UNIVERSITEIT GENT

FACULTY OF ENGINEERING

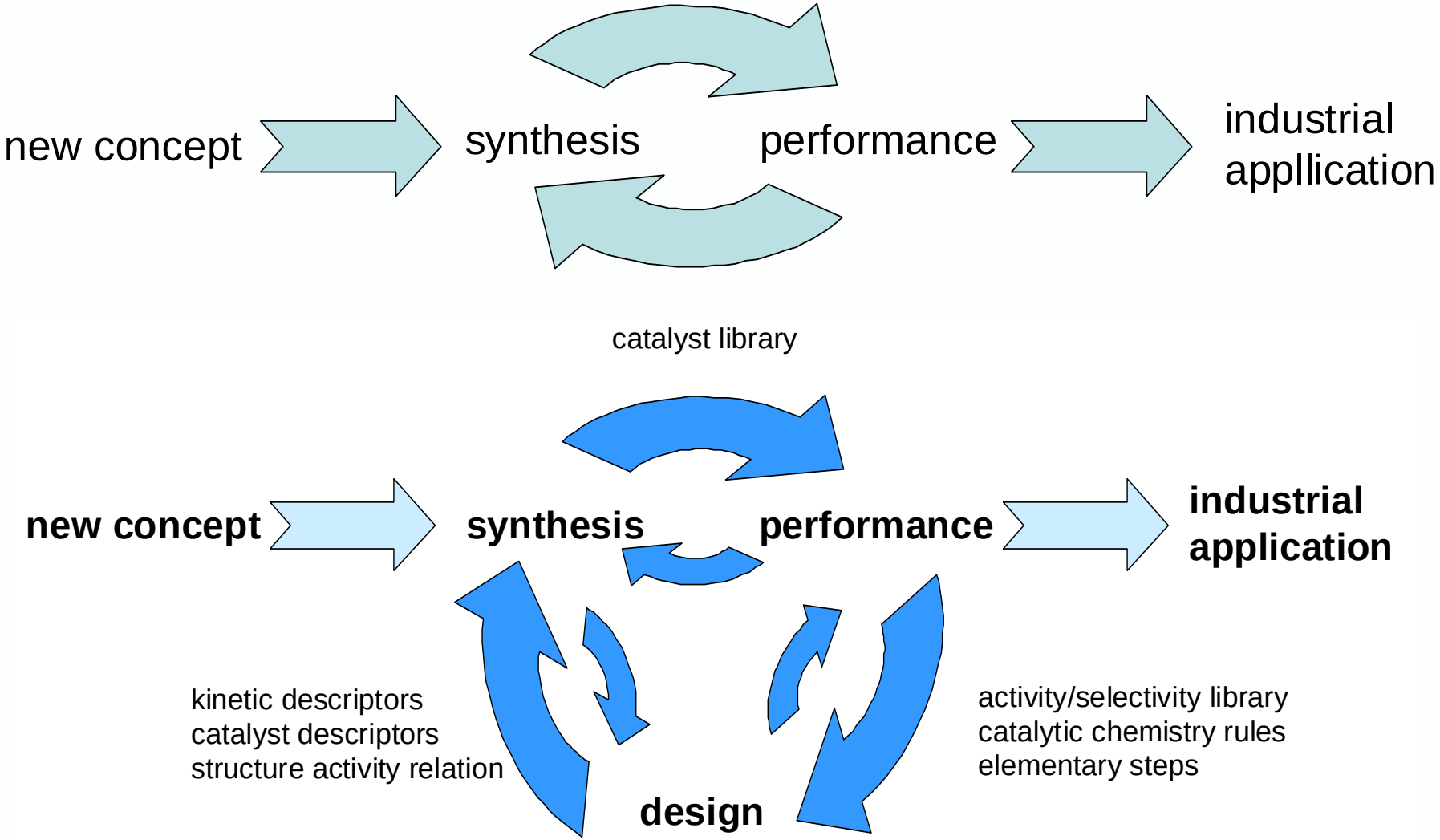
Single-Event Microkinetic Assisted Design of New and Improved Catalytic Materials

J. W. Thybaut and Guy B. Marin

Laboratory for Chemical Technology
http://www.lct.UGent.be

IDECAT
Integrated Design of Catalytic Nanomaterials for a Sustainable Production

model based catalyst design



SEMK: application domains

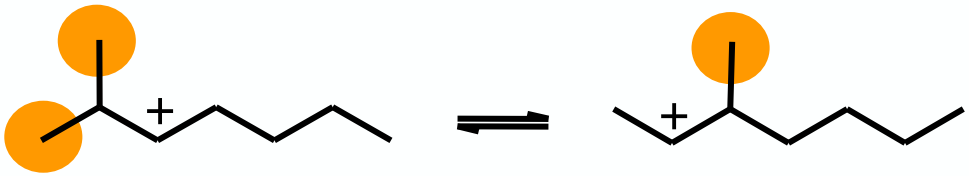
- thermal cracking
- acid catalysis
  - catalytic cracking
  - methanol to olefins
- metal catalysis
  - Fischer Tropsch synthesis
  - hydrogenation
- bifunctional catalysis
  - hydrocracking
  - catalytic reforming

essential features

- large number of species
- large number of elementary steps
- limited number of reaction families defined based on
  - reaction type
    - alkyl shift, PCP branching, β-scission,…
    - methylene insertion, reductive elimination,…
  - types of intermediates involved
    - carbon atom type in reactive moiety of reactant and product
- accounting for symmetry effects

single-event = accounting for symmetry

- reaction family of s,s methylshift



- rate coefficient

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

$$S = -\ln \sigma_{global} + \tilde{S}$$

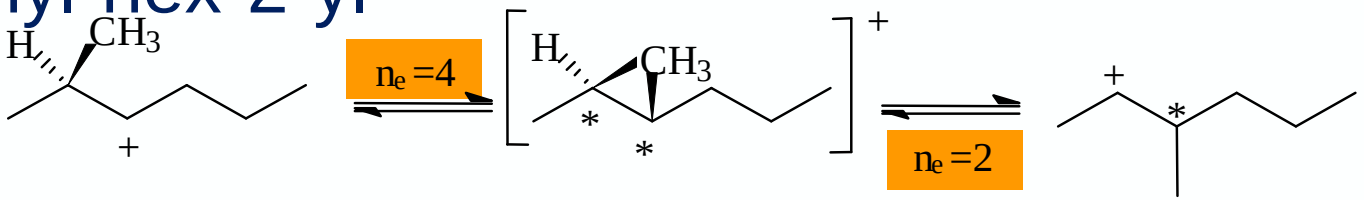
- writing symmetry explicitly

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

$$k = n_e \tilde{k}_{MS}(s;s)$$

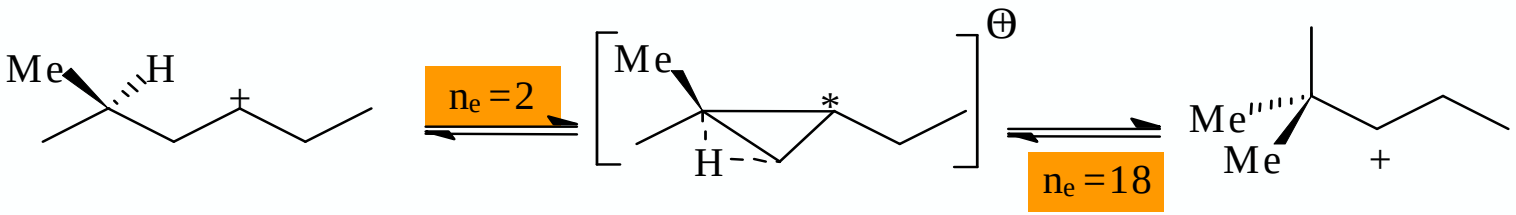
number of single events determination

- alkyl shift from 2methyl-hex-3-yl to 3methyl-hex-2-yl



$\sigma = 3^3$ $\quad \sigma = \frac{3^3}{4}$ $\quad \sigma = \frac{3^3}{2}$

- PCP branching from 5methyl-hex-3-yl to 2,2dimethylpent-3-yl

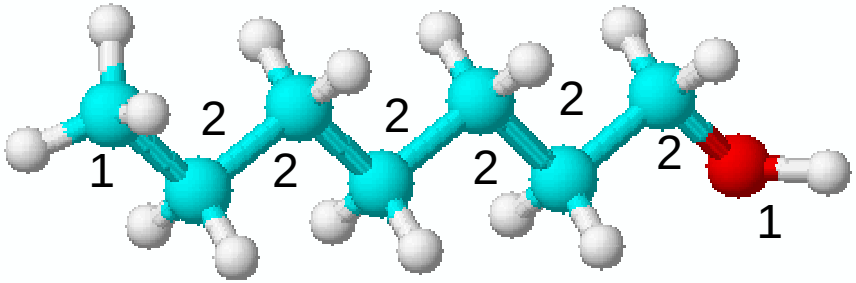


$\sigma = 3^3$ $\quad \sigma = \frac{3^3}{2}$ $\quad \sigma = 3^5$

outline

- necessary tools
  - reaction network generation
  - thermodynamic data generation
  - simulation and regression
- case 1: hydroconversion
  - USY-zeolite: free carbenium ion chemistry
  - ZSM-22: shape selectivity
- case 2: Fischer Tropsch synthesis
  - Fe and Co catalysts

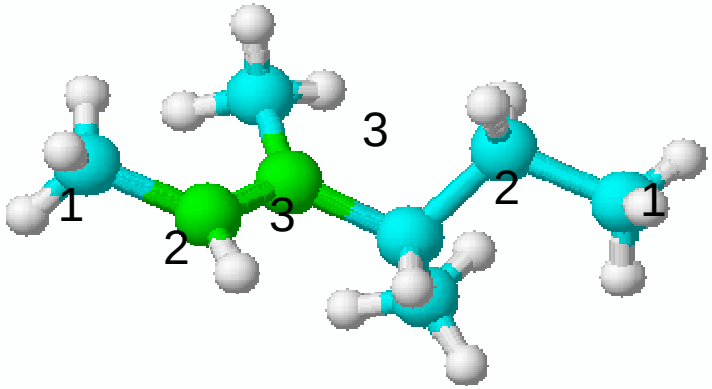
network generation: label representation



0

1 2 2 2 2 2 2 1

26 26 26 26 26 26 26 24

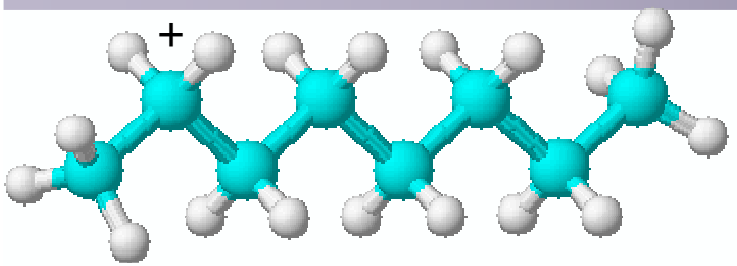


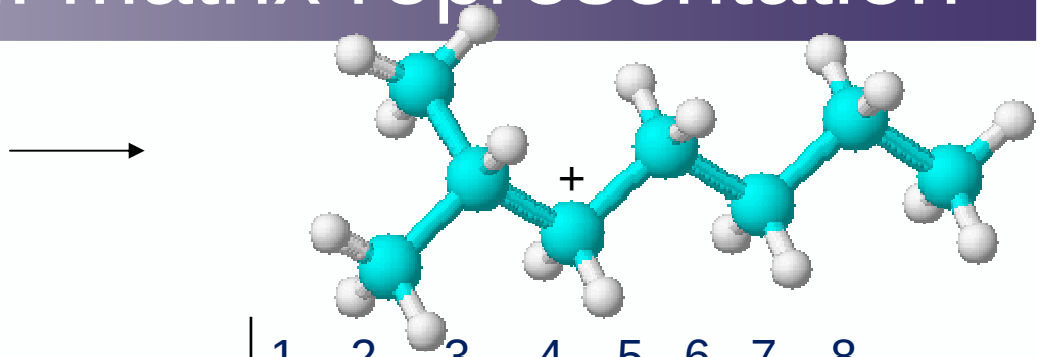
0

1 2 3 3 2 1 1 1

26 25 25 26 26 26 26 26

network generation: matrix representation



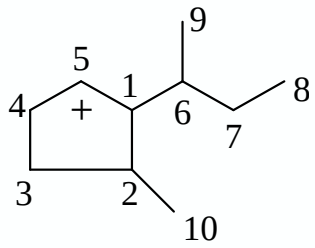


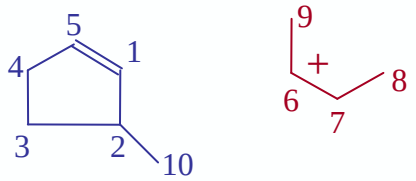
	1	2	3	4	5	6	7	8	
1		1							
2	1		1						+2
3		1		1					
4			1		1				
5				1		1			
6					1		1		
7						1		1	
8							1		
	2								
	1	2	2	2	2	2	2	1	
	26	26	26	26	26	26	26	26	

