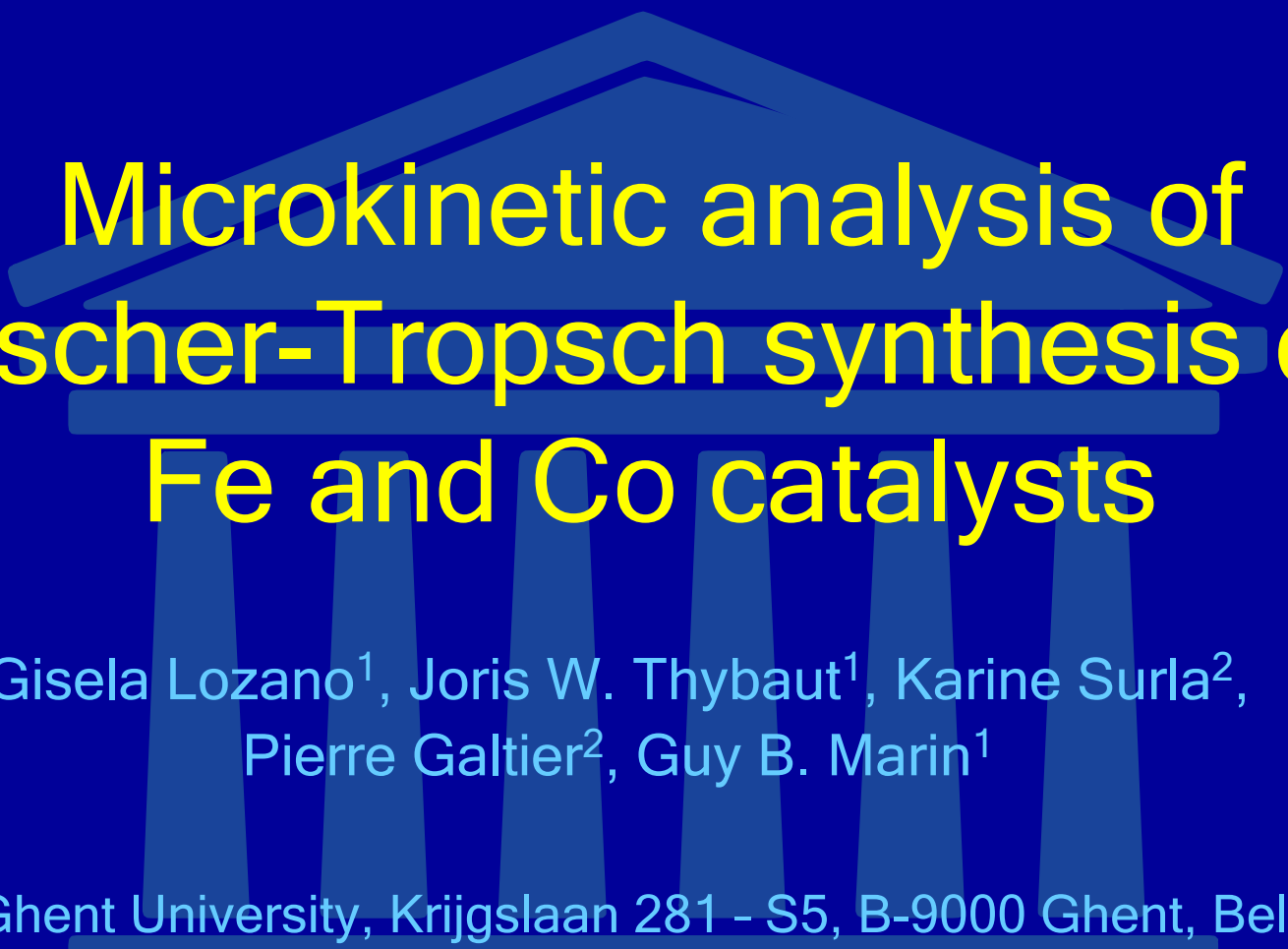




Microkinetic analysis of Fischer-Tropsch synthesis on Fe and Co catalysts

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¹LPT, Ghent University, Krijgslaan 281 - S5, B-9000 Ghent, Belgium

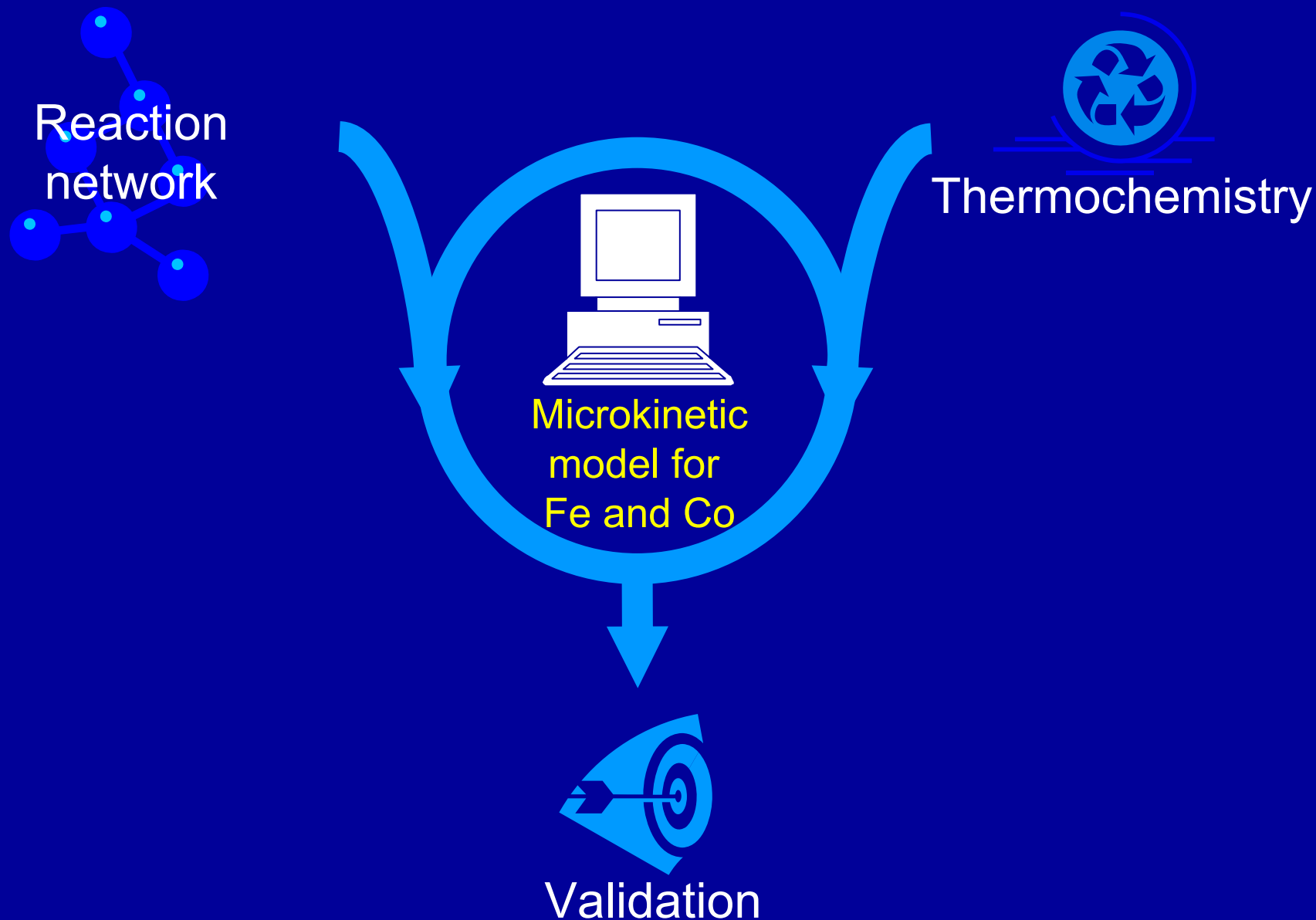
²Institut Français du Pétrole, B.P. 3, 69390 Vernaison, France

