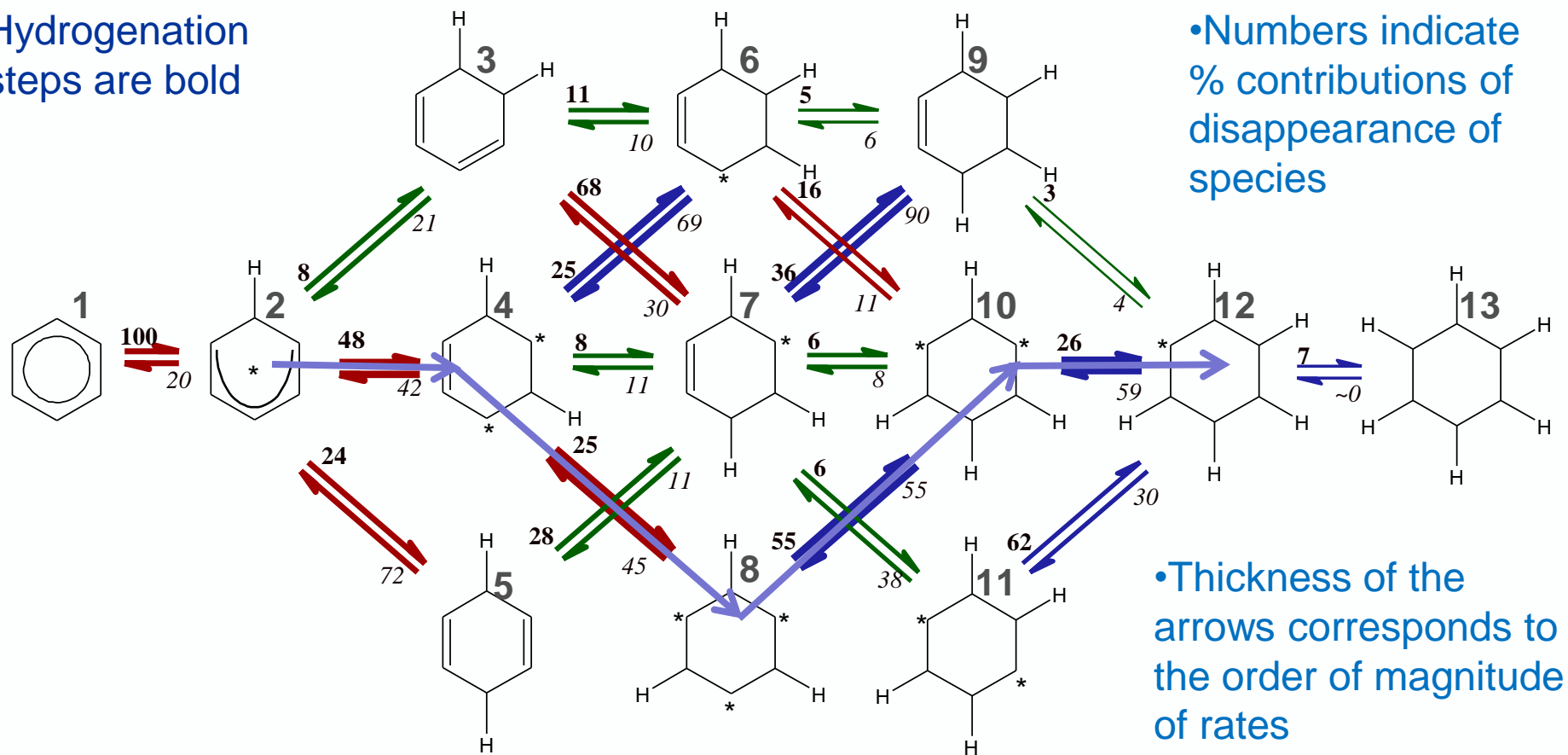
Model selection: Surface concentration

	Original model: unconstrained regression	Simplified model: $Ea(2,2) = Ea(0,2) < Ea(1,2)$
B (1)	9.8	1.2
BH (2)	15.0	8.8
13CHD (3)	13.0	6.2
13DHB (4)	7.2	15.7
14CHD (5)	3.6	8.4
123THB (6)	11.2	5.0
124THB (7)	12.7	24.6
135THB (8)	1.2	9.7
CHE (9)	9.7	4.0
1235THB (10)	5.6	9.2
1245THB (11)	2.8	4.3
c-Hexyl (12)	8.3	2.7
CHA (13)	~0	~0

448 K

Original model

Simplified model

Quantum chemical pathway

⇨ low

⇨ low

Reaction path analysis: simplified model

Hydrogenation steps are bold

•Numbers indicate % contributions of disappearance of species

•Thickness of the arrows corresponds to the order of magnitude of rates

Contribution analysis for benzene hydrogenation on Pt/ZSM-22 at 498 K for 48% conversion

Energy profile along dominant reaction

- Introduction
- Reaction network
  - reaction family definition
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  - rate equations
- Parameter calculation and estimation
  - experimental data
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- Conclusions

Conclusions

- SEMK methodology is successfully extended for aromatics hydrogenation

- The simplified version of the model is preferred in which a pathway of meta-position hydrogen addition is followed in accordance with quantum chemical calculation

- Catalyst surface is mainly occupied by hydrocarbon species with relatively low mobility

- Hydrogen addition reactions on a Pt surface are practically thermoneutral

THANK YOU