	1	2	3	4	5	6	7	8	
1		1							
2	1		1					1	
3		1		1					
4			1		1				+2
5				1		1			
6					1		1		
7						1			
8		1							
	4								
	1	3	2	2	2	2	1	1	
	26	26	26	26	26	26	26	26	

reaction network generation

A^2 – I : identification of the next nearest neighbours





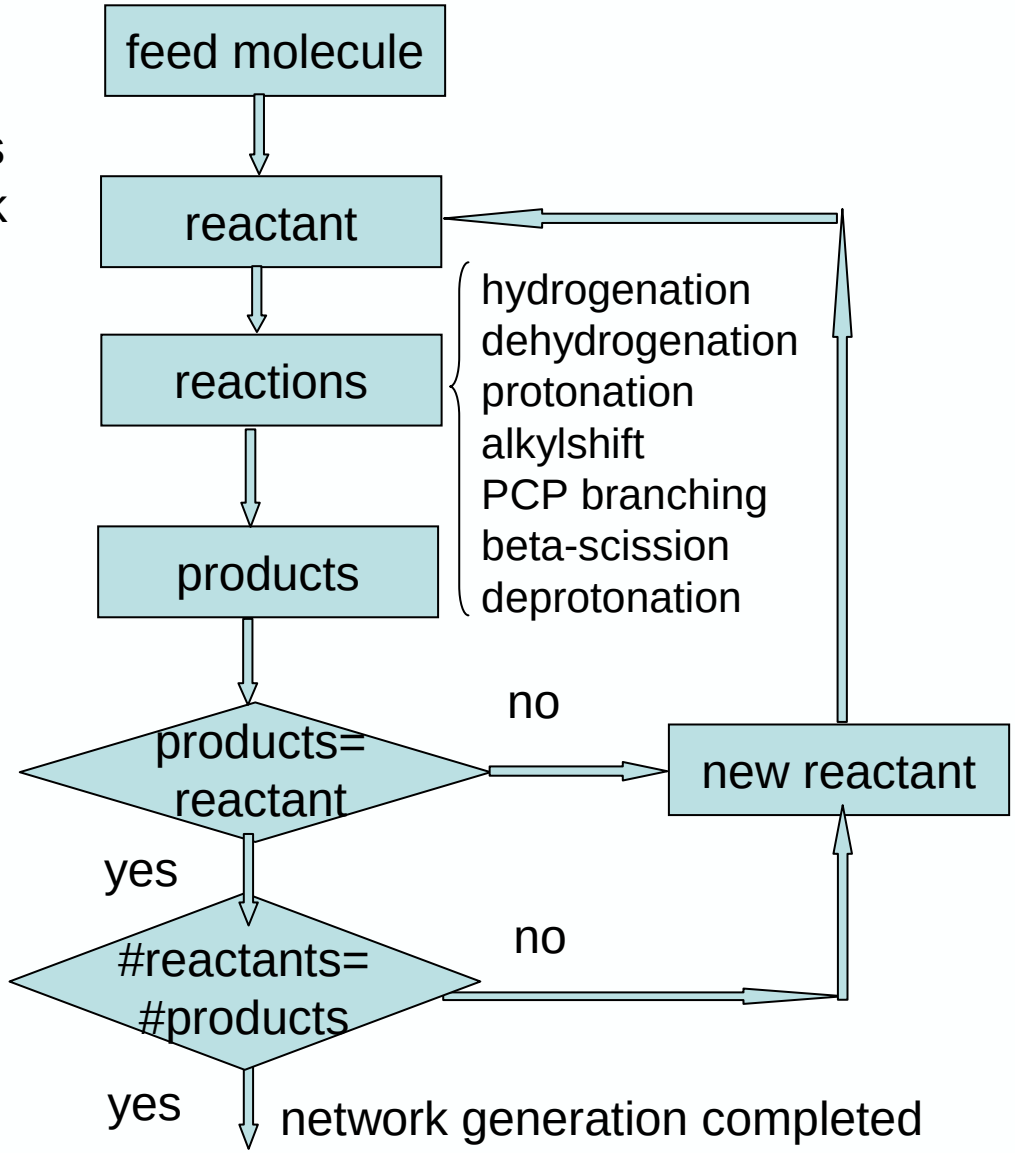
	1	2	3	4	5	6	7	8	9	10
1	0	1	0	0	1	1	0	0	0	0
2	1	0	1	0	0	0	0	0	0	1
3	0	1	0	1	0	0	0	0	0	0
4	0	0	1	0	1	0	0	0	0	0
5	1	0	0	1	0	0	0	0	0	0
6	1	0	0	0	0	0	1	0	1	0
7	0	0	0	0	0	1	0	1	0	0
8	0	0	0	0	0	0	1	0	0	0
9	0	0	0	0	0	1	0	0	0	0
10	0	1	0	0	0	0	0	0	0	0

	1	2	3	4	5	6	7	8	9	10
1	0	1	0	0	1	**0**	0	0	0	0
2	1	0	1	0	0	0	0	0	0	1
3	0	1	0	1	0	0	0	0	0	0
4	0	0	1	0	1	0	0	0	0	0
5	1	0	0	1	0	0	0	0	0	0
6	**0**	0	0	0	0	0	1	0	1	0
7	0	0	0	0	0	1	0	1	0	0
8	0	0	0	0	0	0	1	0	0	0
9	0	0	0	0	0	1	0	0	0	0
10	0	1	0	0	0	0	0	0	0	0

network generation algorithm

specify - feedstock &
- reaction families
in the network

reactant 1
product 1 reactant 2
product 2
product 3
product 4
product 5



network generation results

- feedstock: n-nonane

0
1 2 2 2 2 2 2 2 1
26 26 26 26 26 26 26 26 26

- final results:
  - n-nonane hydrocracking
    - paraffins: 44
    - olefin: 175
    - carbenium ions: 138

    } products

    - hydrogenation: 175
    - dehydrogenation: 175

    } metal catalysed reactions

    - protonation: 262
    - hydride shifts: 174
    - alkyl shifts: 182
    - PCP branching: 272
    - PCB branching: 254
    - beta scission: 53
    - deprotonation: 262

    } acid catalysed reactions

- feedstock: n-nonadecane

0
1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 1
26 26 26 26 26 26 26 26 26 26 26 26 26 26 26 26 26 26

- final results:
  - n-nonadecane hydrocracking
    - paraffins: 1981
    - olefin: 25065
    - carbenium ions: 20437

    - hydrogenation: 25065
    - dehydrogenation: 25065

    - protonation: 42600
    - hydride shifts: 33352
    - alkyl shifts: 12470
    - PCP branching: 15970
    - PCB branching: 20300
    - beta scission: 6429
    - deprotonation: 42600

thermodynamic data generation

- acid catalysis
  - enthalpy, entropy and specific heat capacity of alkanes and alkenes: group contribution method (Benson)
  - recognition of contributions from label representation
  - carbenium ions: from alkenes and standard protonation enthalpy
- metal catalysis
  - gas phase species: group contribution
  - surface species: UBI-QEP + assessment degrees of freedom

thermodynamic data: UBI/QEP

- heats of formation of surface species from atomic chemisorption enthalpies

$$E_{a,for} = fn\left(\Delta H^0_{r,surf}\right)$$

$$E_{a,rev} = E_{a,for} - \Delta H^0_{r,surf}$$

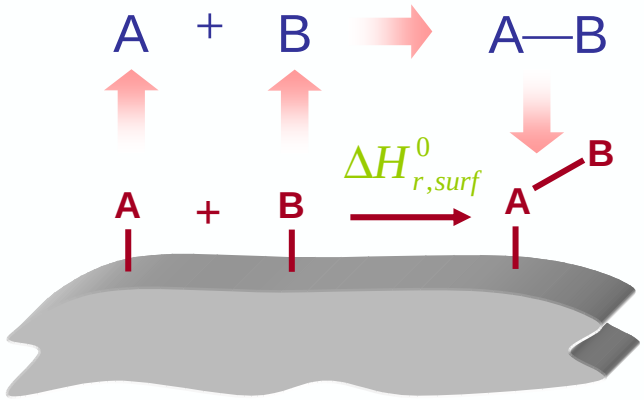
$$\Delta H^0_{r,surf} = \Delta H^0_{r,gas} + \sum_{i=1}^{nreact} \upsilon_i Q_i - \sum_{j=1}^{nprod} \upsilon_j Q_j$$

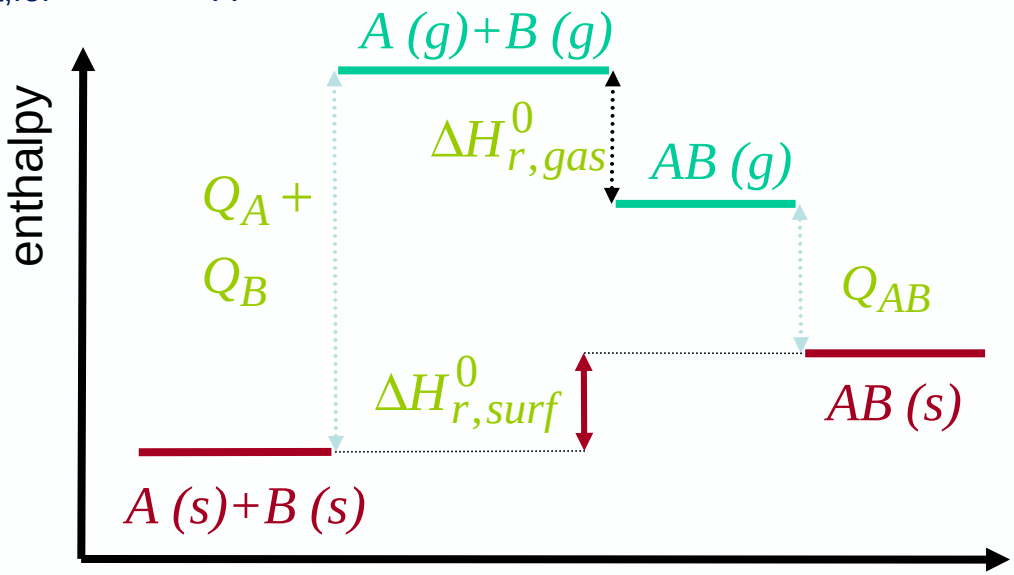
$$Q_{AB} = \frac{Q_A}{Q_A + D_{AB}}$$

"strong" chem. enthalpy

$$Q_A = (Q_C, Q_H, Q_O, ..)$$

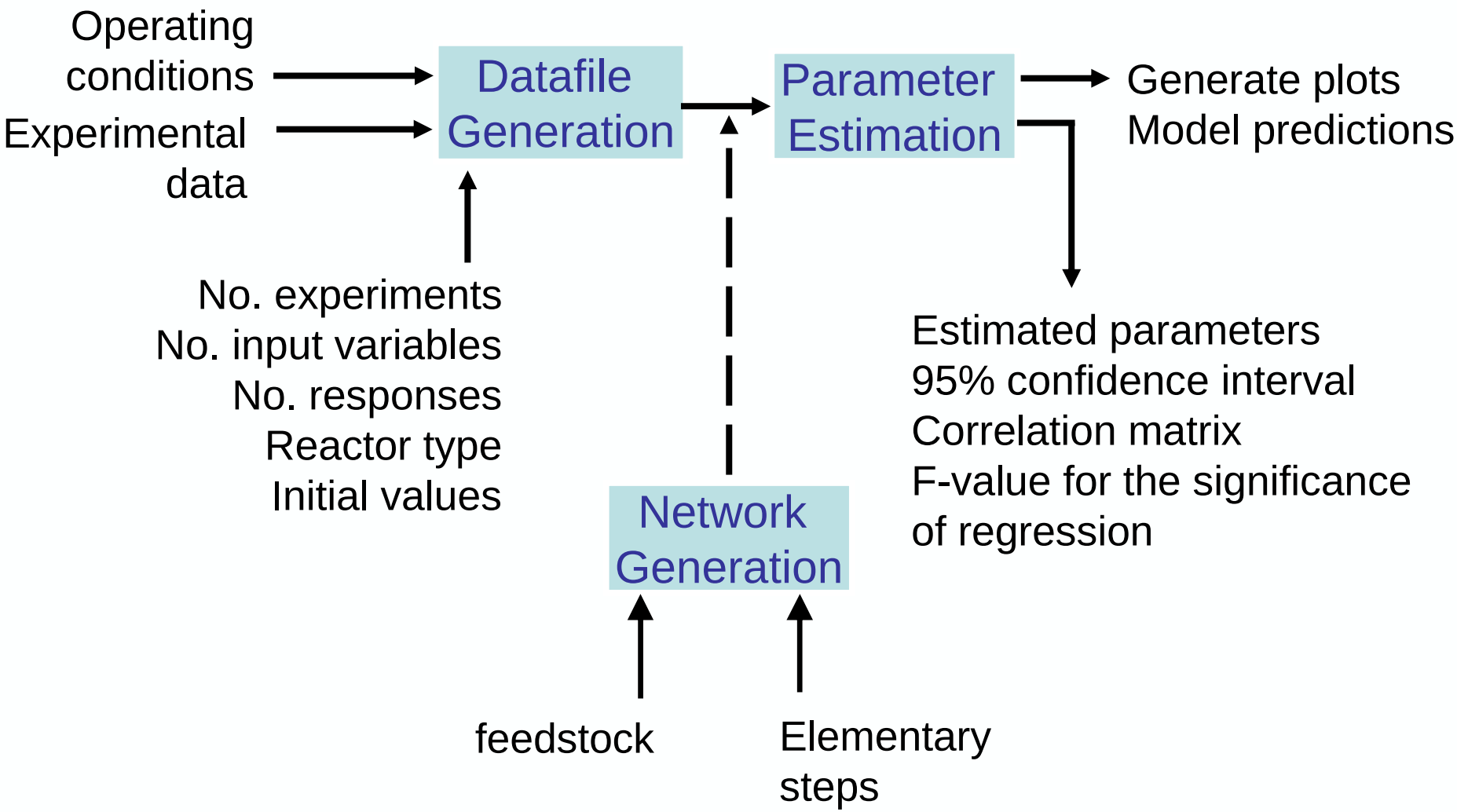
- adjustable parameters: $E_{a,for}$ and Q_A





Shustorovich et al., Surface Science Reports 31 (1998)

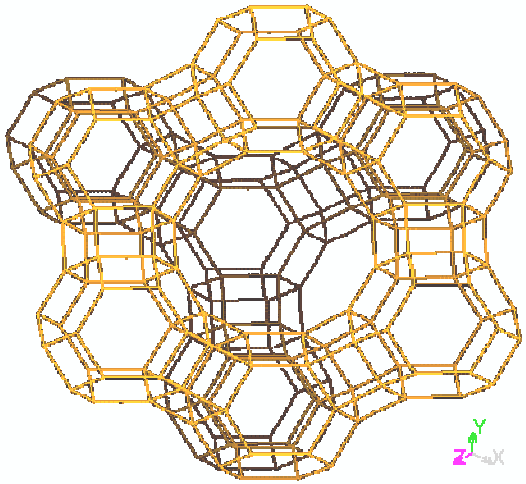
µKinetic Engine

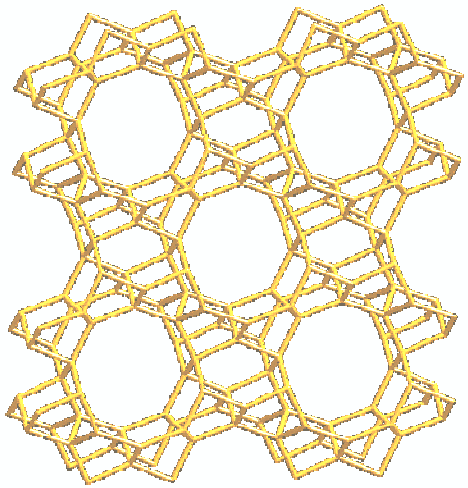


outline

- necessary tools
  - reaction network generation
  - thermodynamic data generation
  - simulation and regression
- case 1: hydroisomerization/-cracking
  - USY-zeolite: free carbenium ion chemistry
  - ZSM-22: shape selectivity
- case 2: Fischer Tropsch synthesis
  - Fe and Co catalysts