EUROPACAT-VIII
26 - 31 August 2007, Turku, Finland

Fischer-Tropsch synthesis



General scheme - Objective



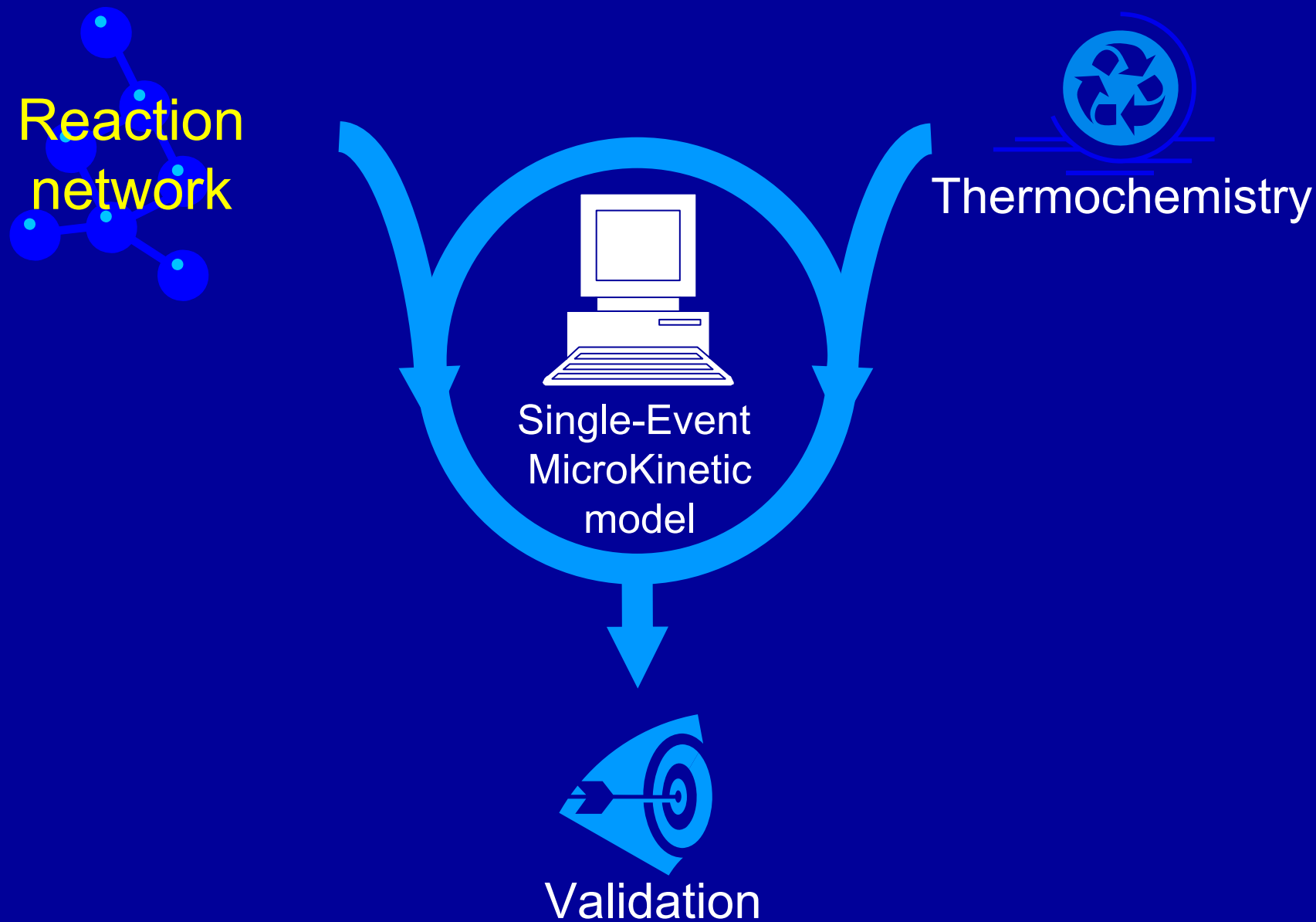
Single-Event MicroKinetics

- Microkinetic model accounts for the rate of every elementary step → detailed selectivities → potential tool to design more performing catalysts
- Single-Event MicroKinetics (SEMK) consist of extracting the **symmetry factors** from the entropic contribution

$$k = \frac{\sigma_{glob,r}}{\sigma_{glob,\neq}} \frac{k_B T}{h} \exp(\Delta \tilde{S}^{0,\neq} / R) \exp(-\Delta H^{0,\neq} / R T)$$
$$\tilde{k} = \tilde{A} \exp(-E_a / R T)$$

- Unique **single-event rate coefficient** for each reaction family

General scheme



Reaction network

Chain initiation

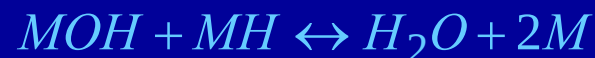
Chemisorption/dissociation



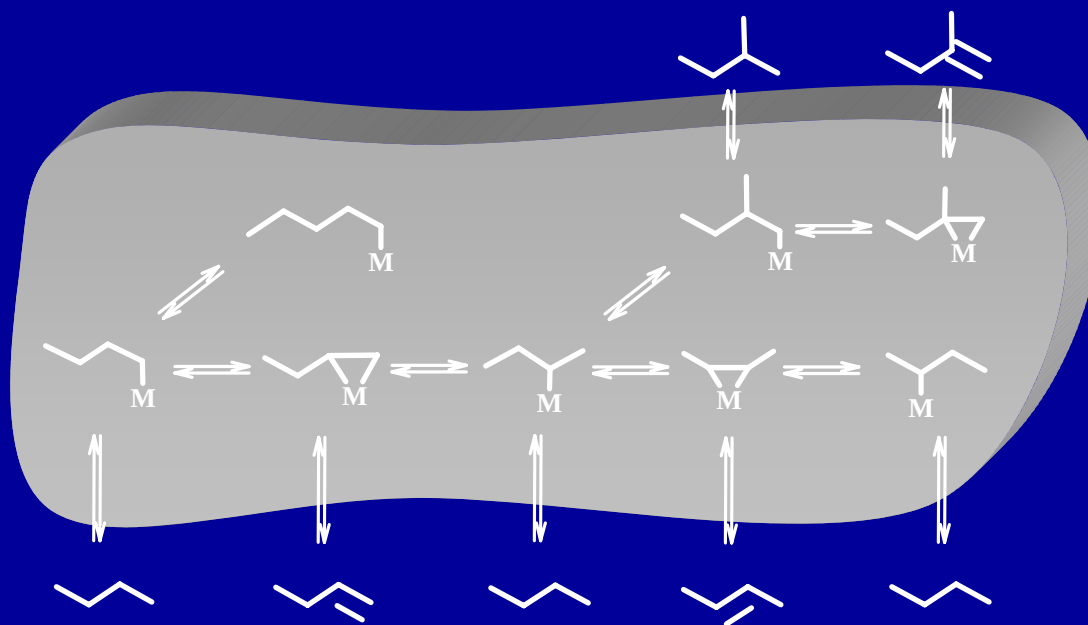
Formation building blocks



Formation of water



Chain growth and termination



Reaction network

Chain initiation

Chemisorption/dissociation



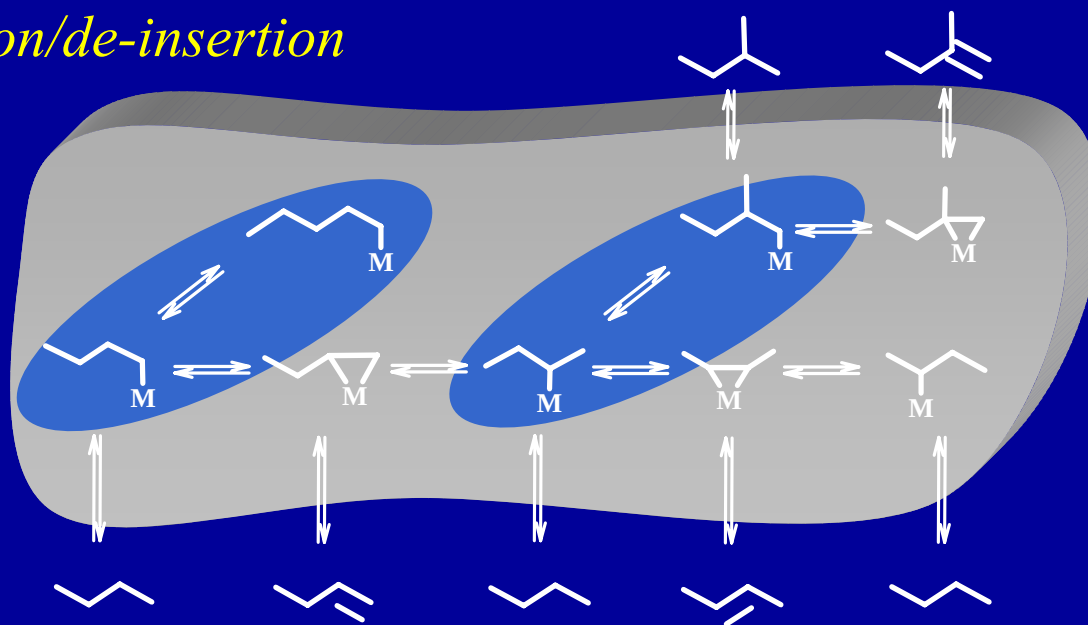
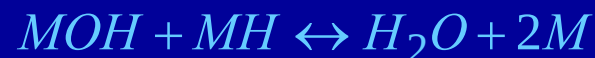
Chain growth and termination

