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

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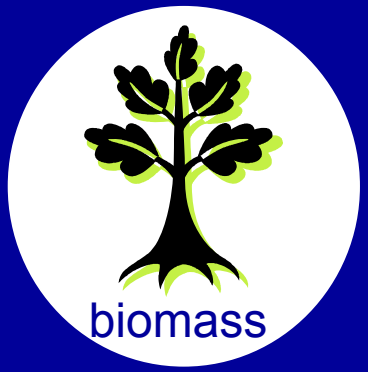
EUROPACAT-VIII

26 - 31 August 2007, Turku, Finland

Fischer-Tropsch synthesis

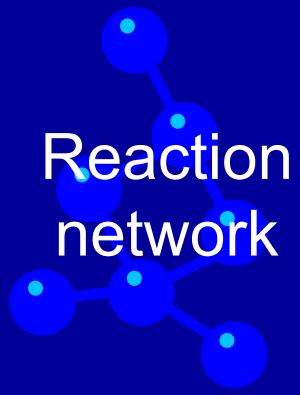


Commercially in operation in South Africa and Malaysia

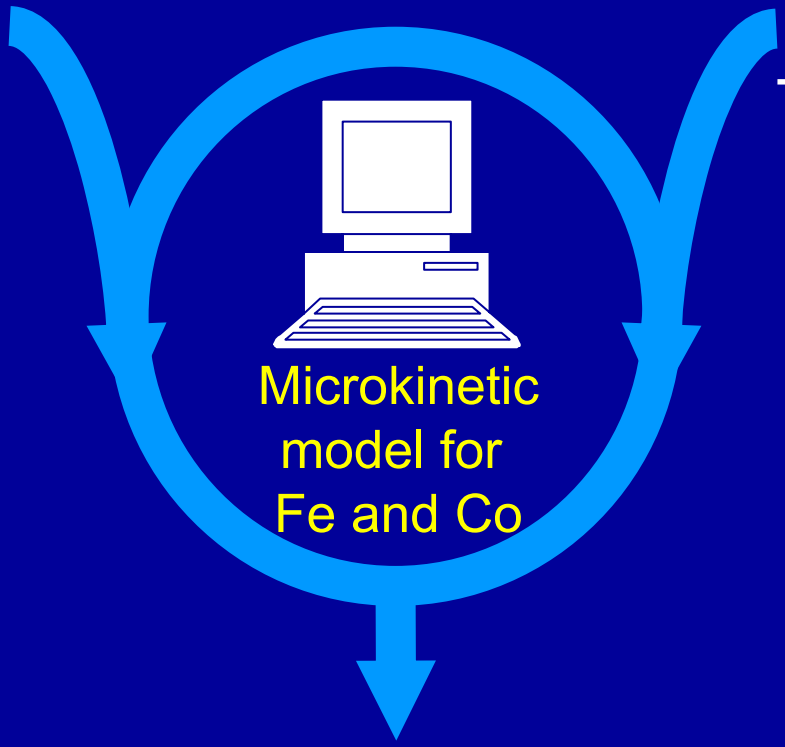
GTL Bintulu (Malaysia)

$$nCO + 2nH_2 \rightarrow -(CH_2)_n- + nH_2O$$

General scheme - Objective

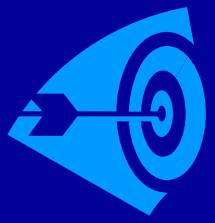


Reaction network



Microkinetic model for Fe and Co

Thermochemistry



Validation

Single-Event MicroKinetics

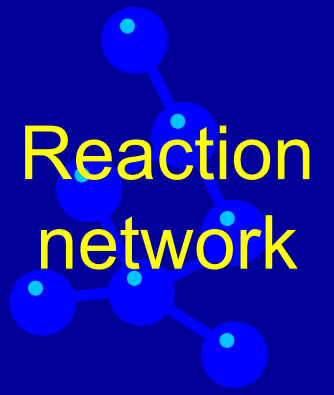
- Microkinetic model accounts for the rate of every elementary step → detailed selectivities → potential tool to design more performing catalysts
- Single-Event MicroKinetics (SEMK) consist of extracting the symmetry factors from the entropic contribution