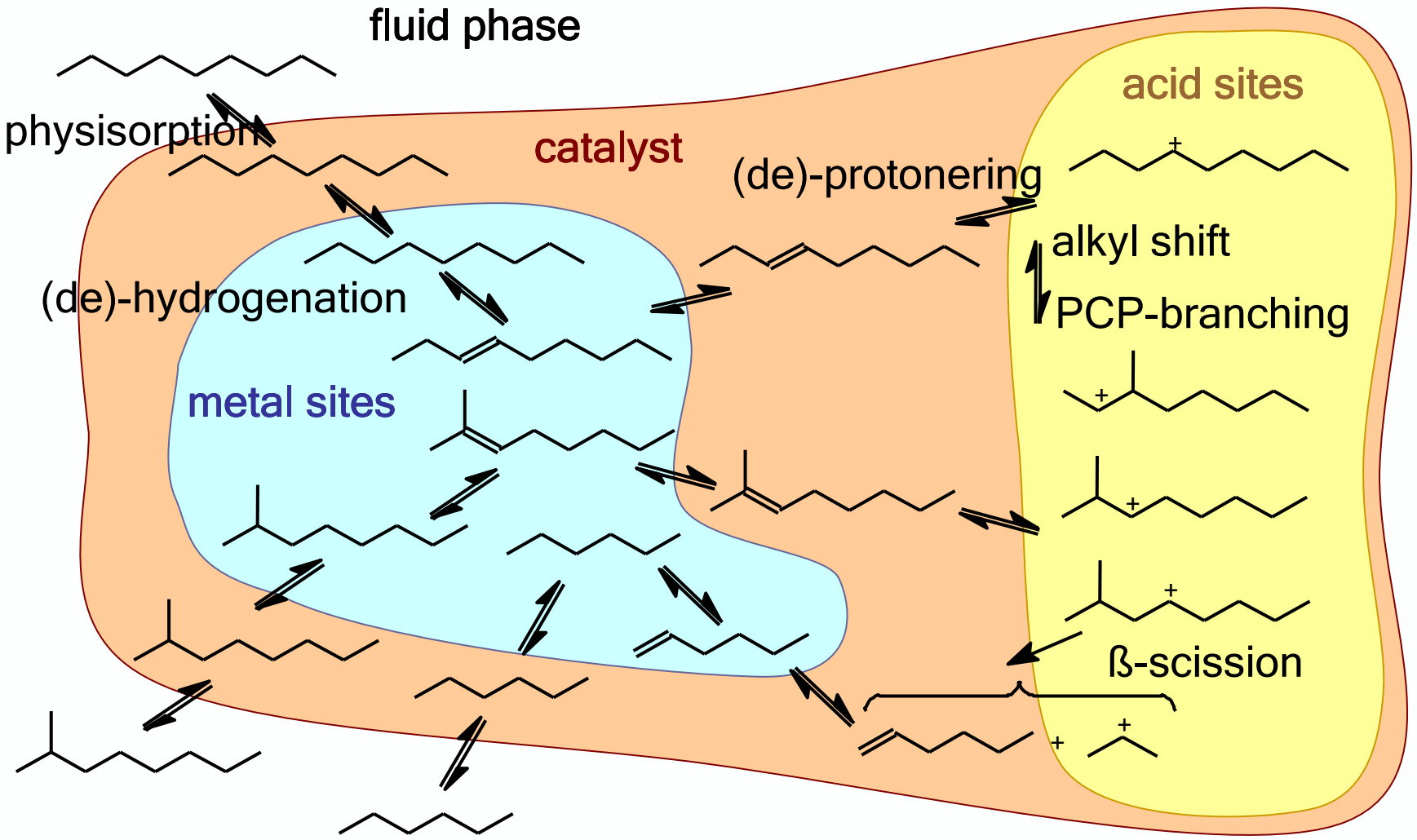
catalysts in hydrocracking





- USY
  - no shape selectivity
  - tuning acidity by dealumination
- ZSM-22
  - shape selectivity
  - enhanced monobranched isomer yield
  - suppressed cracking

hydroisomerization/-cracking



building blocks rate equation

alkyl-shift
PCP-branching
β-scission

$$r = n_e \tilde{k} C_{R^+}$$

(de)-protonation

$$C_{R^+} = \frac{C_t K_{prot} C_O}{1 + K_{prot} C_O} \cong C_t K_{prot} C_O$$

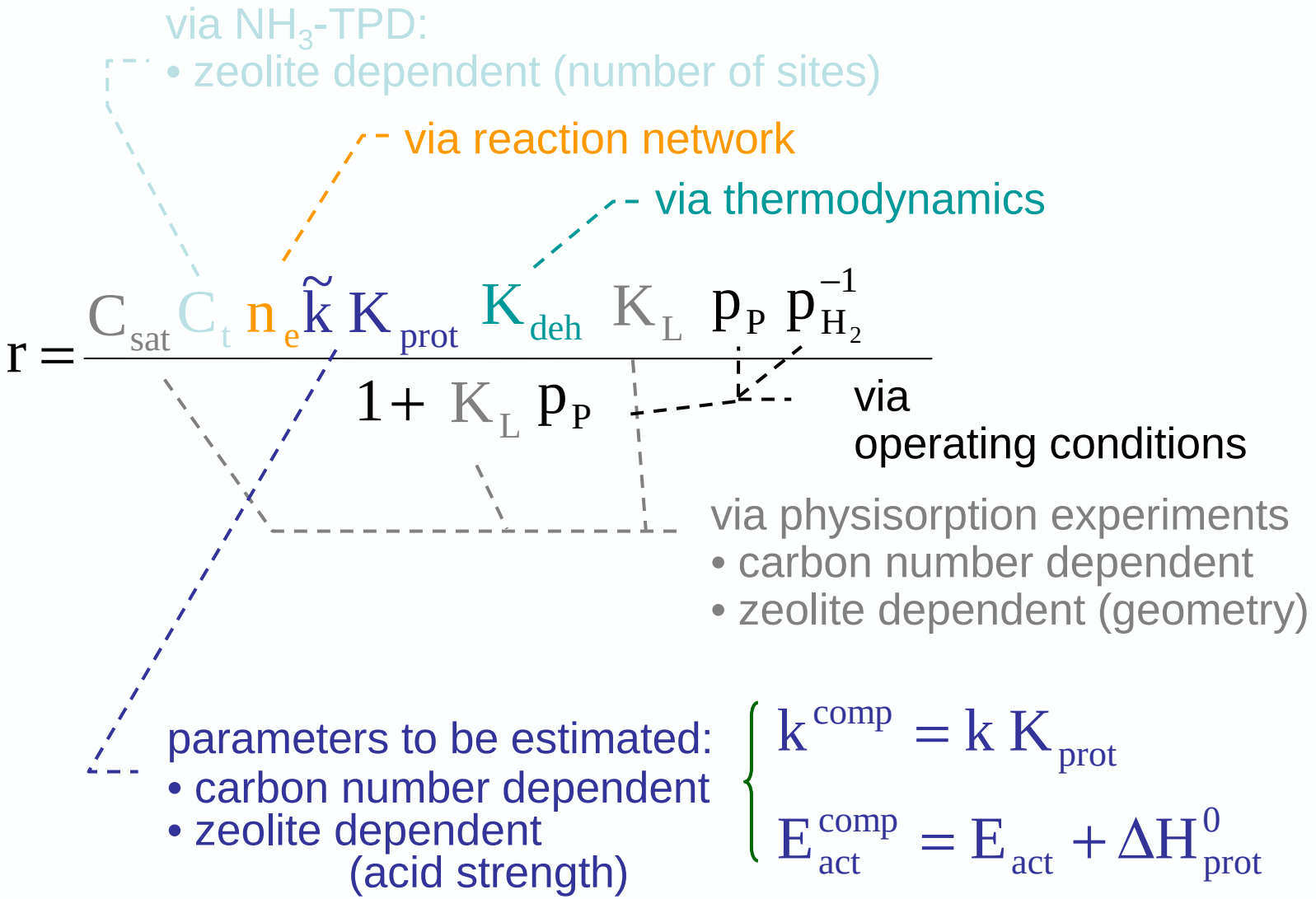
(de)-hydrogenation

$$C_O = \frac{K_{deh} C_P}{p_{H_2}}$$

physisorption

$$C_P = \frac{C_{sat} K_L p_P}{1 + K_L p_P}$$

detailed rate equation



net rates of formation

summation of all elementary steps

$$R_{P_i} = \sum_k R^{AS/PCP/\beta}_{R^+_{i,k}} + \sum_j R^{\beta}_{O_{i,j}}$$

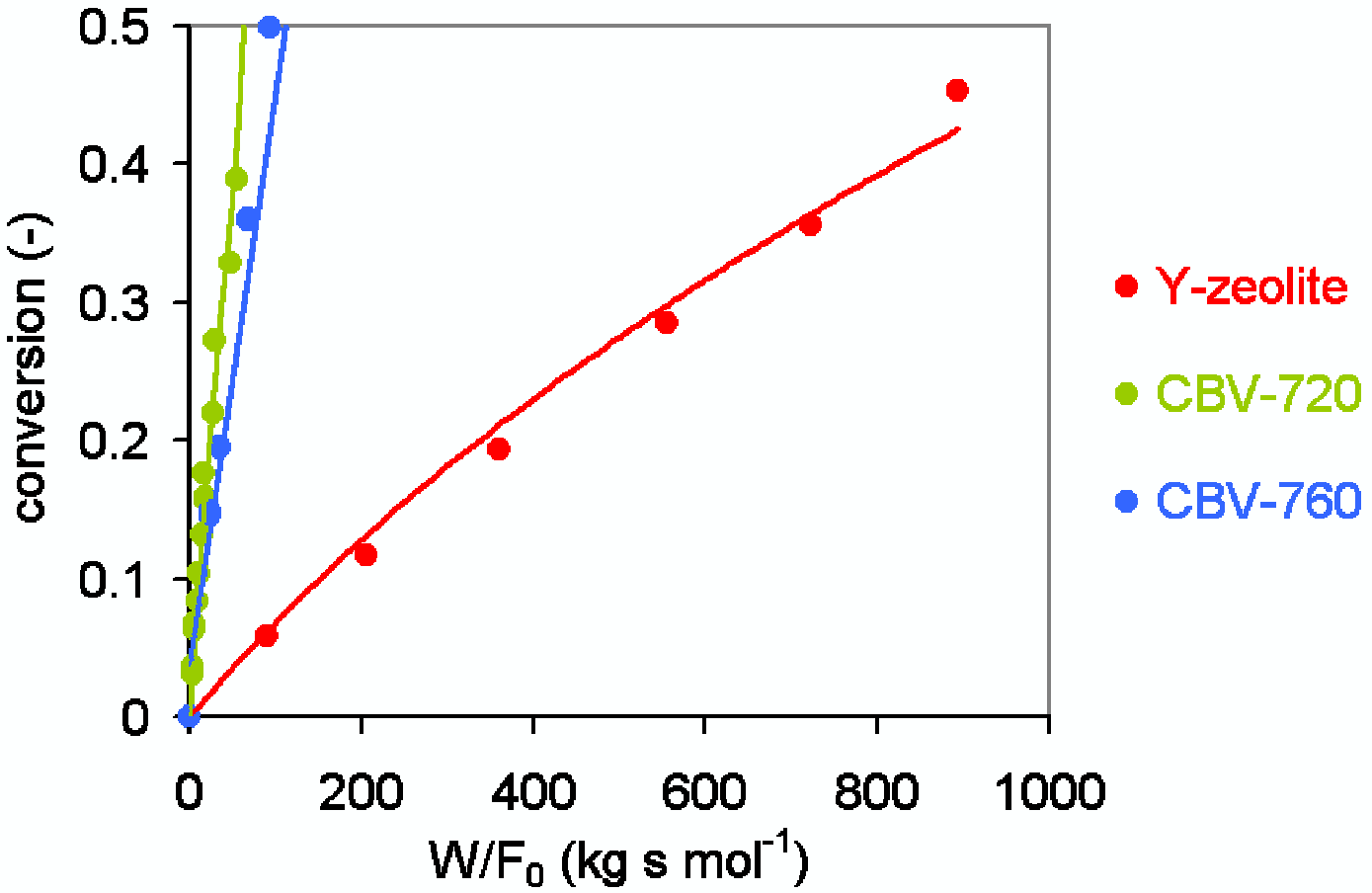
$$R^{\beta}_{O_{i,j}} = \sum_l \sum_o r^{\beta}\left(m_{l,o}; m_{q,r}, O_{i,j}\right)$$

$$R^{AS/PCP/\beta}_{R^+_{i,k}} = \sum_l \sum_o r^{AS/PCP}\left(m_{l,o}; m_{i,k}\right) - \sum_l \sum_o r^{AS/PCP}\left(m_{i,k}; m_{l,o}\right) + \sum_l \sum_o r^{\beta}\left(m_{l,o}; m_{i,k}, O_{u,v}\right) - \sum_l \sum_o r^{\beta}\left(m_{i,k}; m_{l,o}, O_{u,v}\right)$$

reference parameter values

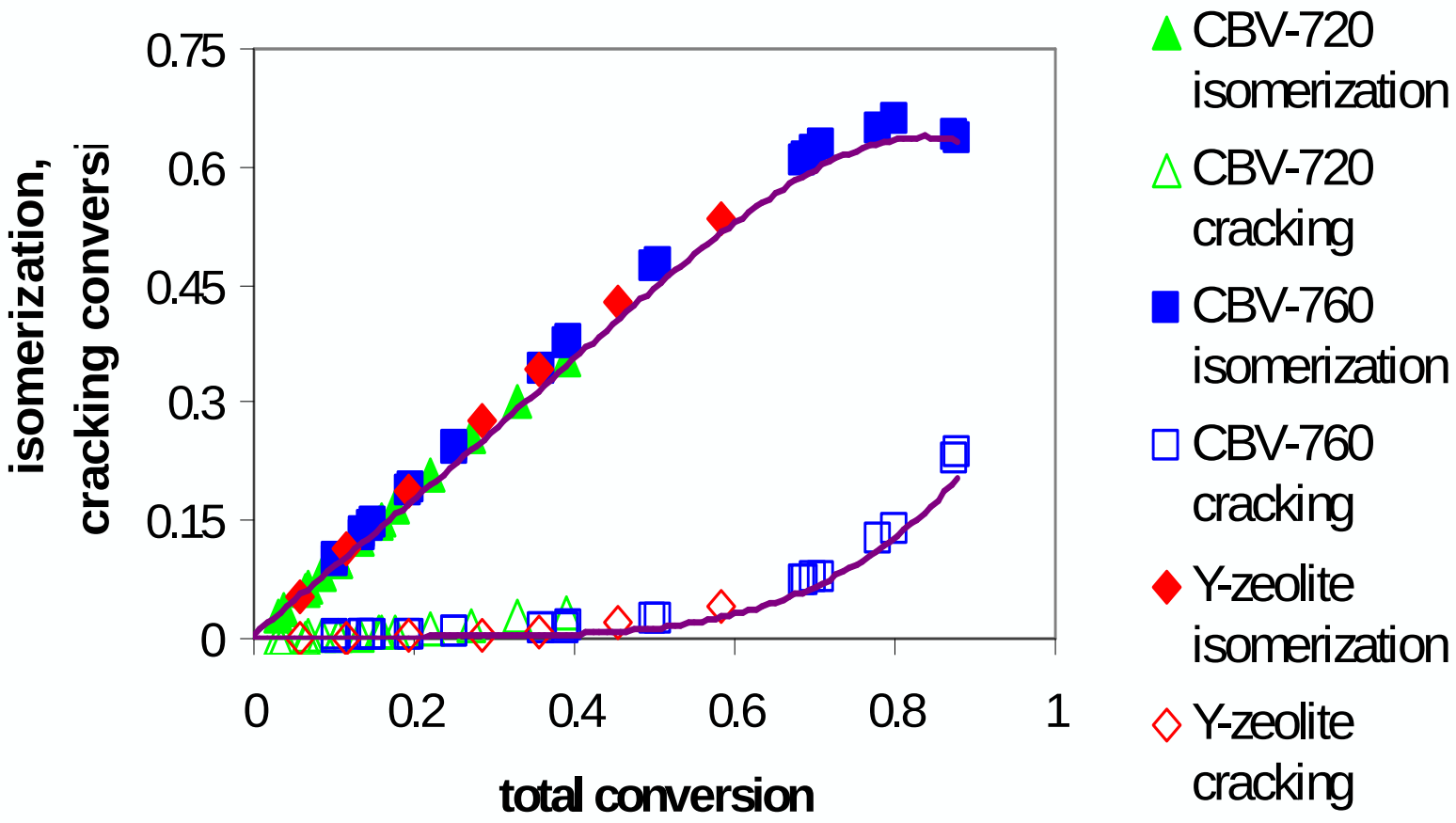
<table>
<tr><th></th><th>Alkylshift</th><th>PCP-branching</th><th>β-scission</th><th>protonation</th></tr>
<tr><td></td><td colspan="4">kJ mol^{-1}</td></tr>
<tr><td>(s;s)</td><td>76.4 (±0.7)^{a}</td><td>104.7 (±0.3)</td><td>139.8 (±0.7)</td><td rowspan="2">-59.2^{c} (±0.3)</td></tr>
<tr><td>(s;t)</td><td rowspan="2">72.2 ^{b} (±0.3)</td><td rowspan="2">95.6^{b} (±0.3)</td><td>127.3 (±1.1)</td></tr>
<tr><td>(t;s)</td><td>148.6 (±0.5)</td><td rowspan="2">-94.0^{d} (±0.5)</td></tr>
<tr><td>(t;t)</td><td>101.5 (±0.3)</td><td>127.3 (±0.9)</td><td>128.6 (±0.9)</td></tr>
</table>