Methylene insertion/de-insertion

Formation building blocks



Formation of water



Reaction network

Chain initiation

Chemisorption/dissociation



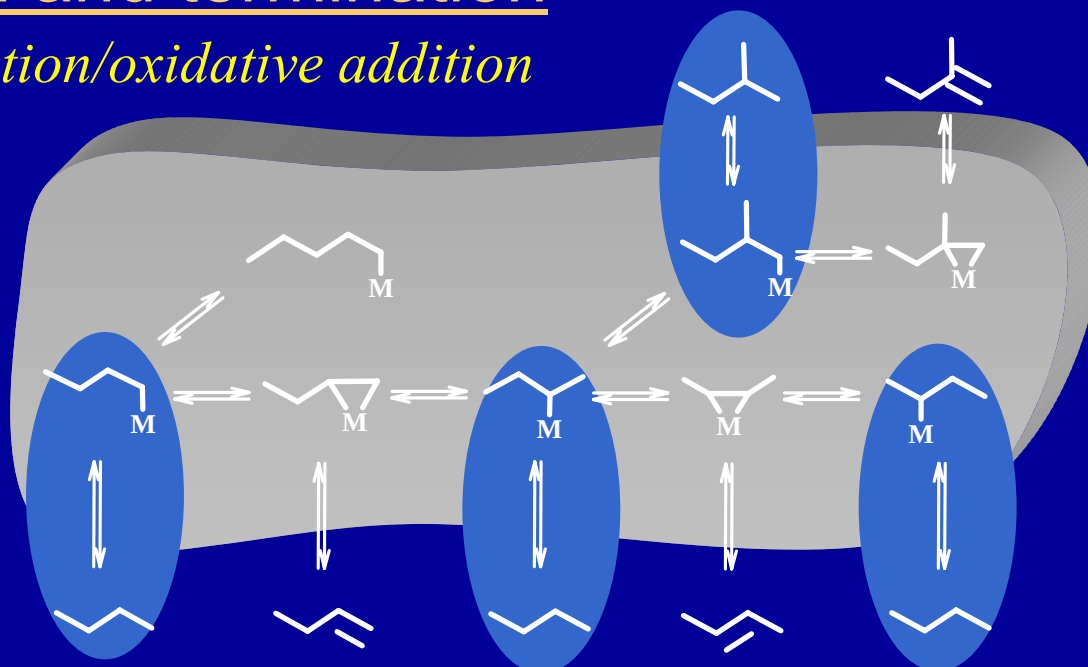
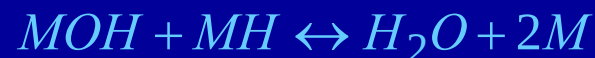
Chain growth and termination

Reductive elimination/oxidative addition

Formation building blocks



Formation of water



Reaction network

Chain initiation

Chemisorption/dissociation



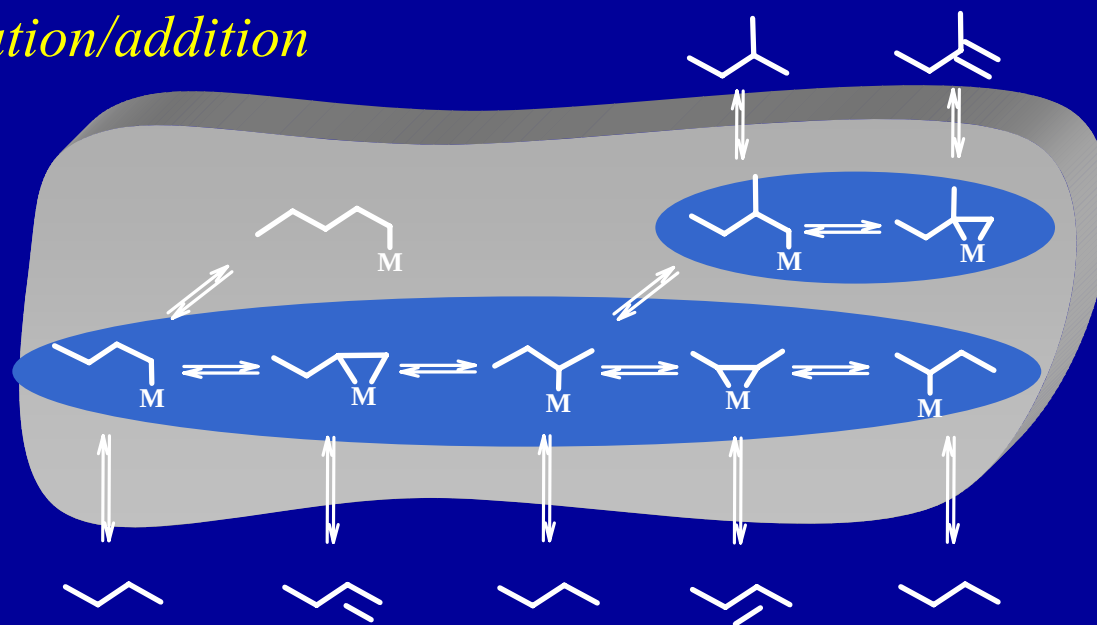
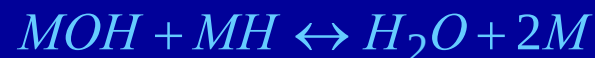
Chain growth and termination

β -hydride elimination/addition

Formation building blocks



Formation of water



Reaction network

Chain initiation

Chemisorption/dissociation



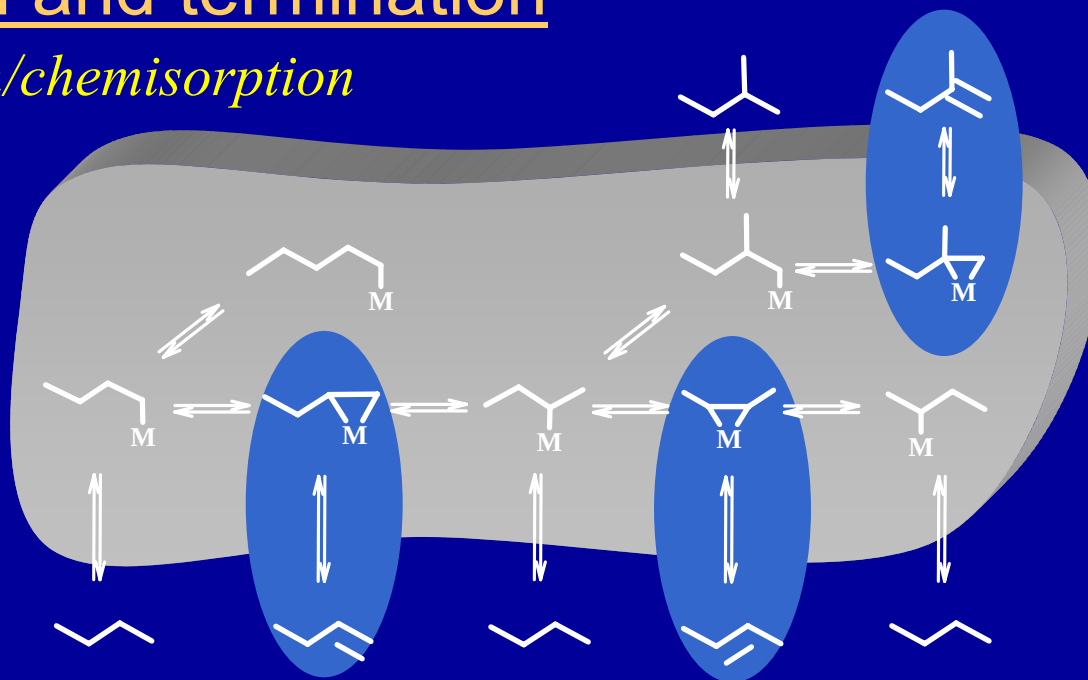
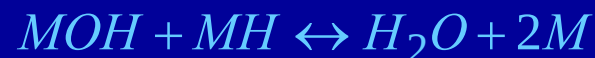
Chain growth and termination