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

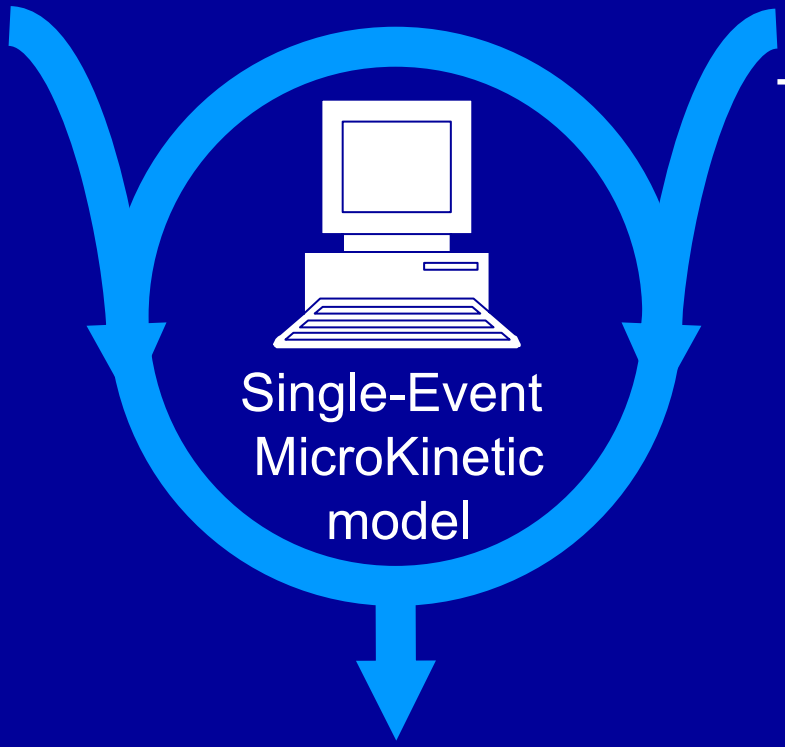
$$\tilde{k} = \tilde{A} \exp\left(-E_a / RT\right)$$