USY: effect Si/Al ratio on activity

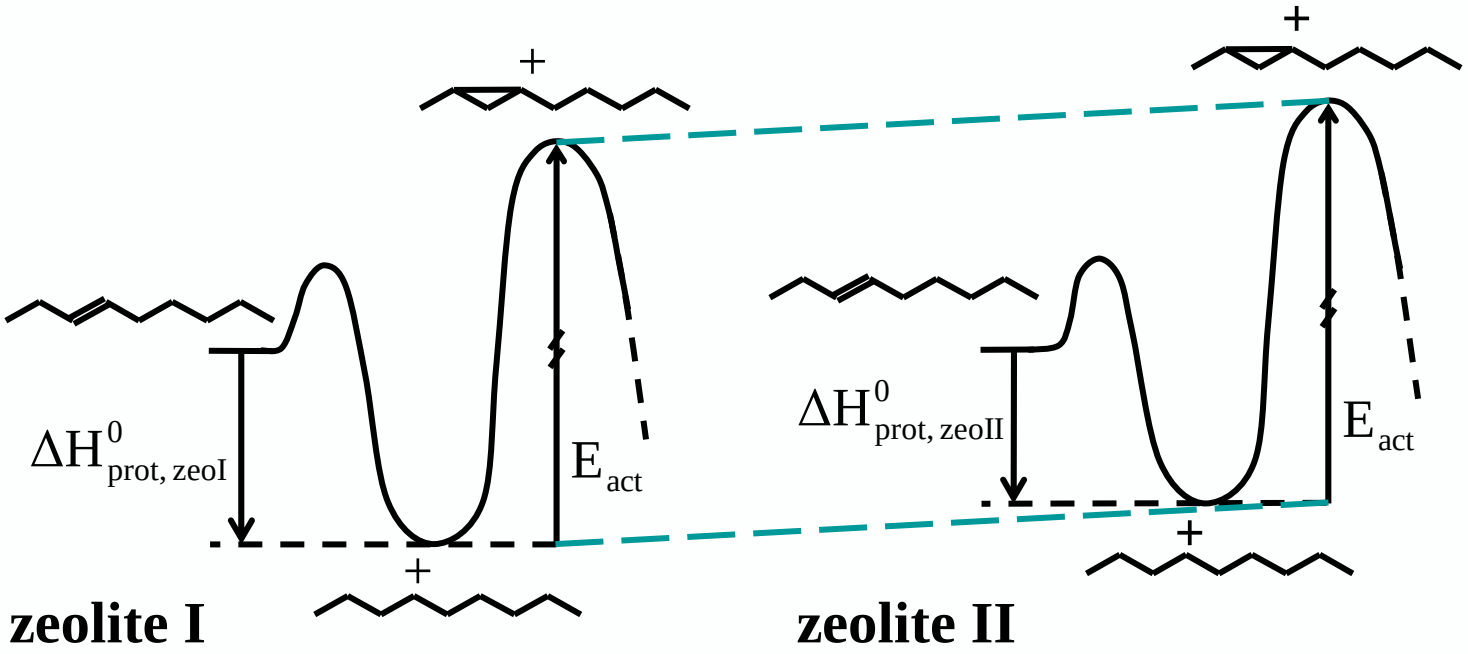


(i) physisorption, (ii) number of sites,
(iii) acid strength

USY: effect Si/Al ratio on selectivity



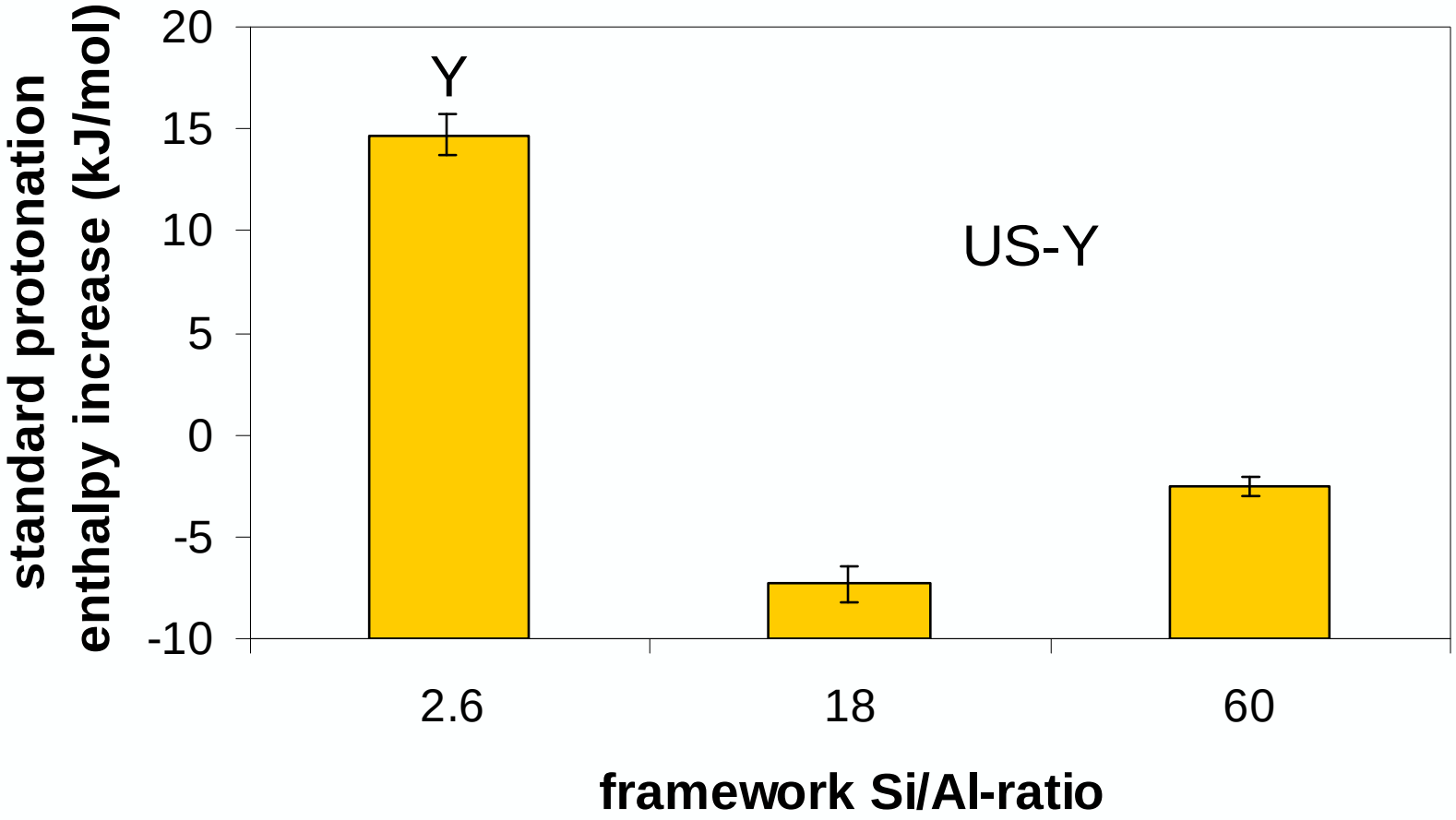
standard protonation enthalpy: catalyst descriptor



same effect of acid strength on stability of reacting carbenium ion and activated complex

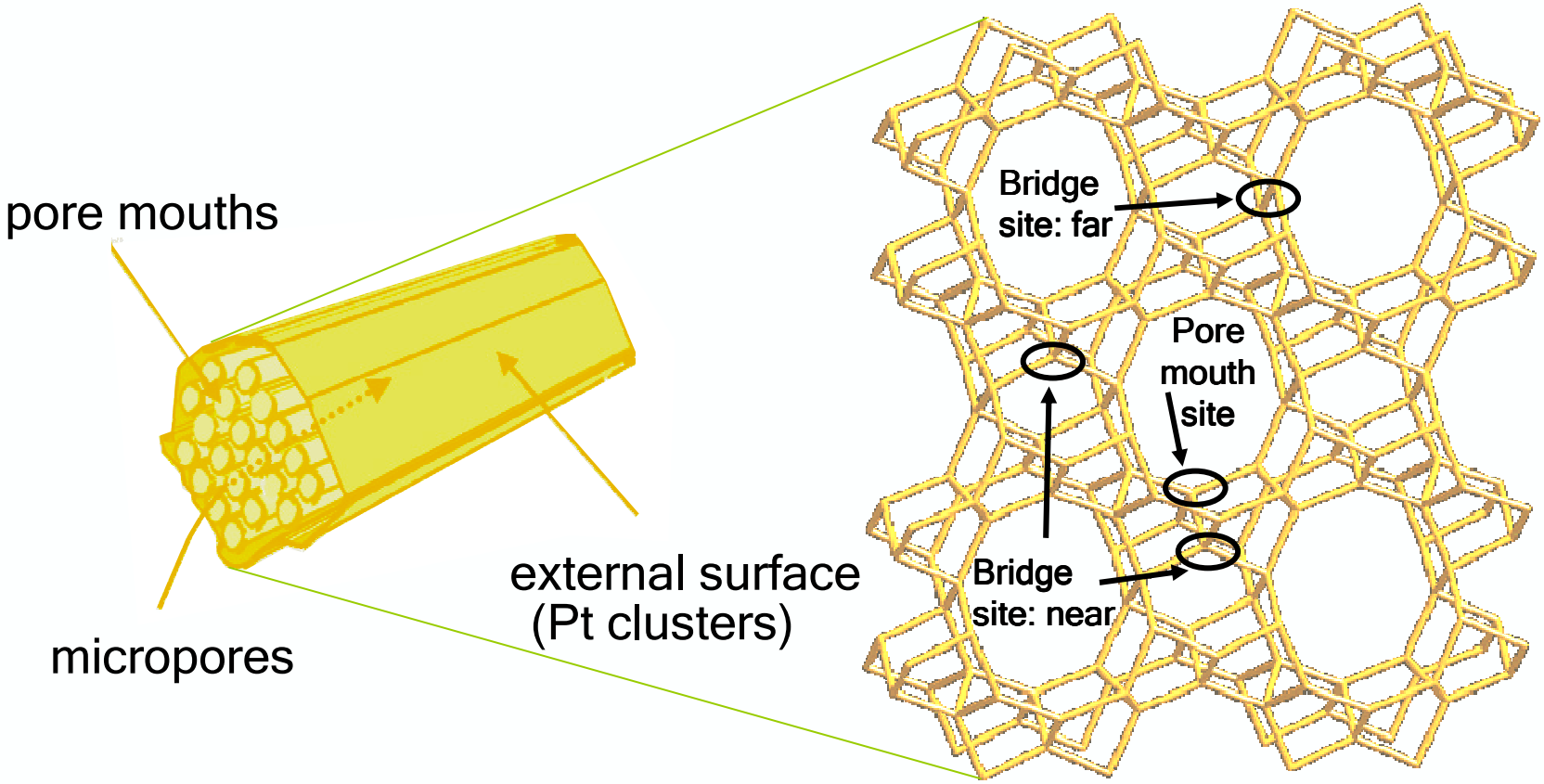
$$E^{comp}_{act,zeo_{II}} - E^{comp}_{act,zeo_{I}} = \Delta H^0_{prot,zeo_{II}} - \Delta H^0_{prot,zeo_{I}} = \Delta(\Delta H^0_{prot})_{zeo_{II}-zeo_{I}}$$

standard protonation enthalpy: catalyst descriptor

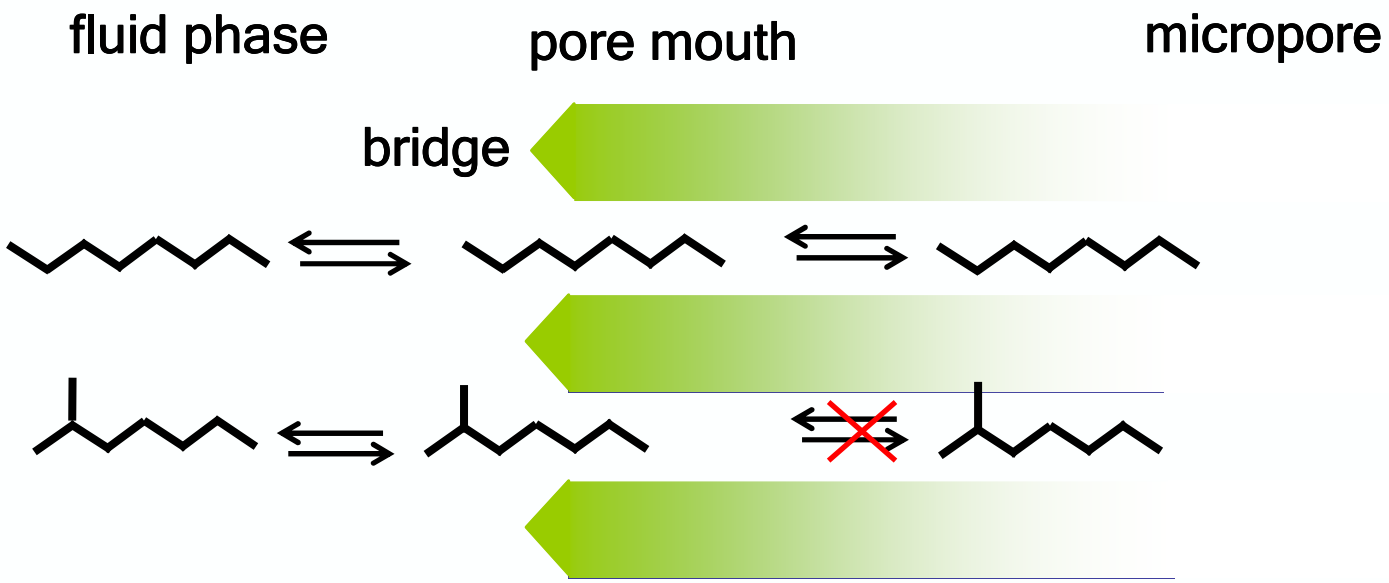


- Y-zeolite: weak acid sites
- intermediate dealumination degree → strongest acid sites