Alkene desorption/chemisorption

Formation building blocks



Formation of water

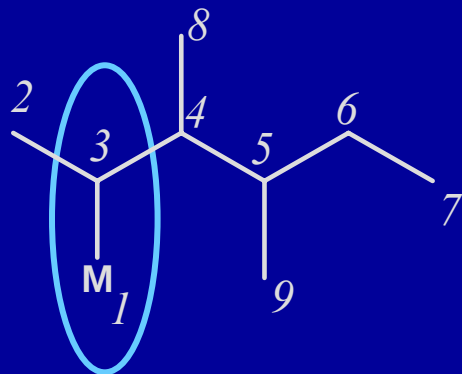


Reaction network

Max. C atom	alkyls	alkanes	alkenes	number elem. steps
8	131	36	94	922
10	528	107	390	3730
12	2084	334	1571	14752

- Numerical representation of molecules:

- Boolean matrices (*chemical transformation*)

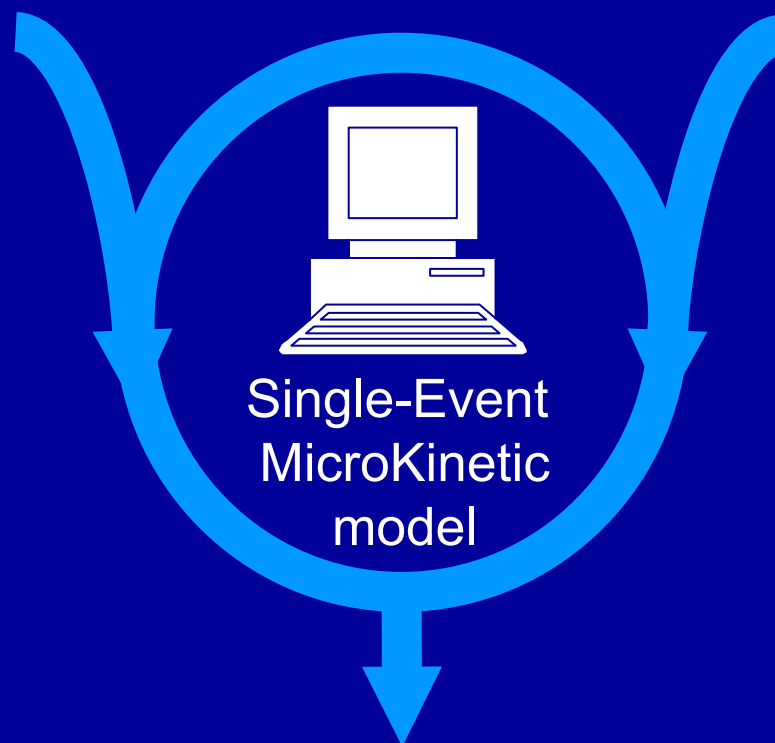
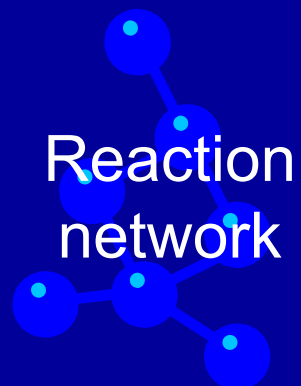


		1	2	3	4	5	6	7	8	9
1	M	0	0	1	0	0	0	0	0	0
2	C	0	0	1	0	0	0	0	0	0
3	C	1	1	0	1	0	0	0	0	0
4	C	0	0	1	0	1	0	0	1	0
5	C	0	0	0	1	0	1	0	0	1
6	C	0	0	0	0	1	0	1	0	0
7	C	0	0	0	0	0	1	0	0	0
8	C	0	0	0	1	0	0	0	0	0
9	C	0	0	0	0	1	0	0	0	0

- Standardized labels (*storage*)

1	1	3	3	3	2	1	1	1
25	28	26	28	28	28	28	28	28

General scheme



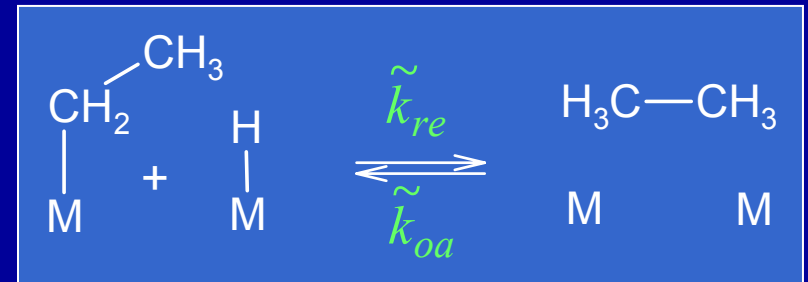
Model equations

Gas-phase compounds

$$\frac{dx_i}{d(W/F_{CO,ini})} = R_i$$

Surface intermediates

$$R_i = 0$$



$$R_{alkane,l} = \sum_{i=1}^{n_{alkyls}} \frac{1}{2} z \frac{\sigma_r}{\sigma_{\neq}} \tilde{k}_{re,M-alkyls} C_{M-alkyl_{i \rightarrow l}} \frac{C_{M-H}}{C_{M_{tot}}} - \frac{1}{2} z \frac{\sigma_r}{\sigma_{\neq}} \tilde{k}_{oa,alkanes} P_{alkane,l} C_M \frac{C_M}{C_{M_{tot}}}$$

- Probability of finding occupied/unoccupied neighbour surface atoms
- Single-event kinetic coefficient: $\tilde{k} = \tilde{A} \exp(-E_a/RT)$
- Thermodynamic consistency guaranteed by pple microscopic reversibility

$$\tilde{A}_{rev} = \tilde{A}_{for} / \exp(\Delta \tilde{S}_r^0 / R) \quad E_{a,rev} = E_{a,for} - \Delta H_r^0$$

Pre-exponential factors

$$\tilde{A}_{for} = \frac{k_B T}{h} \exp\left(\frac{\Delta\tilde{S}^{0,\neq}}{R}\right)$$

$$\tilde{A}_{rev} = \tilde{A}_{for} / \exp(\Delta\tilde{S}_r^0 / R)$$

$$\Delta\tilde{S}^{0,\neq} = \tilde{S}_{TS}^0 - \sum_{i=1}^{nreact} \nu_i \tilde{S}_i^0$$

$$\Delta\tilde{S}_r^0 = \sum_{i=1}^{nprod} \nu_i \tilde{S}_i^0 - \sum_{j=1}^{nreact} \nu_j \tilde{S}_j^0$$

$$\tilde{S}_{i/TS}^0 = \tilde{S}_{i/TS,gas}^0 + \Delta\tilde{S}_{chem}^0$$

Benson GAV stable molecules and radicals

- Entropy change associated to the chemisorption step proportional to the **loss of translational entropy**
- Single pre-exponential factors per reaction family
- **Fixed kinetic parameters** in the model

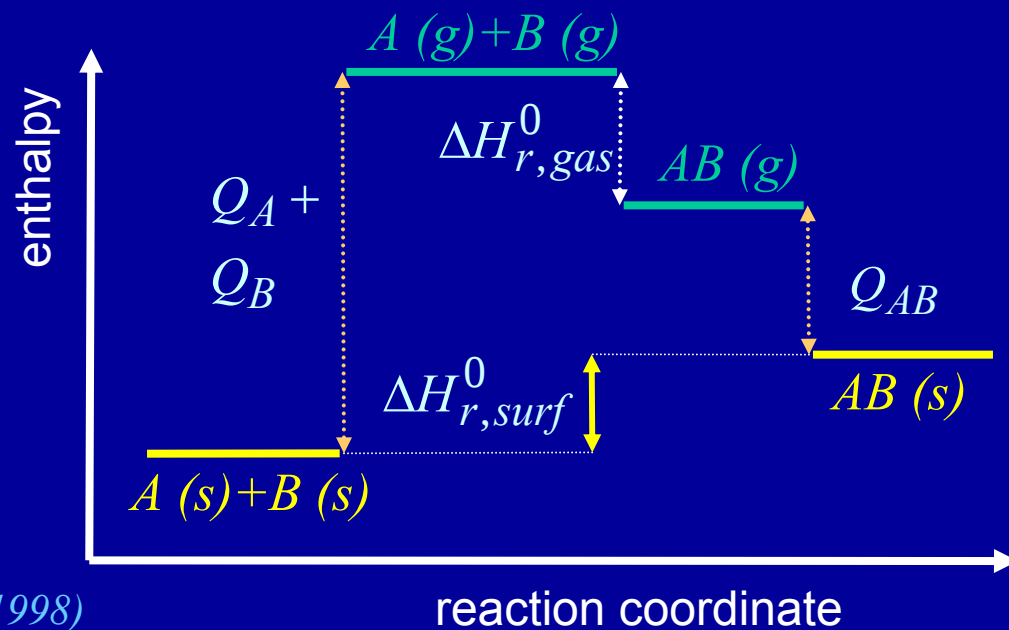
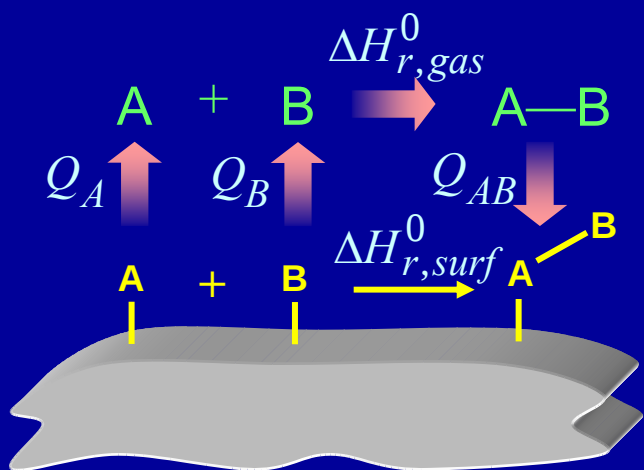
Thermochemistry