- Unique single-event rate coefficient for each reaction family

General scheme

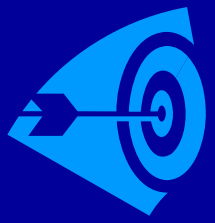


Reaction network



Single-Event MicroKinetic model

Thermochemistry



Validation

Reaction network

Chain initiation

Chemisorption/dissociation

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

$$CO + 2M \leftrightarrow MMCO$$

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

Chain growth and termination

Formation building blocks

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

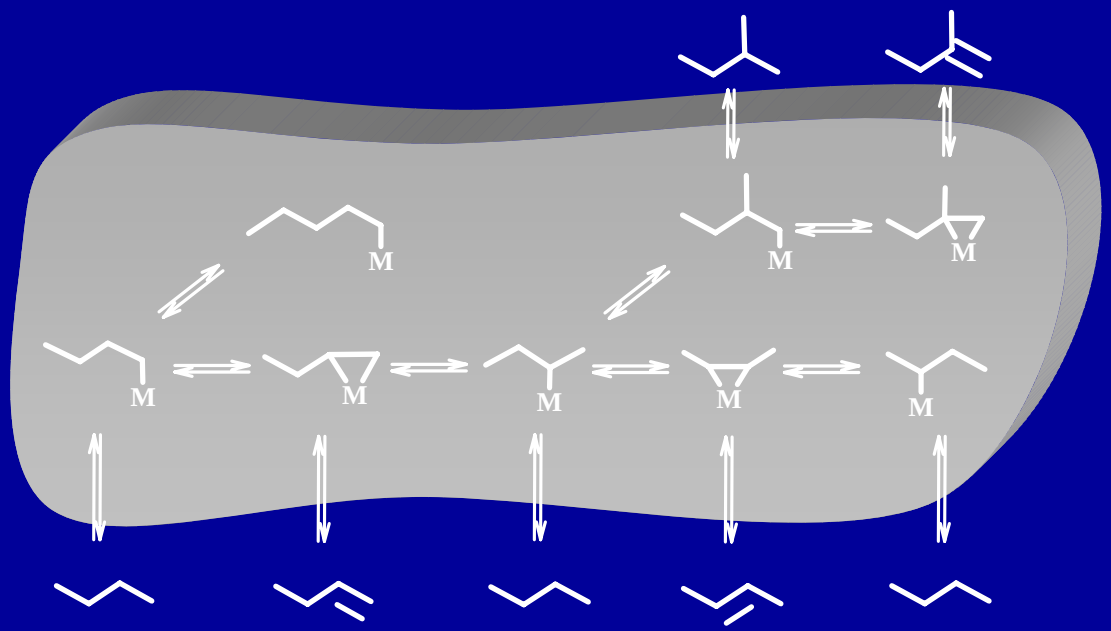
$$MMMCH + MH \leftrightarrow MMCH_2 + 2M$$

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

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

Methylene insertion/de-insertion

Formation building blocks

$MMMC + MH \leftrightarrow MMMCH + M$

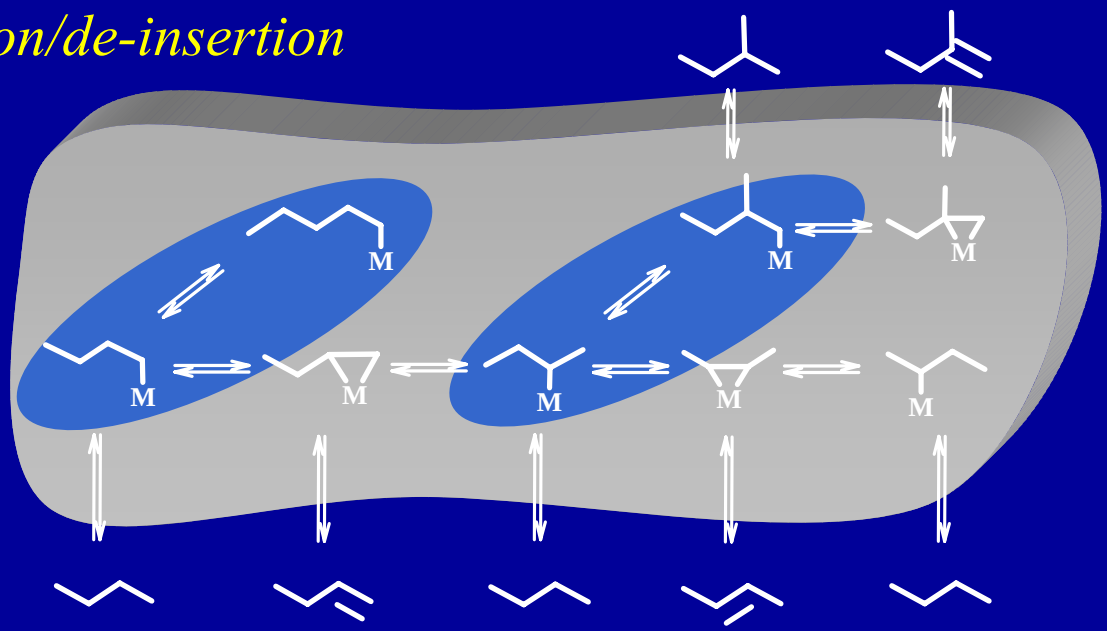
$MMMCH + MH \leftrightarrow MMCH_2 + 2M$