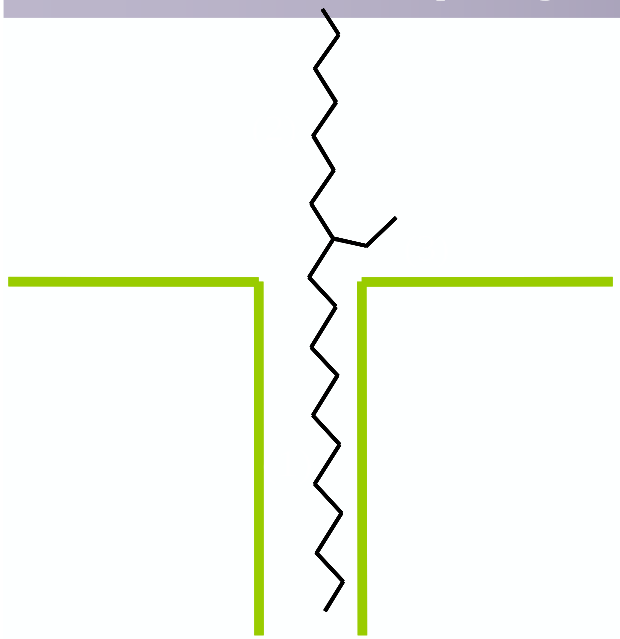
Pt/H-ZSM-22


pore mouths
micropores
external surface
(Pt clusters)
Bridge
site: far
Pore
mouth
site
Bridge
site: near

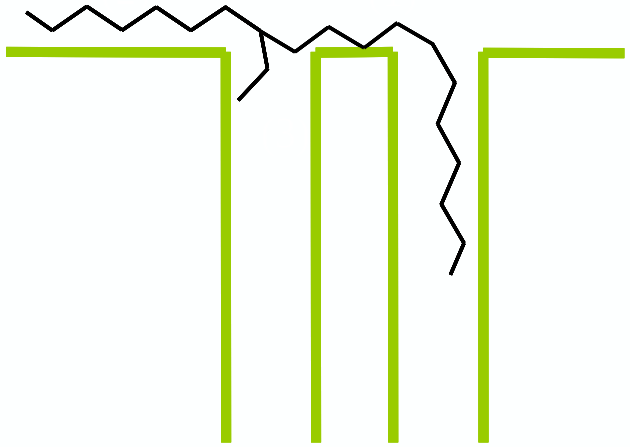
physisorption on ZSM-22



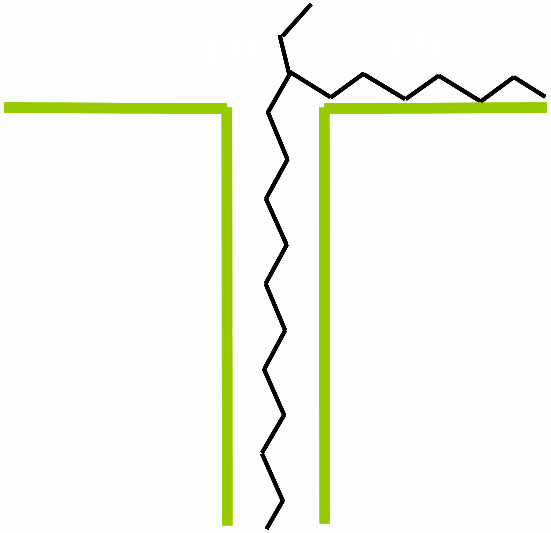
physisorption on ZSM-22



Low interaction mode



High interaction mode (2 pore mouths)



High interaction mode (1 pore mouth)

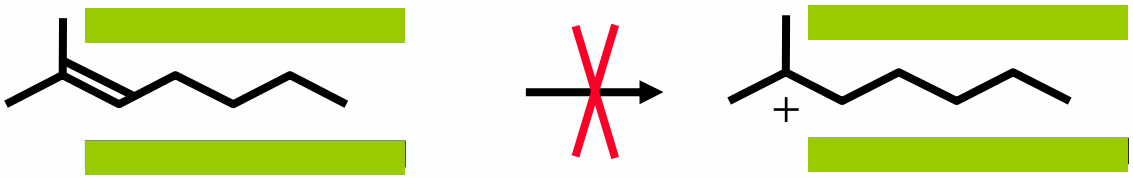
Laxmi Narasimhan et al. J.Catal.,218, 135-147 (2003)

pore mouth catalysis

product shape selectivity:

- methyl shifts excluded

- tertiary carbenium ions cannot be stabilized

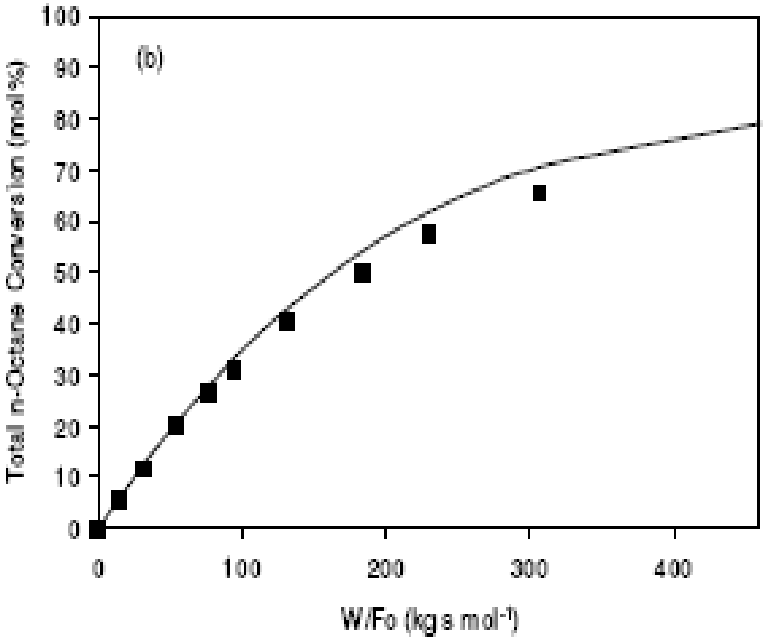


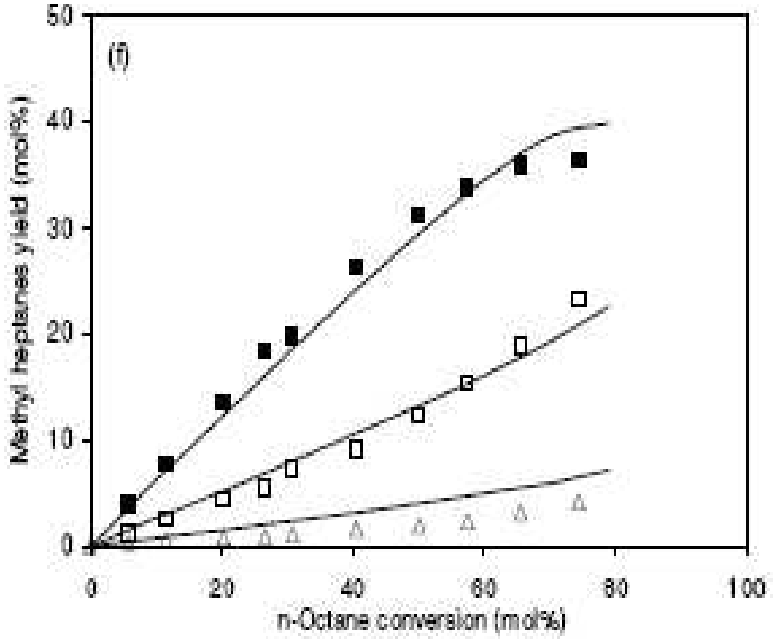
J. A. Martens et al. Appl. Catal. 1991

shape selectivity in SEMK

- reaction network
  - exclusion of tertiary carbenium ions
  - no alkyl shifts at pore mouth sites
  - cracking to primary carbenium ions in pore mouths
- physisorption
  - various physisorption modes
  - pronounced differences between isomers
- protonation
  - depends on the number of carbon atoms inside the pore mouth

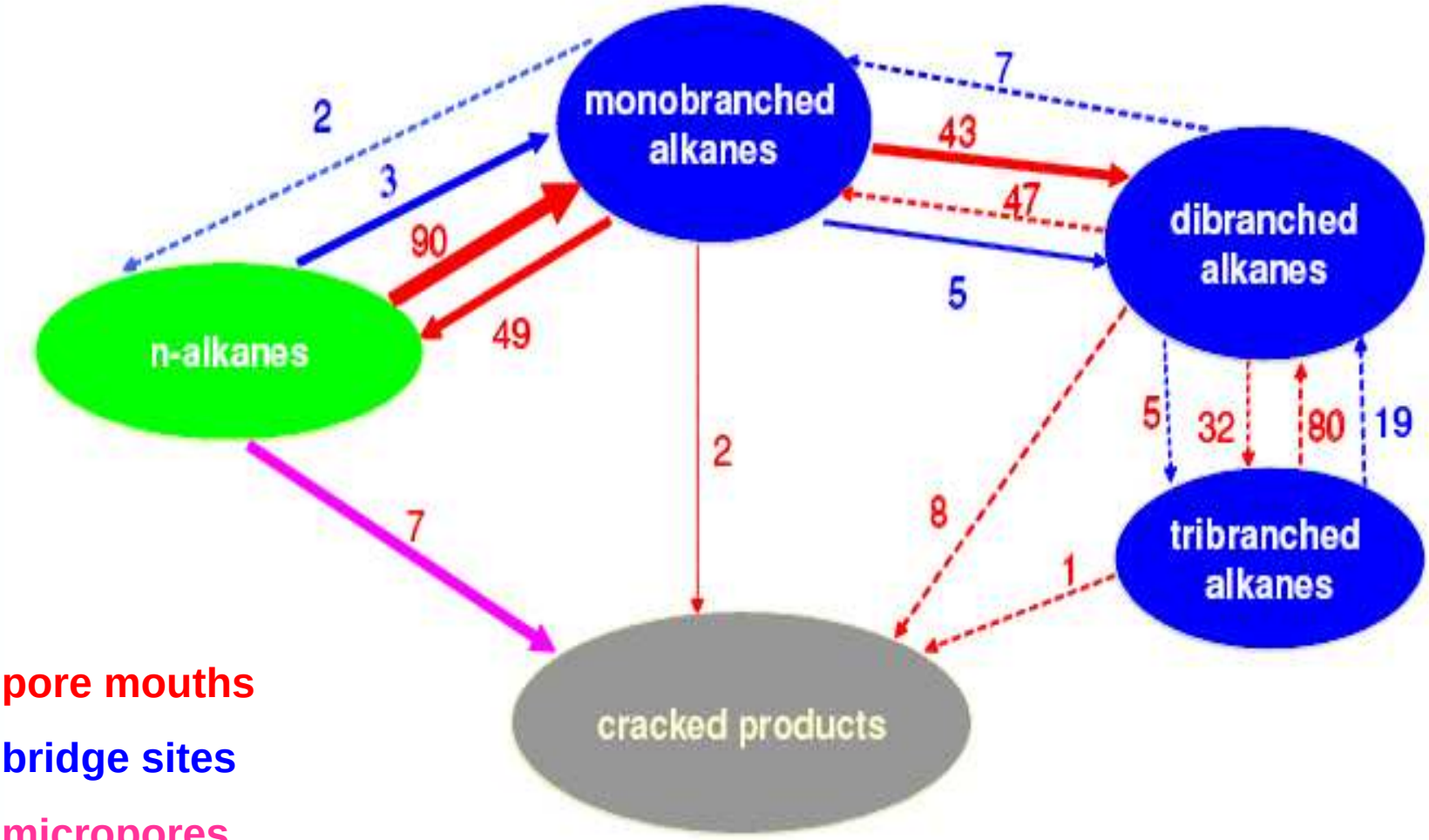
ZSM-22 parameter estimates



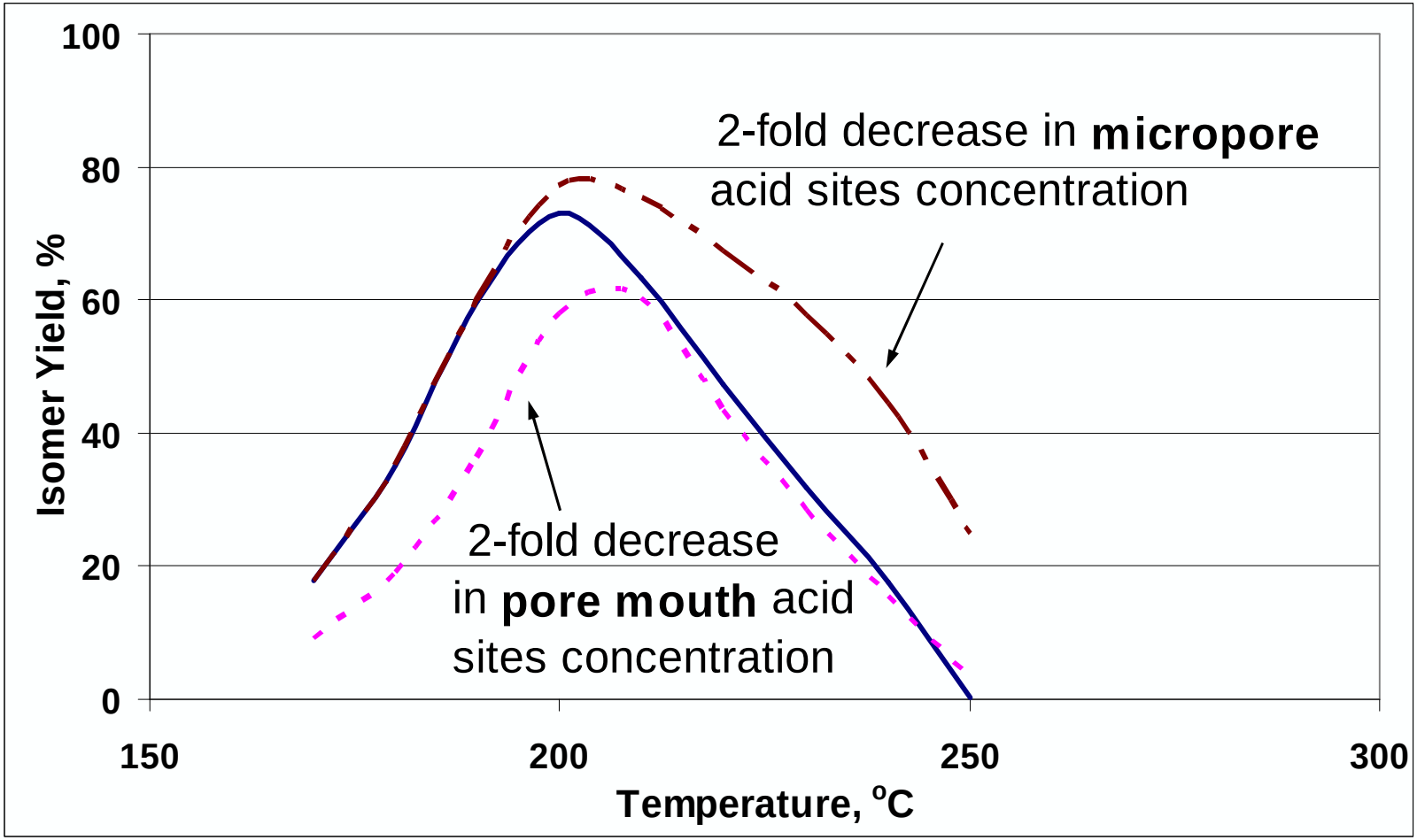


$\Delta H_{prot_{pm/mp}}$	$\Delta H_{prot_{bs}}$	$h_{in_{ref}}^{prot}$	$E_{\beta(s;p)}$
kJ mol^{-1}			
-61.0 (±0.5)	-53.1 (±3.0)	-2.4 (±0.3)	-177.5 (±0.3)