- Calculated by phenomenological method (UBI/QEP)

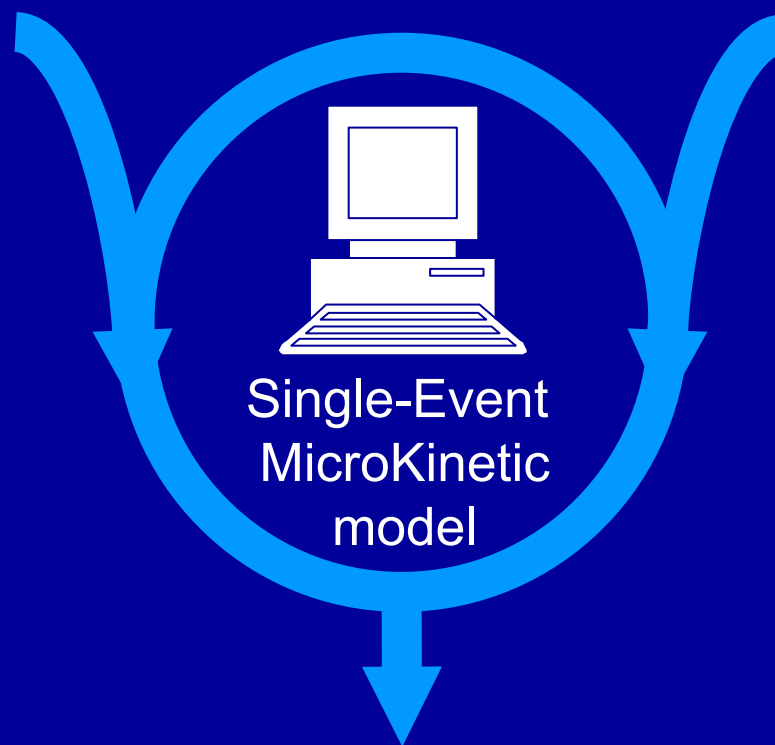
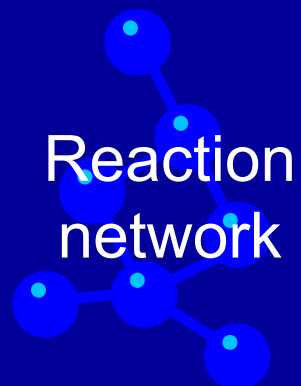
$$\Delta H_{r,surf}^0 = \Delta H_{r,gas}^0 + \sum_{i=1}^{n_{react}} \nu_i Q_i - \sum_{j=1}^{n_{prod}} \nu_j Q_j$$

$$Q_{AB} = \frac{Q_A}{Q_A + D_{AB}} \quad (\text{"strong" chem. enthalpy})$$

- Adjustable parameters: $Q_A = (Q_C, Q_H, Q_O, \dots)$



General scheme



Validation on Fe and Co

Iron

- **Water-Gas Shift** (iron oxide phase, formate mechanism, 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)

Parameter estimation

Reaction family/ elem. reaction	$\tilde{A}_{for}$ ($\text{bar}^{-1}\text{s}^{-1}$ or s^{-1})	$E_{a,for} / Q$ (kJ/mol)	
		Fe	Co
$H_2 + 2M \leftrightarrow 2MH$	$3.1 \cdot 10^8$	0.0	0.0
$CO + 2M \leftrightarrow MMCO$	$2.2 \cdot 10^7$	0.0	0.0
$MMCO + 3M \leftrightarrow MMMC + MMO$	$1.3 \cdot 10^{13}$	56.8 ± 0.5	52.8 ± 6.2
$MMMC + MH \leftrightarrow MMMCH + M$	$8.8 \cdot 10^{14}$	77.7 ± 0.7	74.3 ± 10.3
$MMMCH + MH \leftrightarrow MMCH_2 + 2M$	$5.7 \cdot 10^{11}$	11.9 ± 0.1	12.2 ± 2.0
$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$	$2.3 \cdot 10^{11}$	61.9 ± 0.5	71.9 ± 3.1
$MMO + MH \leftrightarrow MOH + 2M$	$1.3 \cdot 10^{12}$	103.8 ± 1.0	107.0 ± 6.6
$MOH + MH \leftrightarrow H_2O + 2M$	$2.4 \cdot 10^{11}$	86.2 ± 0.6	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

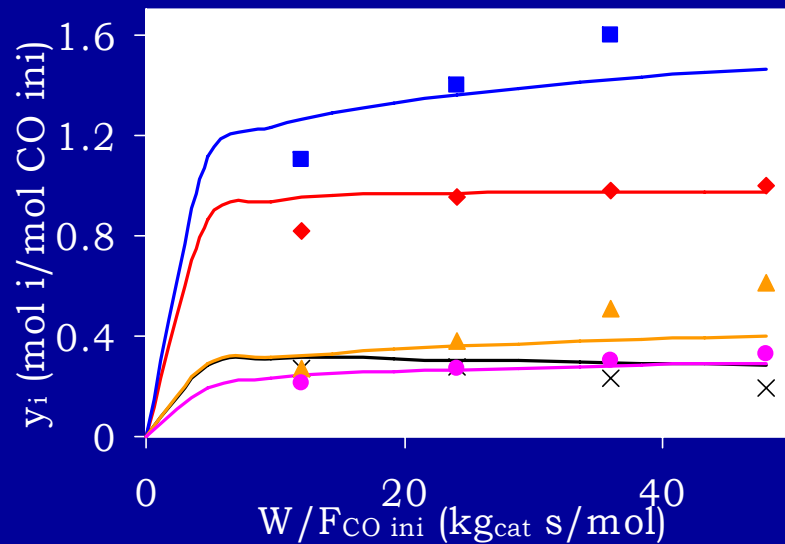
Parameter estimation

<i>Reaction family/ elem. reaction</i>	$\tilde{A}_{for}$ ($\text{bar}^{-1}\text{s}^{-1}$ or s^{-1})	$E_{a,for} / Q$ (kJ/mol)	
		<i>Fe</i>	<i>Co</i>
$MC_nH_{2n+1} + MMCH_2 \leftrightarrow$ $MC_{n+1}H_{2n+3} + 2M$	$8.9 \cdot 10^9$	44.8 ± 0.4	43.5 ± 2.0
$MC_nH_{2n+1} + MH \leftrightarrow C_nH_{2n+2} + 2M$	$2.1 \cdot 10^{10}$	117.8 ± 0.7	103.6 ± 2.0
$MC_nH_{2n+1} + M \leftrightarrow MC_nH_{2n} + MH$	$1.1 \cdot 10^{10}$	96.3 ± 0.5	86.1 ± 1.4
$MC_nH_{2n} \leftrightarrow C_nH_{2n} + M$	$1.3 \cdot 10^{13}$	-	-