$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$

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

Reductive elimination/oxidative addition

Formation building blocks

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

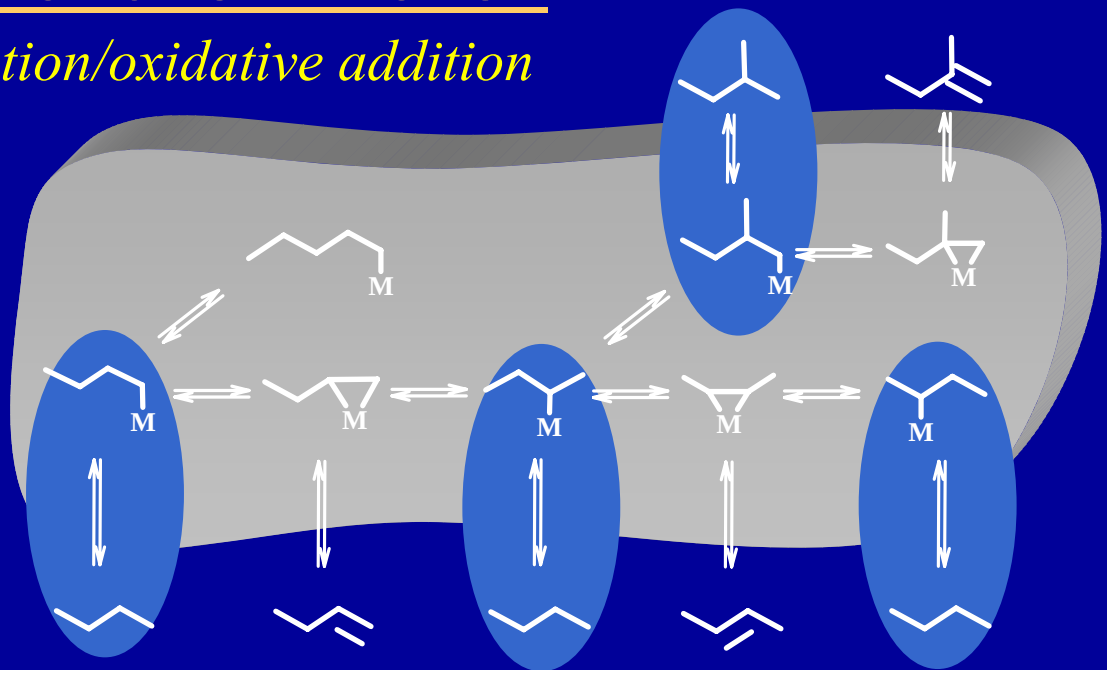
$$MMMCH + MH \leftrightarrow MMCH_2 + 2M$$

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

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 elimination/addition

Formation building blocks

$MMMC + MH \leftrightarrow MMMCH + M$

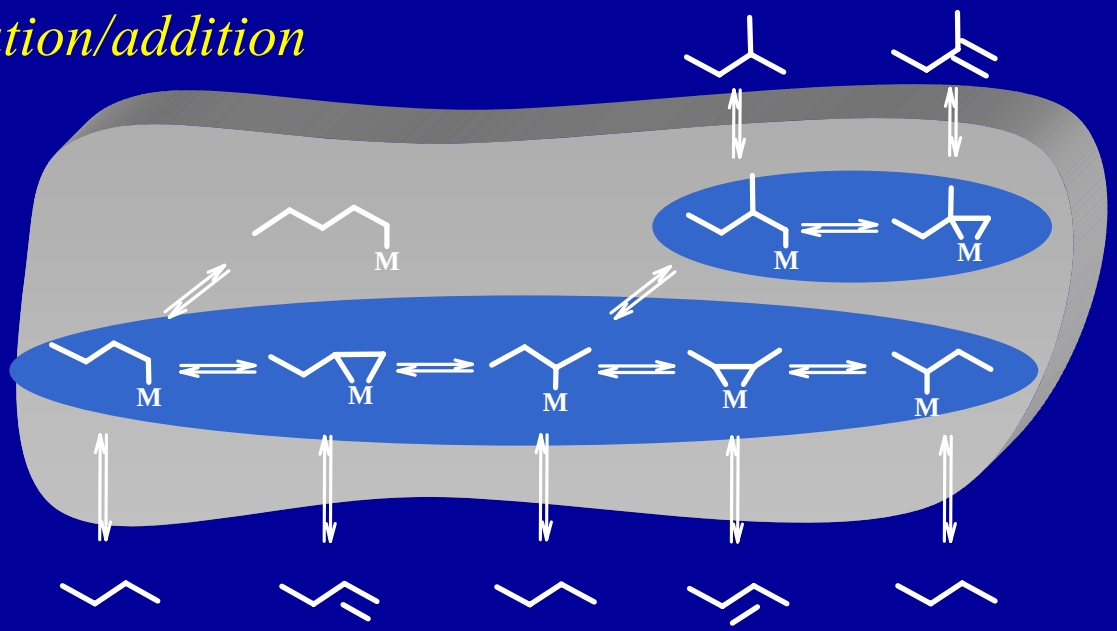
$MMMCH + MH \leftrightarrow MMCH_2 + 2M$