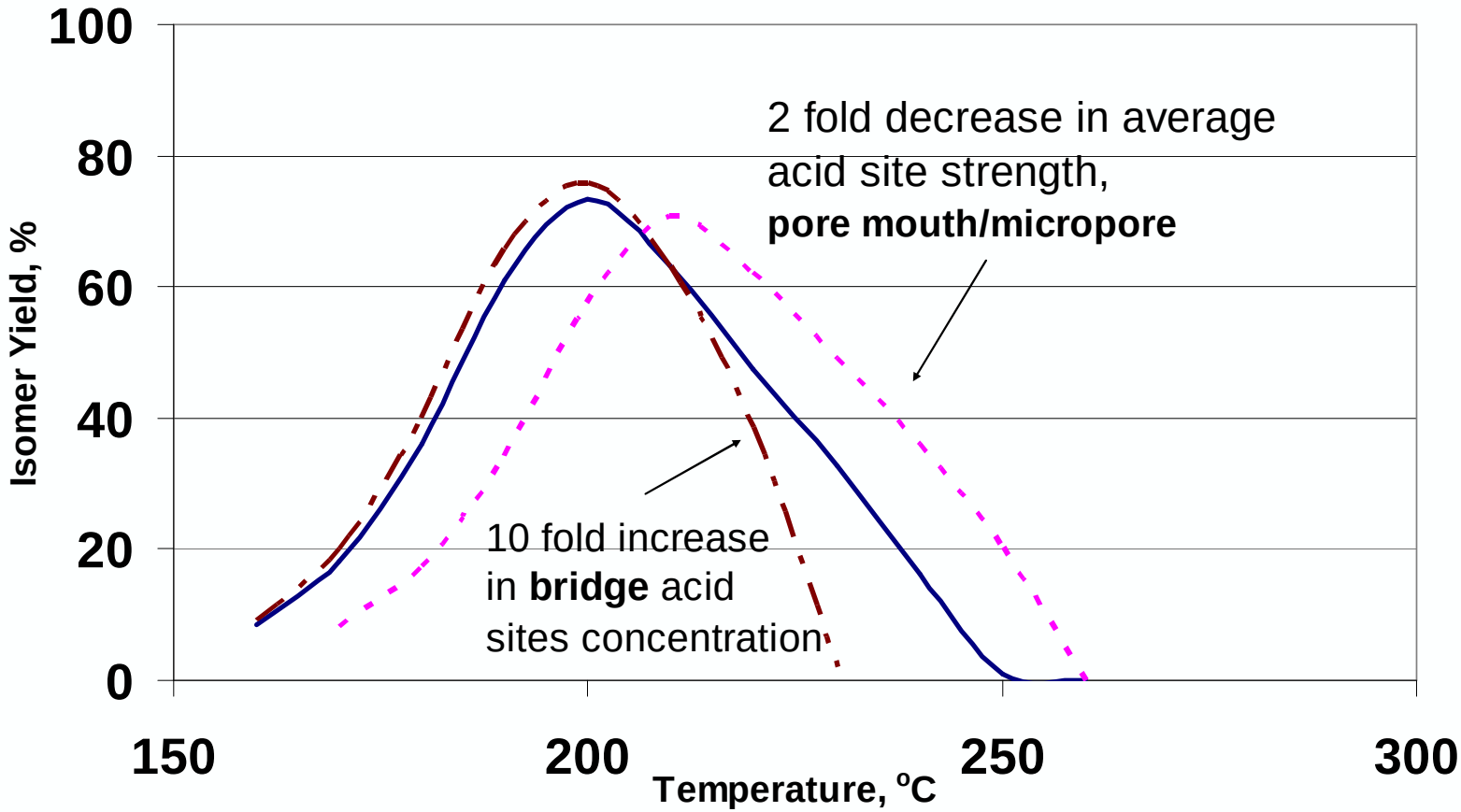
contribution analysis



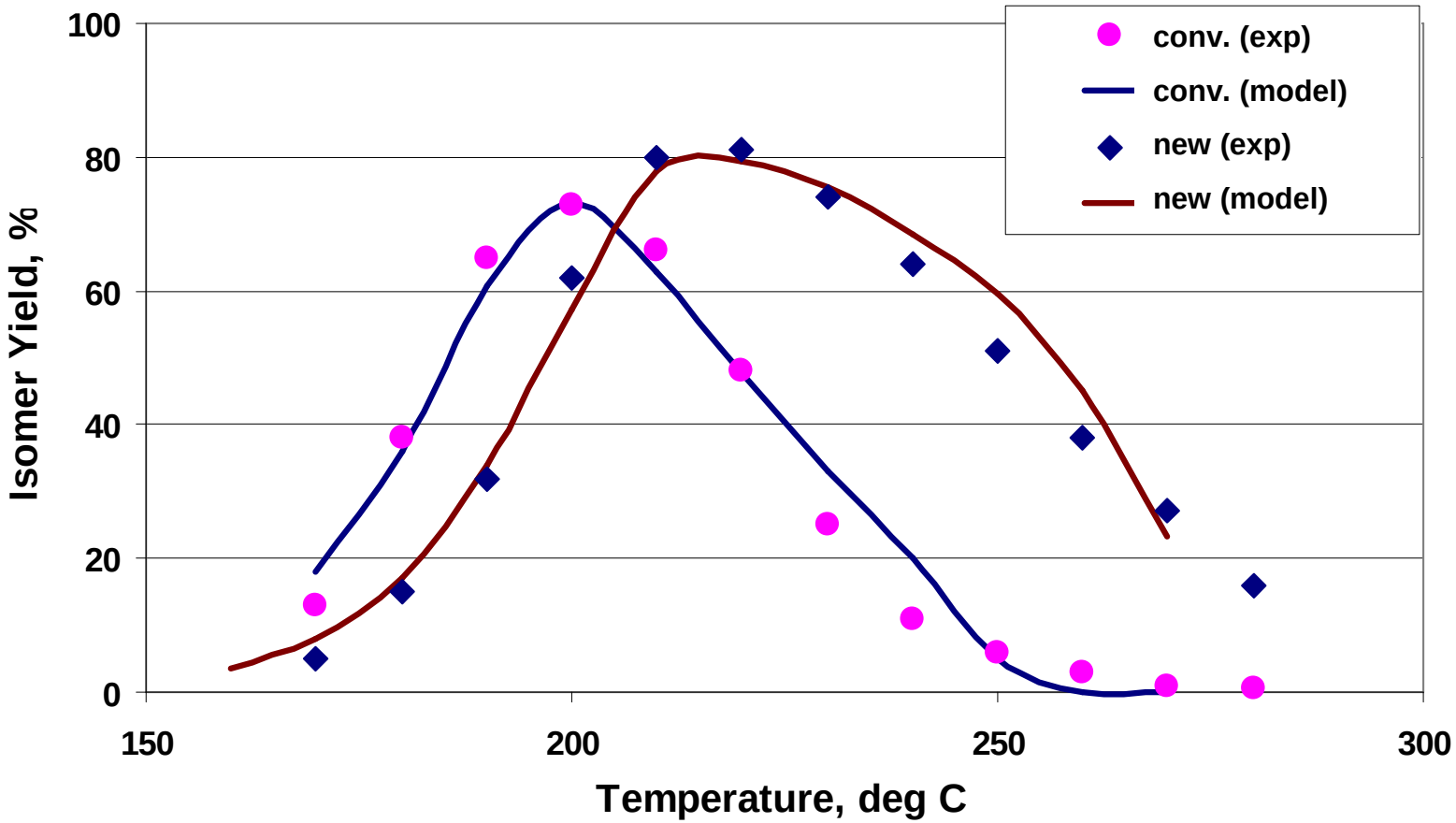
effect of acid site concentration



effect of the strength of the acid sites



new synthesis procedure



outline

- necessary tools
  - reaction network generation
  - thermodynamic data generation
  - simulation and regression
- case 1: hydroisomerization/-cracking
  - USY-zeolite: free carbenium ion chemistry
  - ZSM-22: shape selectivity
- case 2: Fischer Tropsch synthesis
  - Fe and Co catalysts

Reaction network

Chain initiation

Chemisorption/dissociation

$$H_2 + 2M \leftrightarrow 2MH$$

$$CO + 2M \leftrightarrow MMCO$$

$$MMCO + 3M \leftrightarrow MMMC + MMO$$

Formation building blocks

$$MMMC + MH \leftrightarrow MMMCH + M$$

$$MMMCH + MH \leftrightarrow MMCH_2 + 2M$$

$$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$$

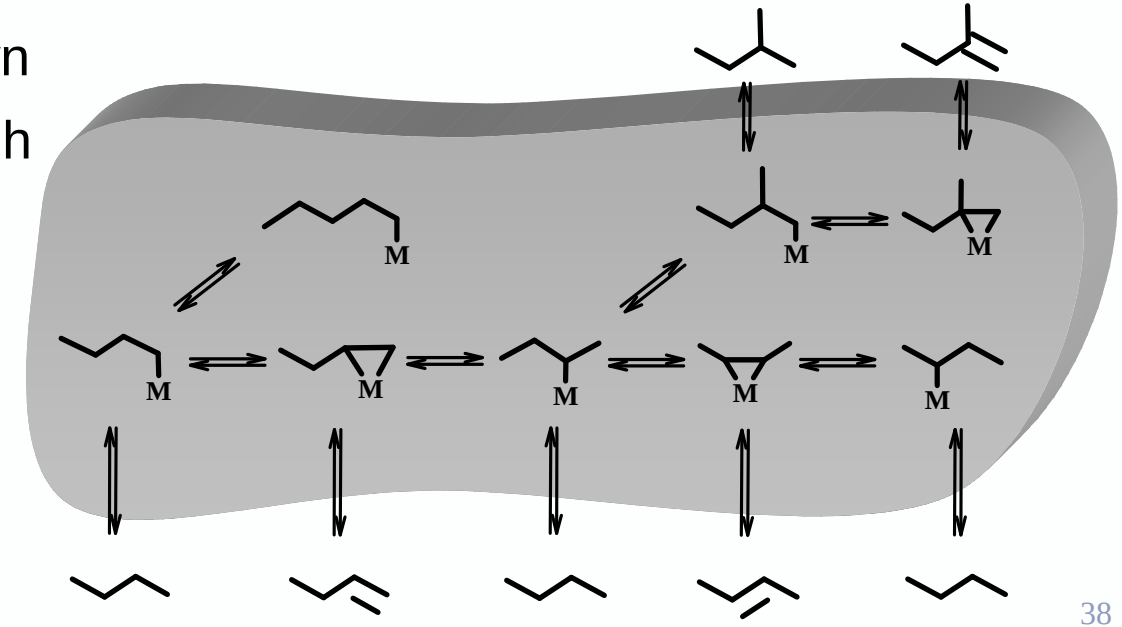
Formation of water

$$MMO + MH \leftrightarrow MOH + 2M$$

$$MOH + MH \leftrightarrow H_2O + 2M$$

Chain growth and termination

- Mechanistic details still unknown
- Chain growth on surface through stepwise addition of carbon monomers
- Anderson-Schulz-Flory product distribution → chain growth probability independent of *cn*