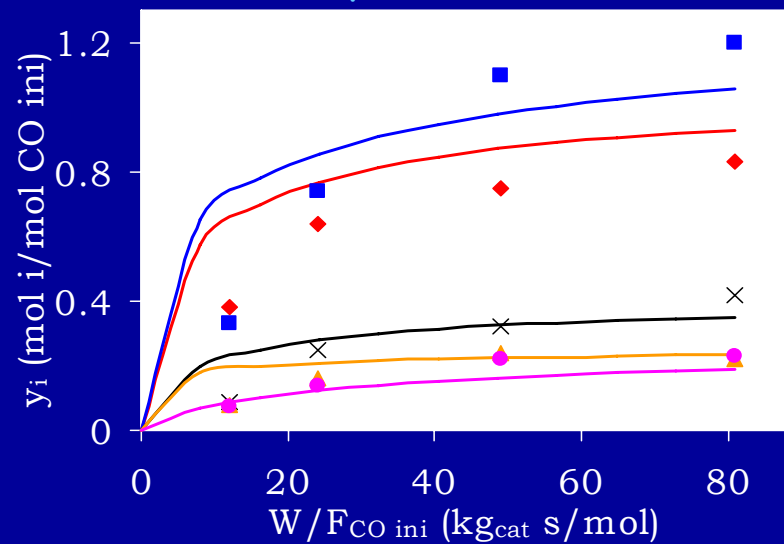
- Significant changes only in atomic chemisorption enthalpies and in elementary steps determining the product distribution (catalyst dependent parameters)

Model validation on Fe

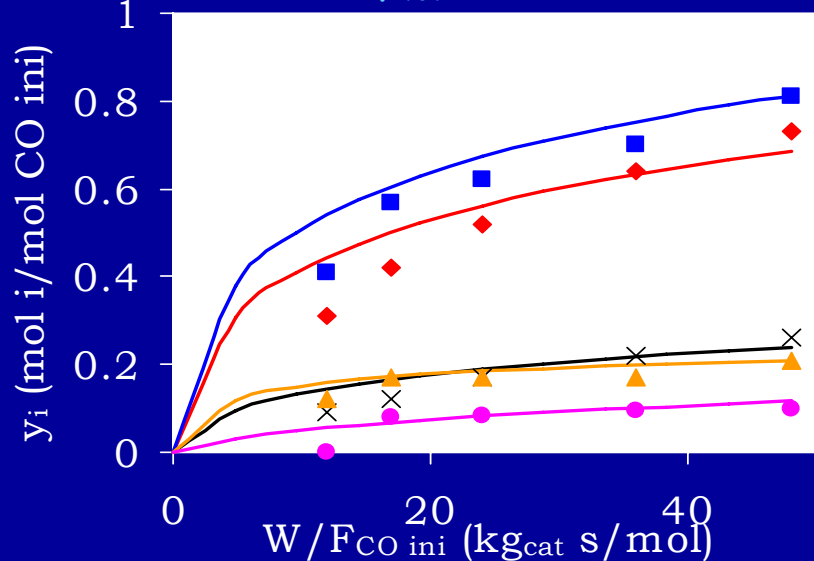
$T=623\text{K}; p_{\text{tot}}=21\text{bar}; H_2/CO=3$



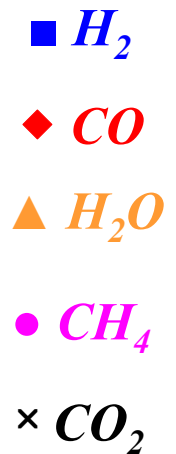
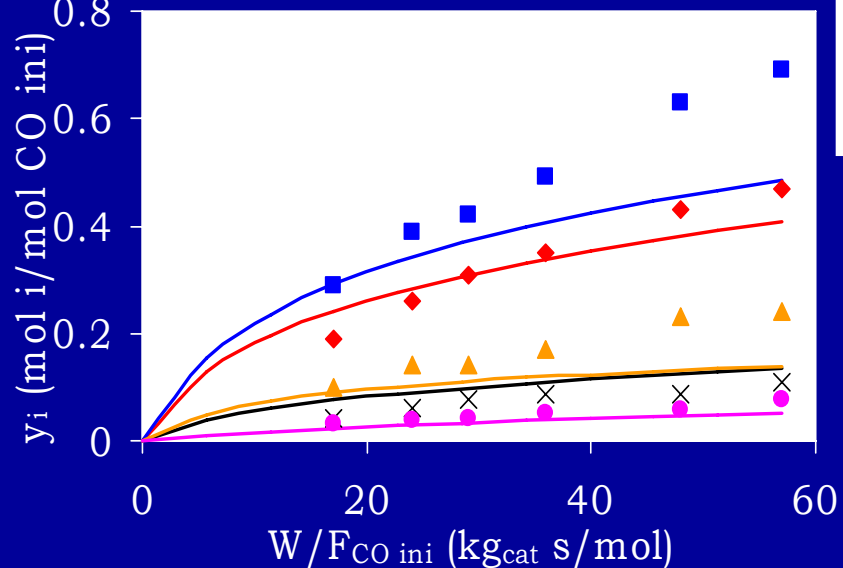
$T=573\text{K}; p_{\text{tot}}=11\text{bar}; H_2/CO=3$



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

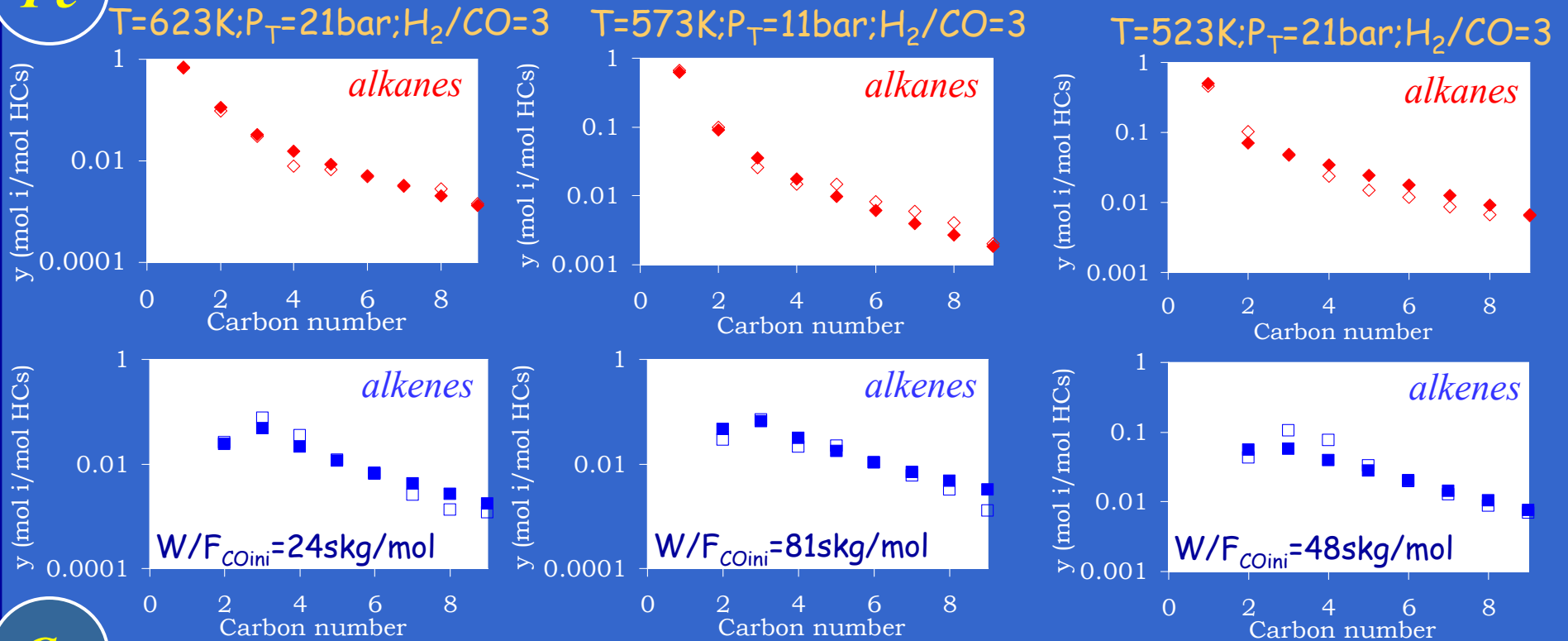


$T=523\text{K}; p_{\text{tot}}=21\text{bar}; H_2/CO=3$

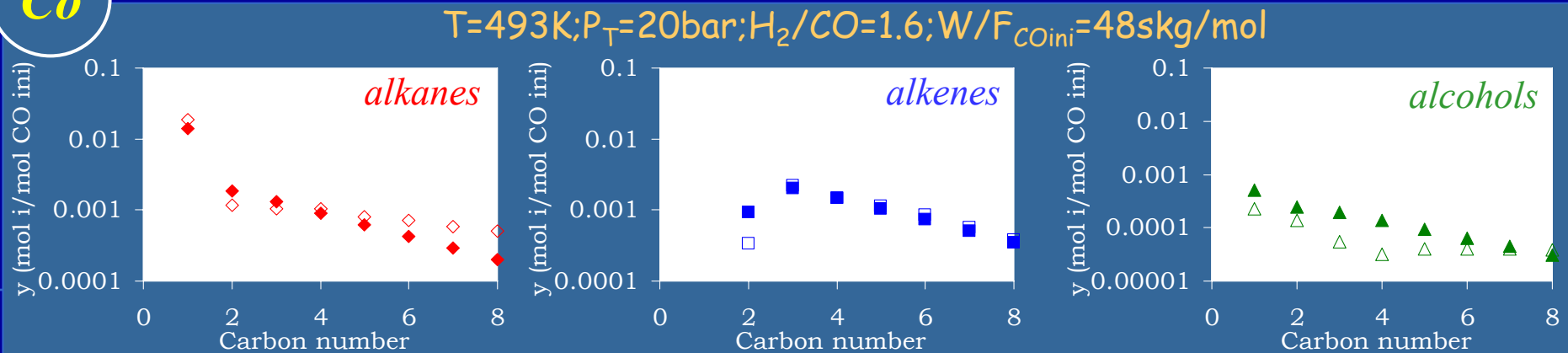


Model validation on Fe and Co

Fe

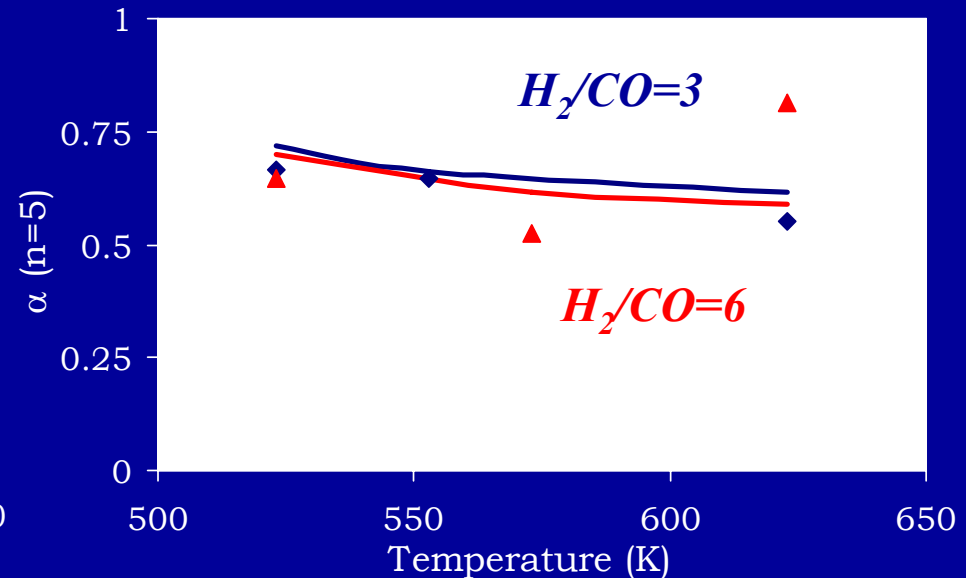
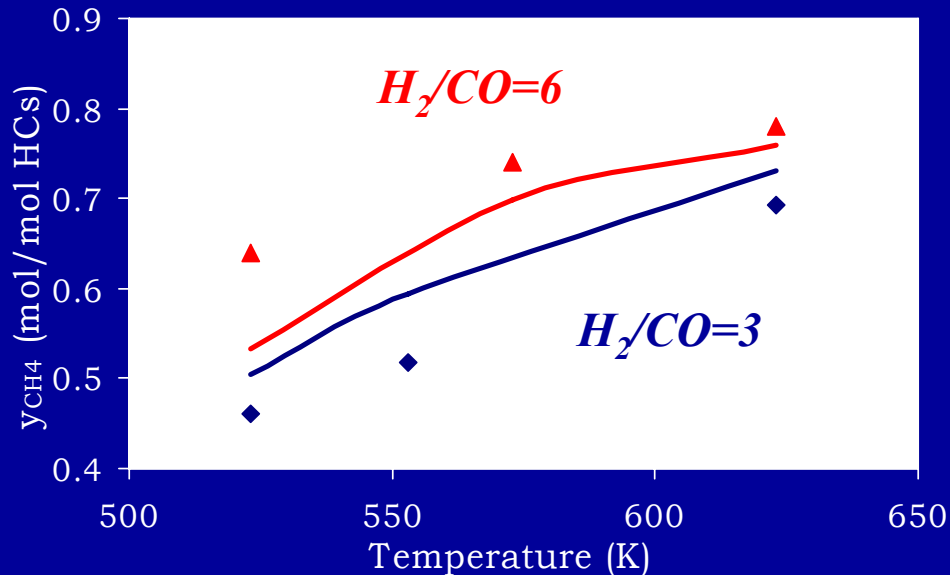


Co



General trends (Fe)

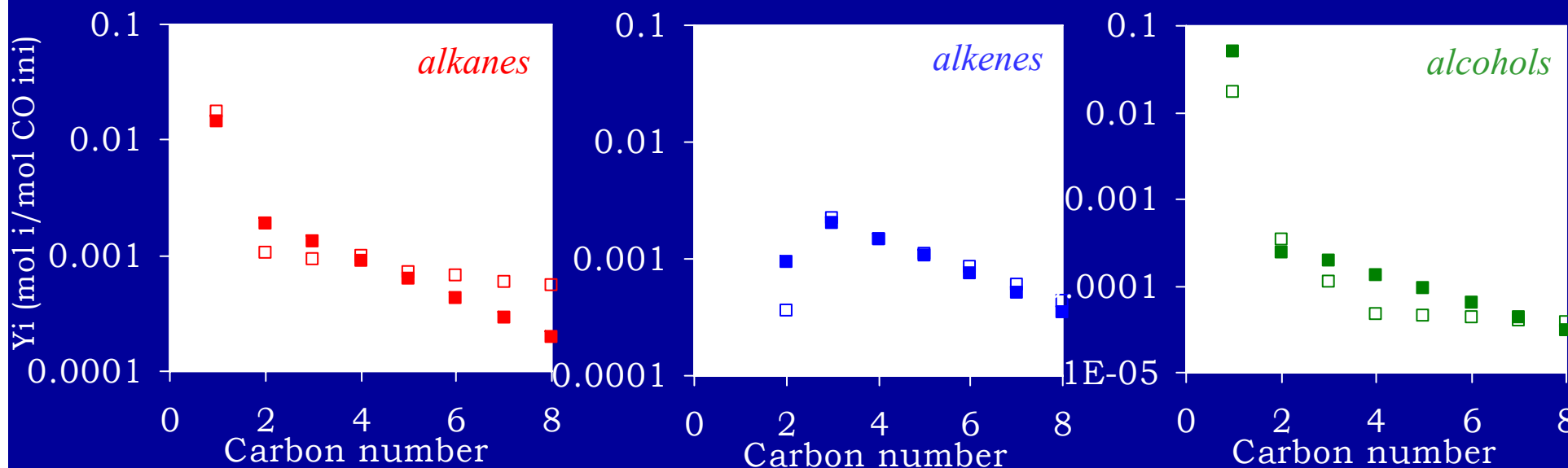
$p_{\text{tot}} = 11 \text{ bar}$; $W/F_{\text{COini}} = 43\text{-}48 \text{ skg/mol}$



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

Secondary reactions (Co)

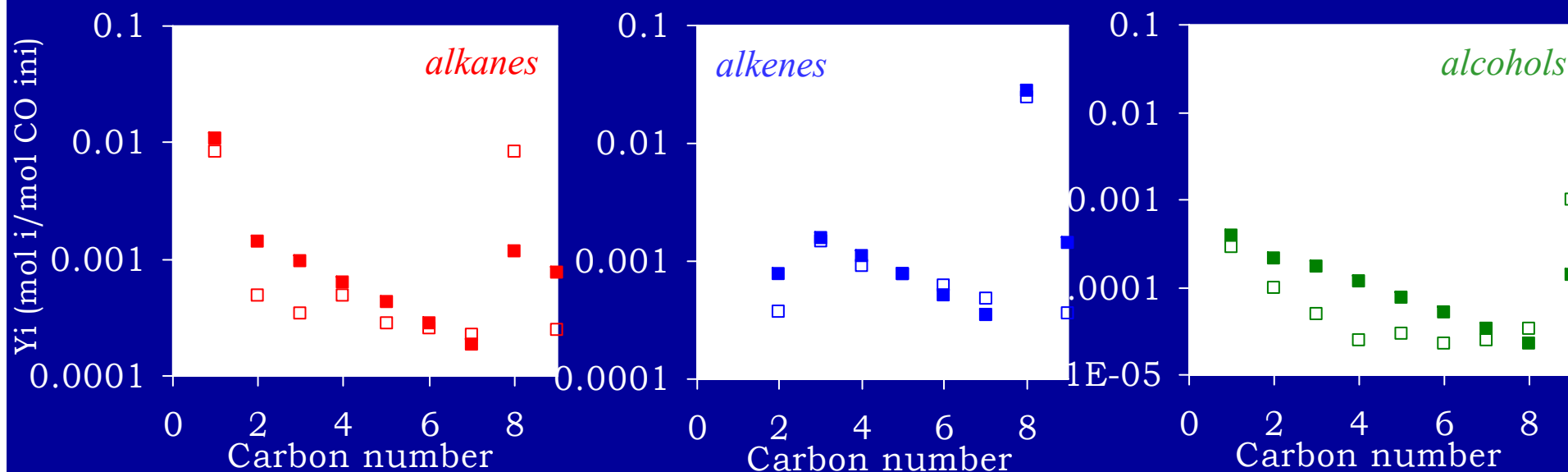
- Methanol addition
 - No effect on product distribution