Reaction network

Chain initiation

Chemisorption/dissociation

$$H_2 + 2M \leftrightarrow 2MH$$

$$CO + 2M \leftrightarrow MMCO$$

$$MMCO + 3M \leftrightarrow MMMC + MMO$$

Formation building blocks

$$MMMC + MH \leftrightarrow MMMCH + M$$

$$MMMCH + MH \leftrightarrow MMCH_2 + 2M$$

$$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$$

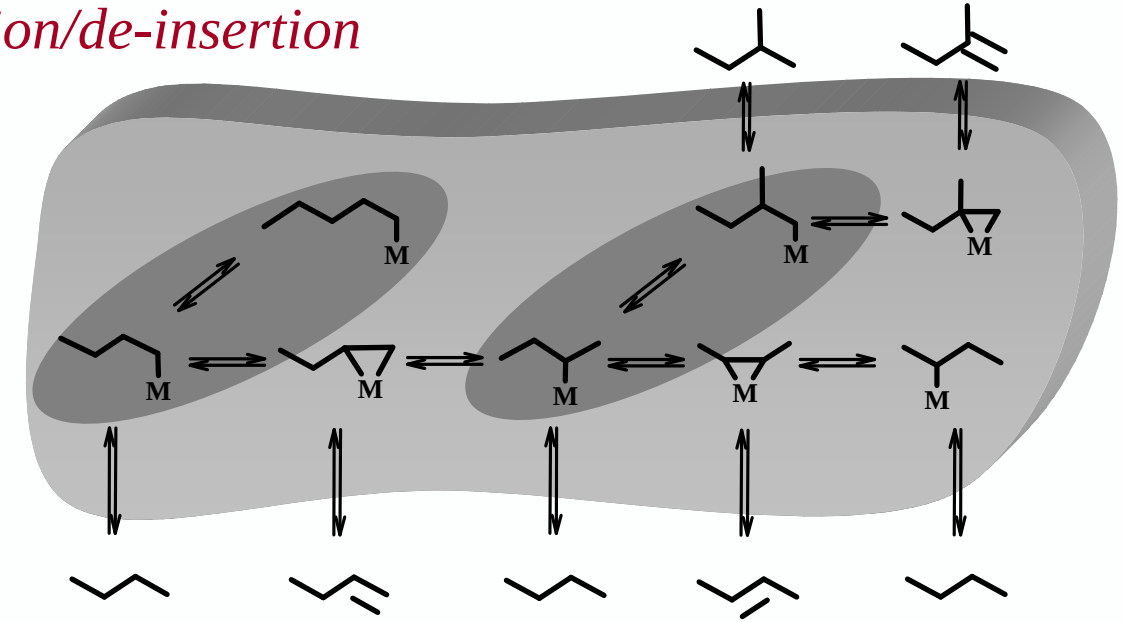
Formation of water

$$MMO + MH \leftrightarrow MOH + 2M$$

$$MOH + MH \leftrightarrow H_2O + 2M$$

Chain growth and termination

Methylene insertion/de-insertion



Reaction network

Chain initiation

Chemisorption/dissociation

$$H_2 + 2M \leftrightarrow 2MH$$

$$CO + 2M \leftrightarrow MMCO$$

$$MMCO + 3M \leftrightarrow MMMC + MMO$$

Chain growth and termination

Reductive elimination/oxidative addition

Formation building blocks

$$MMMC + MH \leftrightarrow MMMCH + M$$

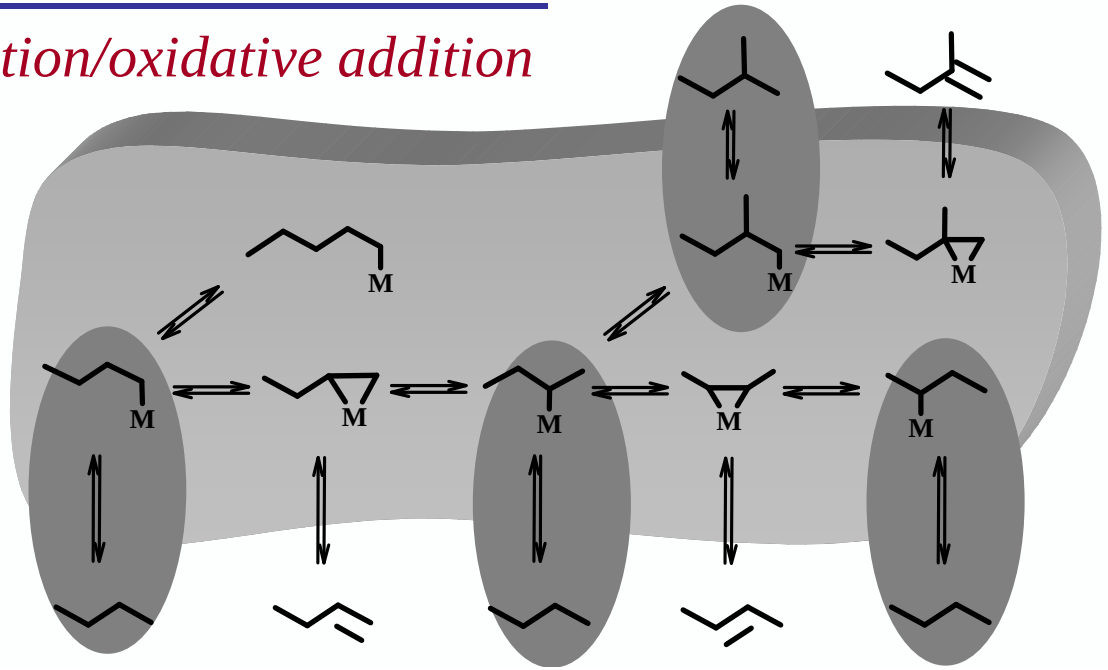
$$MMMCH + MH \leftrightarrow MMCH_2 + 2M$$

$$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$$

Formation of water

$$MMO + MH \leftrightarrow MOH + 2M$$

$$MOH + MH \leftrightarrow H_2O + 2M$$



Reaction network

Chain initiation

Chemisorption/dissociation

$$H_2 + 2M \leftrightarrow 2MH$$

$$CO + 2M \leftrightarrow MMCO$$

$$MMCO + 3M \leftrightarrow MMMC + MMO$$

Chain growth and termination

β-hydride addition/elimination

Formation building blocks

$$MMMC + MH \leftrightarrow MMMCH + M$$

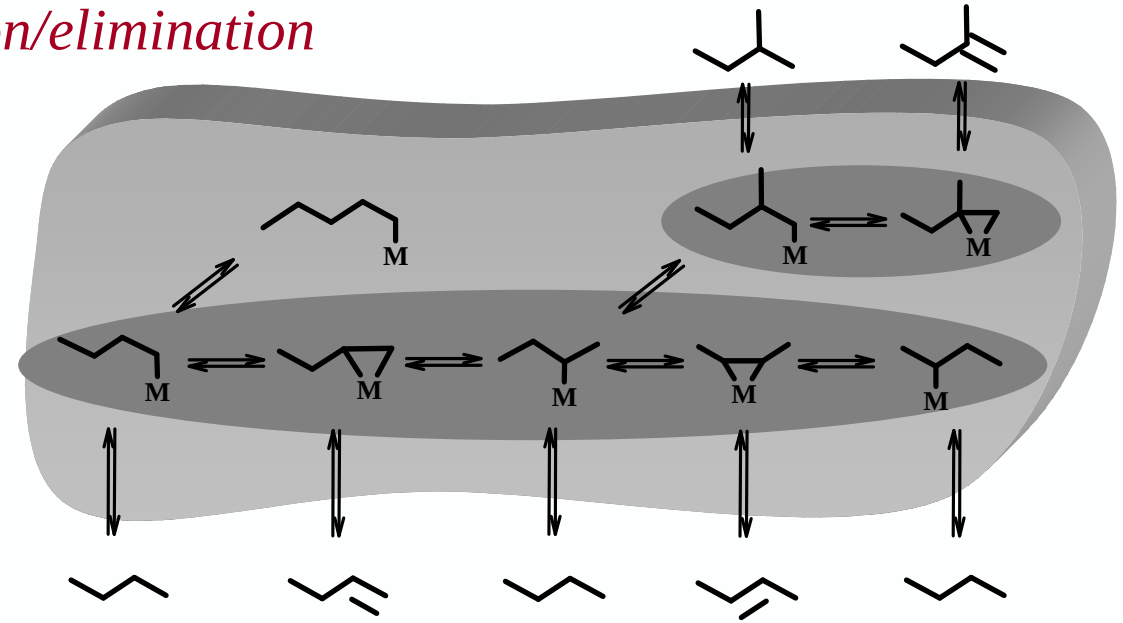
$$MMMCH + MH \leftrightarrow MMCH_2 + 2M$$

$$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$$

Formation of water

$$MMO + MH \leftrightarrow MOH + 2M$$

$$MOH + MH \leftrightarrow H_2O + 2M$$



Reaction network

Chain initiation

Chemisorption/dissociation

$$H_2 + 2M \leftrightarrow 2MH$$

$$CO + 2M \leftrightarrow MMCO$$

$$MMCO + 3M \leftrightarrow MMMC + MMO$$

Formation building blocks

$$MMMC + MH \leftrightarrow MMMCH + M$$

$$MMMCH + MH \leftrightarrow MMCH_2 + 2M$$

$$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$$

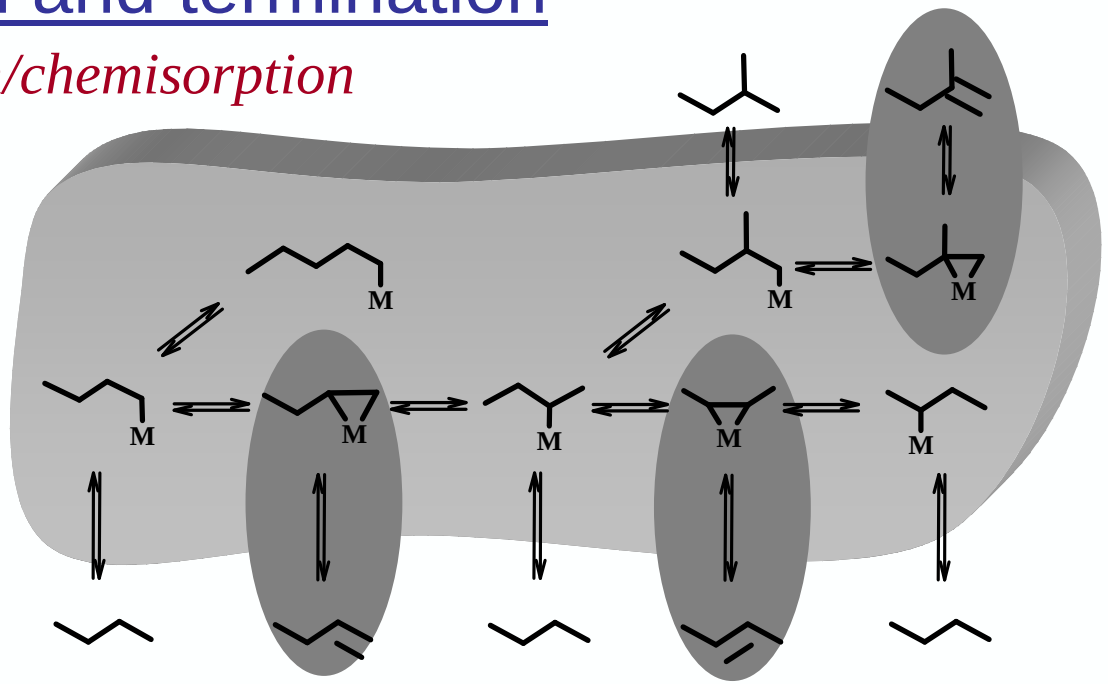
Formation of water

$$MMO + MH \leftrightarrow MOH + 2M$$

$$MOH + MH \leftrightarrow H_2O + 2M$$

Chain growth and termination

Alkene desorption/chemisorption



Validation Fe and Co catalyst

Iron

- Water-Gas Shift (formate mechanism, iron oxide phase, 6 additional elementary reactions)
- Range of experimental conditions:

T (K)	H_2/CO	p_{tot} (bar)	N_{obs}
523-623	2-6	6-21	90

Lox, Ph.D. Thesis, Ghent University (1987)

- Adjustable parameters:
  - Q_C,Q_H,Q_O on iron carbide phase (3)
  - Q_H on iron oxide phase (1)
  - $E_{a,for}$ of kinetically relevant reaction families (10)

Lozano-Blanco et al.,
OGST – Rev. IFP, Vol. 61 (2006), No. 4

Cobalt

- Primary-alcohols (CO insertion mechanism, 3 additional elementary reactions)
- Range of experimental conditions:

T (K)	H_2/CO	p_{tot} (bar)	N_{obs}
493	1.6-2	20	22

Fiore et al., Studies in Surf. Sci. and Cat. (2004)

- Adjustable parameters:
  - Q_C,Q_H,Q_O on cobalt metallic phase (3)
  - $E_{a,for}$ of kinetically relevant reaction families (12)

Validation Fe and Co catalyst

Reaction family/ elem. reaction	$\tilde{A}_{for}$ *(bar^{-1}s^{-1} or s^{-1})*	$E_{a,for}$ / Q ***(kJ/mol)***			
		UBI/QEP	*Estimated*	*UBI/QEP*	*Estimated*
		Fe		***Co***	
$H_2 + 2M \leftrightarrow 2MH$	3.1 10^{8}	0.0	-	0.0	-
$CO + 2M \leftrightarrow MMCO$	2.2 10^{7}	0.0	-	0.0	-
$MMCO + 3M \leftrightarrow MMMC + MMO$	1.3 10^{13}	139.5	56.8±0.5	155.1	52.8±6.2
$MMMC + MH \leftrightarrow MMMCH + M$	8.8 10^{14}	127.6	77.7±0.7	122.3	74.3±10.3
$MMMCH + MH \leftrightarrow MMCH_2 + 2M$	5.7 10^{11}	67.6	11.9±0.1	58.3	12.2±2.0
$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$	2.3 10^{11}	38.1	61.9±0.5	27.2	71.9±3.1
$MMO + MH \leftrightarrow MOH + 2M$	1.3 10^{12}	118.6	103.8±1.0	110.8	107.0±6.6
$MOH + MH \leftrightarrow H_2O + 2M$	2.4 10^{11}	78.0	86.2±0.6	51.8	91.6±24.3
M-C	-	-	639.5±2.1	-	611.2±2.7
M-H	-	-	249.2±0.6	-	243.3±3.2
M-O	-	-	578.8±0.9	-	553.7±6.0

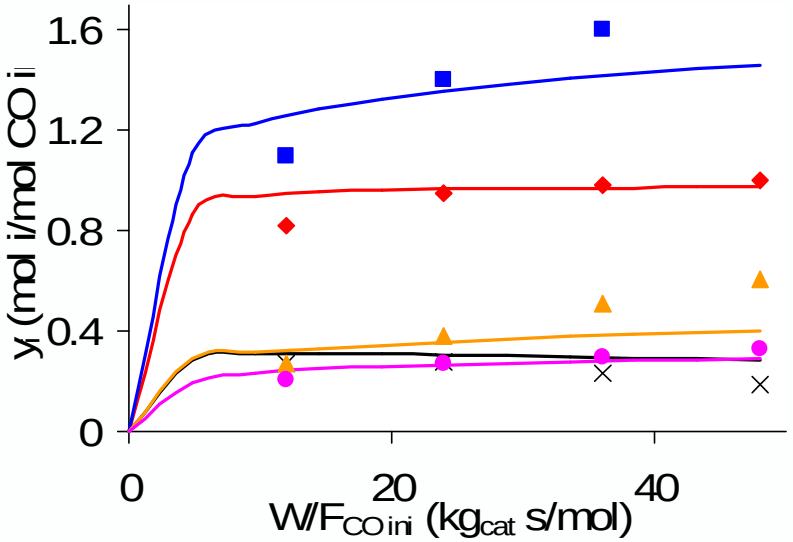
Validation Fe and Co catalyst

Reaction family/ elem. reaction	$\tilde{A}_{for}$ *(bar^{-1}s^{-1} or s^{-1})*	$E_{a,for}$ / Q **(kJ/mol)**			
		UBI/QEP	*Estimated*	*UBI/QEP*	*Estimated*
		Fe		**Co**	
$MC_nH_{2n+1} + MMCH_2 \leftrightarrow MC_{n+1}H_{2n+3} + 2M$	$8.9\ 10^{9}$	8.0	44.8±0.4	0.0	43.5±2.0
$MC_nH_{2n+1} + MH \leftrightarrow C_nH_{2n+2} + 2M$	$2.1\ 10^{10}$	15.5	117.8±0.7	6.4	103.6±2.0
$MC_nH_{2n+1} + M \leftrightarrow MC_nH_{2n} + MH$	$1.1\ 10^{10}$	26.2	96.3±0.5	24.1	86.1±1.4
$MC_nH_{2n} \leftrightarrow C_nH_{2n} + M$	$1.3\ 10^{13}$	62.1	-	57.0	-