$T=493K$; $p_{tot}=20bar$; $H_2/CO=2$; $W/F_{COini}=48skg/mol$

Secondary reactions (Co)

- 1-octene addition
 - Increases selectivities towards n-octane and 1-nonanol



$T=493\text{K}$; $p_{\text{tot}}=20\text{bar}$; $H_2/CO=1.6$; $W/F_{COini}=48\text{skg/mol}$

Conclusions

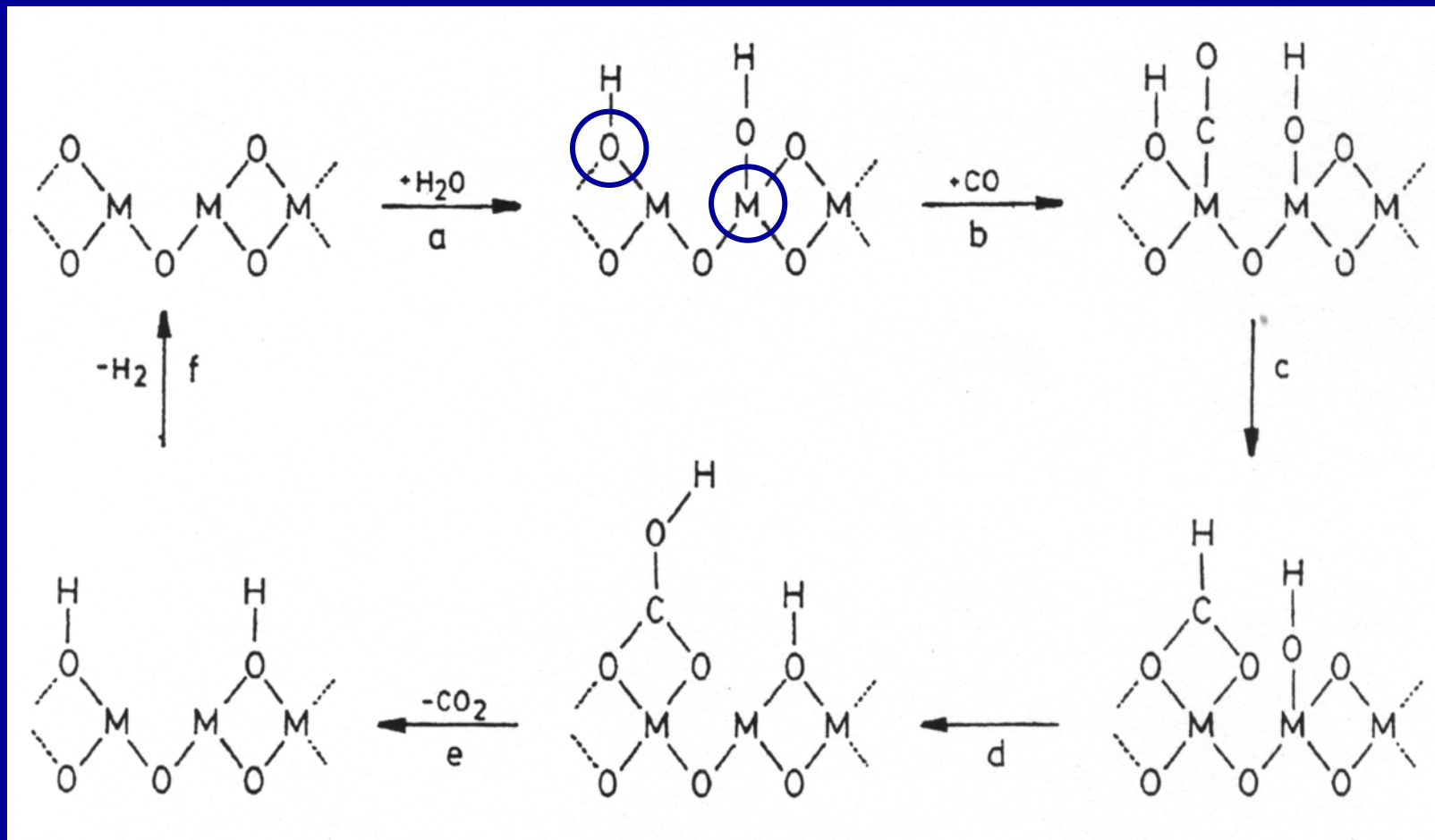
- A single model is able to describe product distributions on Fe and Co catalysts with physically meaningful parameter values
- Single-event concept (entropy differences) allows to describe the typical deviations observed at lower carbon atoms
- 3 activation energies show strong catalyst dependency
- Relations between these activation energies and catalyst properties should be further investigated

Acknowledgements

- Financial support: Institut Français du Pétrole (IFP) and IAP program funded by the Belgian Science Policy
- PoliMi and EniTecnologie

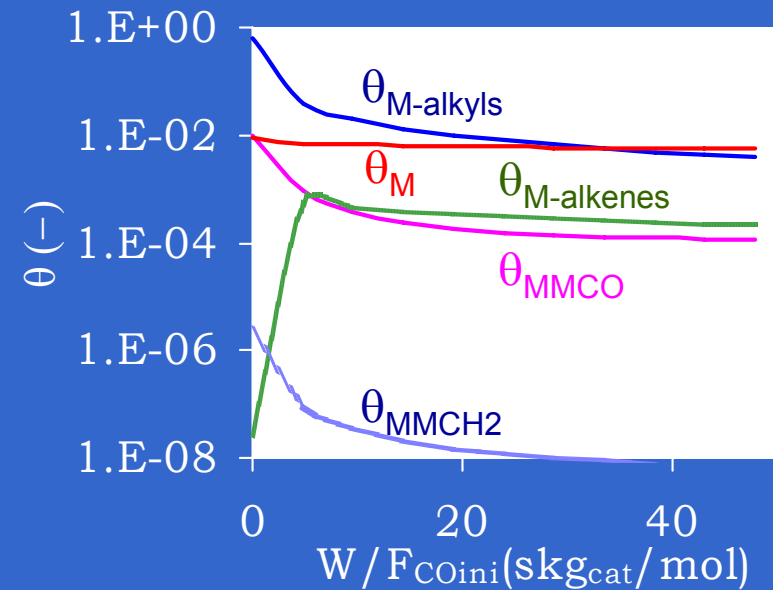
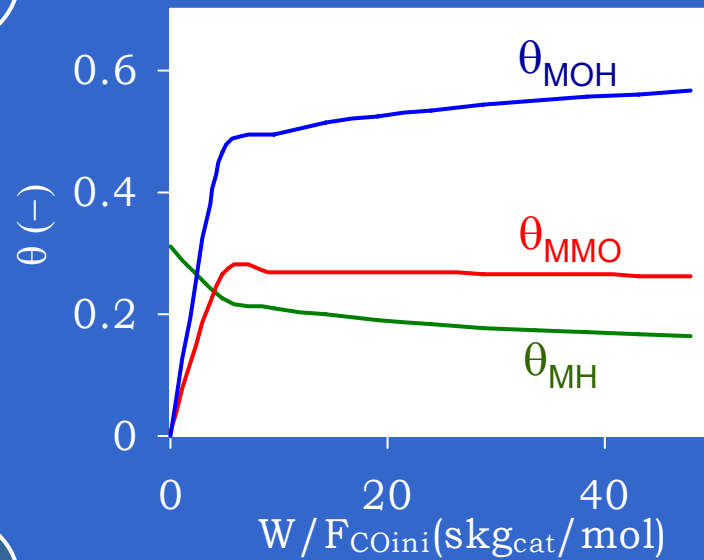
Water-Gas Shift

- Formate mechanism



Surface species

Fe



Co