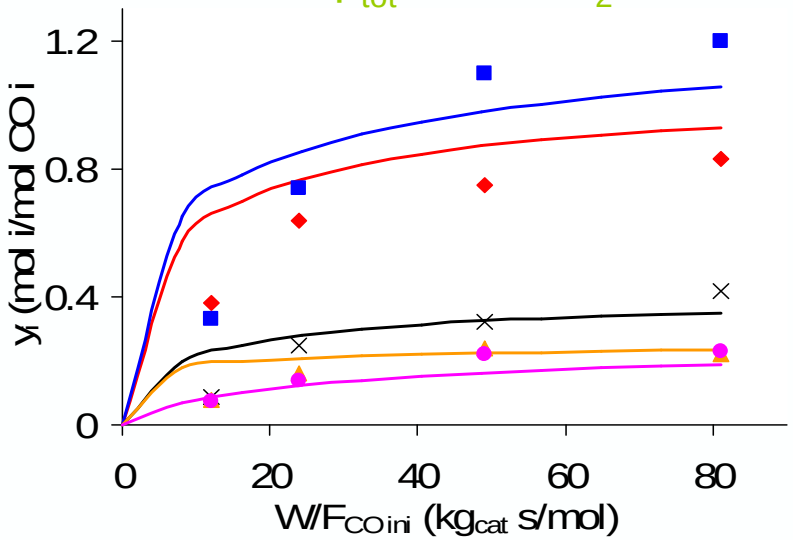
- most significant changes in atomic chemisorption enthalpies and in elementary steps determining the product distribution

Results Fe - Nonisothermal

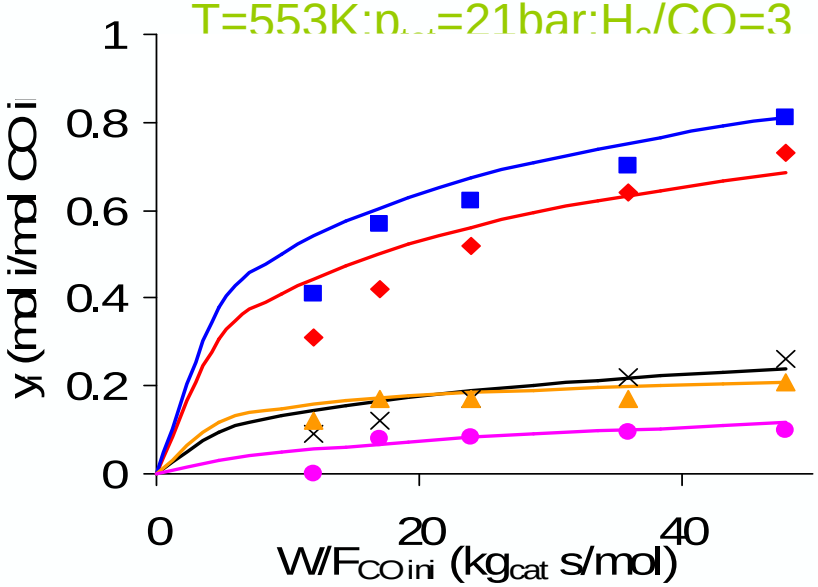
T=623K;p_{tot}=21bar;H_2/CO=3



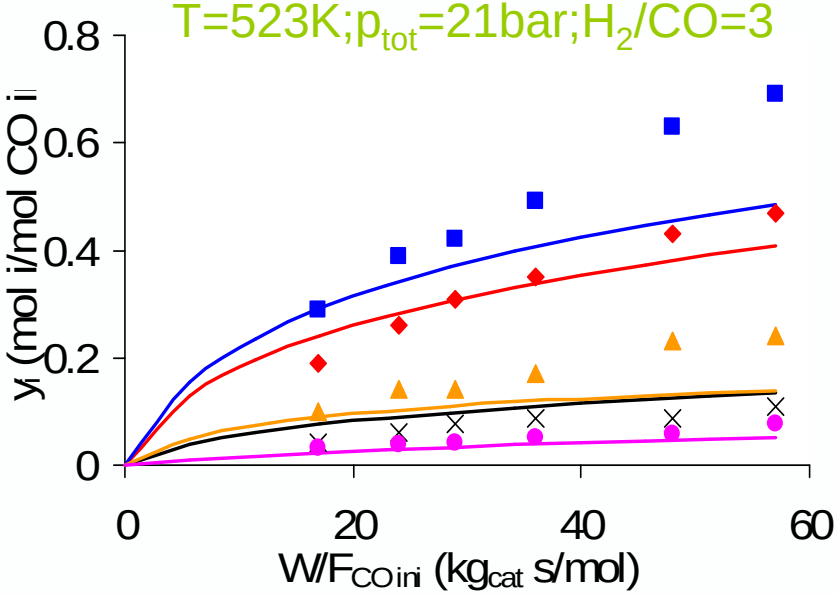
T=573K;p_{tot}=11bar;H_2/CO=3



T=553K;p_{tot}=21bar;H_2/CO=3



T=523K;p_{tot}=21bar;H_2/CO=3



■ H_2

◆ CO

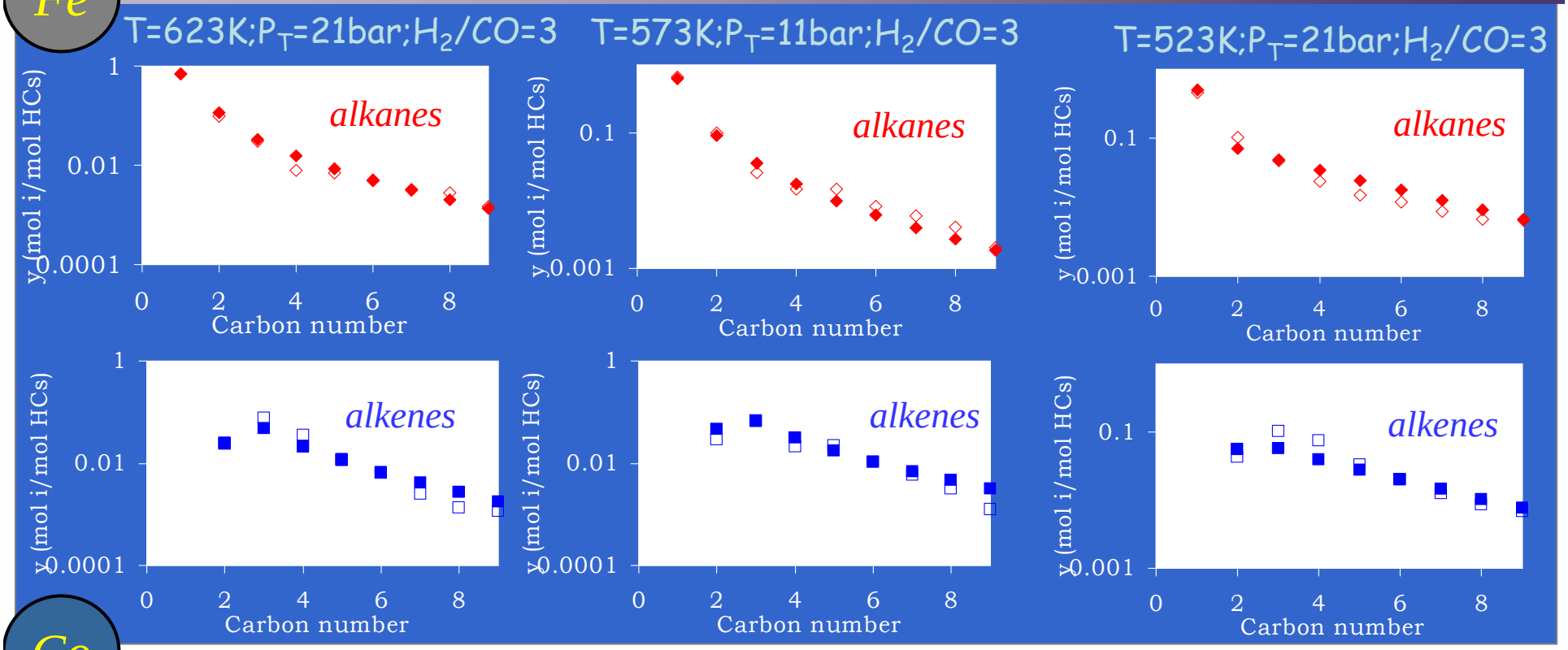
▲ H_2O

● CH_4

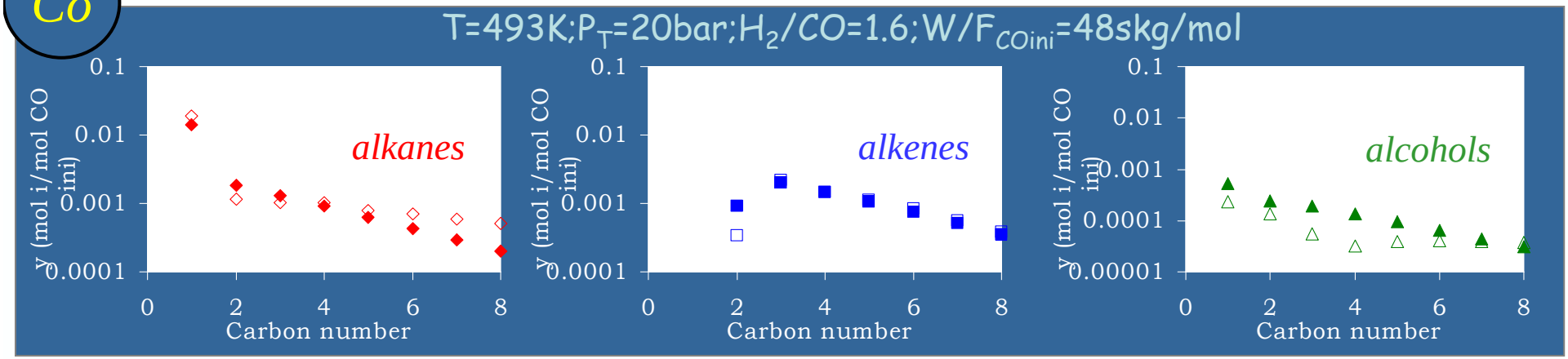
× CO_2

Model validation on Fe and Co

Fe

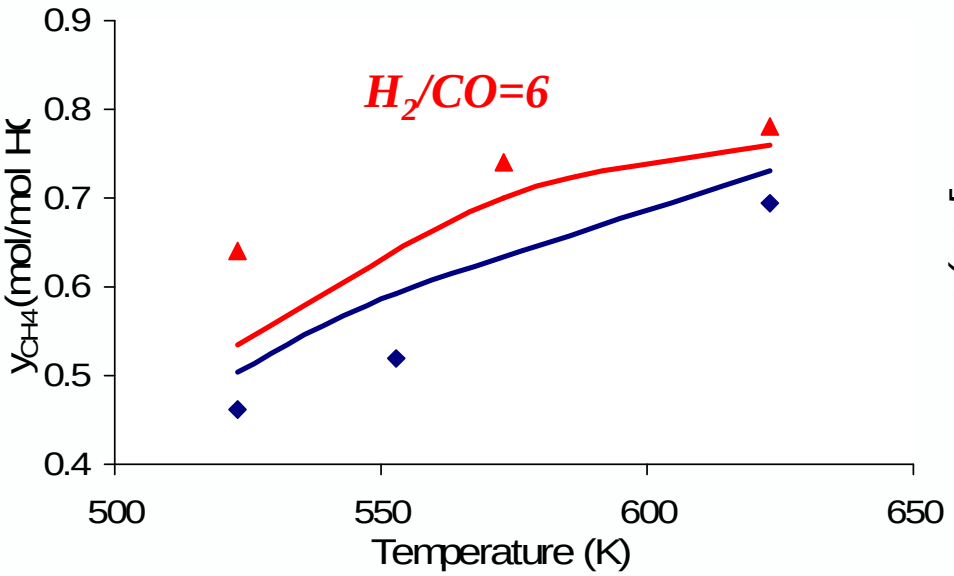


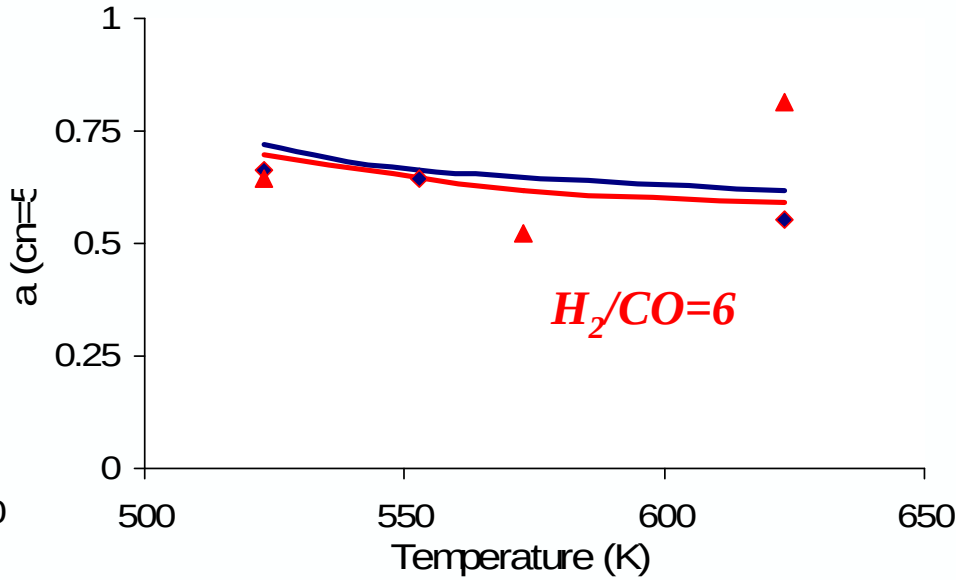
Co



General trends

p_{tot} = 11 bar ; W/F_{COini} = 43-48 skg/mol





- Chain growth probability: $\alpha_n = \dfrac{r_{prop,n}}{r_{prop,n} + r_{term,n}}$
- At higher temperatures more hydrogenated products and lower molecular mass hydrocarbons

$$E_{a,mi}(45kJ/mol) < E_{a,\beta-e}(96kJ/mol) < E_{a,re}(118kJ/mol)$$

conclusions

- SEMK is a versatile methodology for a wide range of processes
- catalyst descriptors account for the effect of the catalyst properties on the kinetics
  - protonation enthalpy, number of sites, physisorption
  - atomic chemisorption enthalpies
- identification of undesired and desired reaction pathways
- enhanced isomerization catalyst

acknowledgements

- Laxmi Narasimhan, Indranil Choudhury (UGent)
- Johan Martens, Pierre Jacobs (KULeuven)
- Gino Baron, Joeri Denayer (VUBrussel)
- David Farrusseng, Claude Mirodatos (IRC Lyon)
- Pierre Galtier, Karine Surla (IFP)

- IAP-program (Belgian Science Policy)
- European Commission (TOPCOMBI)

- Eurokin