$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$

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

Alkene desorption/chemisorption

Formation building blocks

$MMMC + MH \leftrightarrow MMMCH + M$

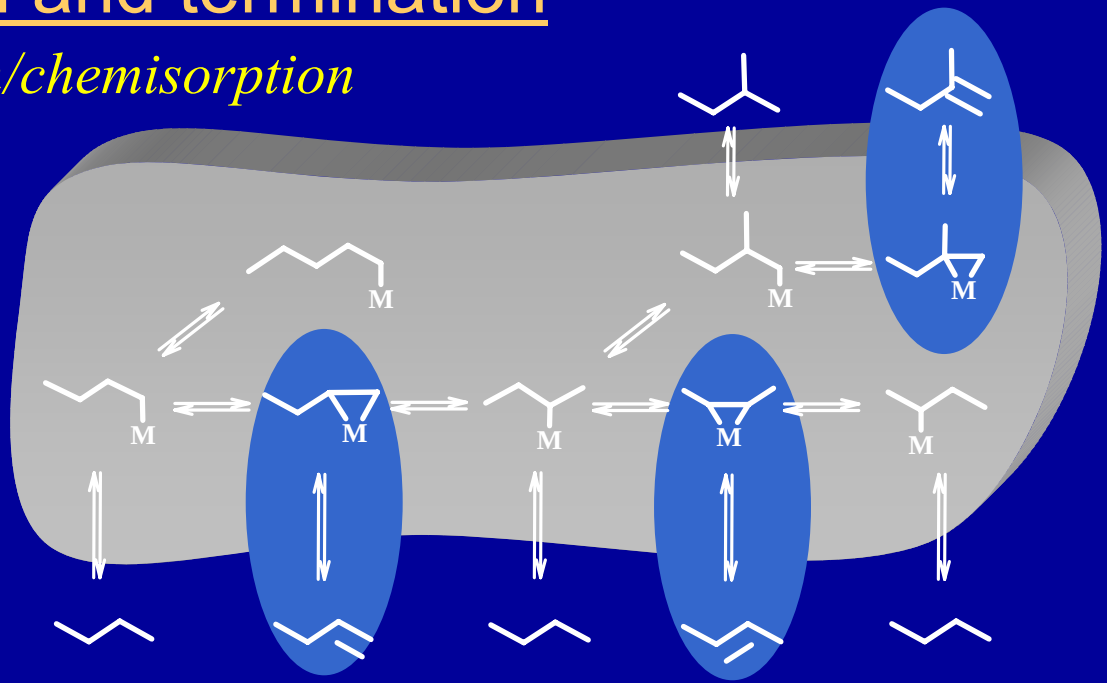
$MMMCH + MH \leftrightarrow MMCH_2 + 2M$

$MMCH_2 + MH \leftrightarrow MCH_3 + 2M$

Formation of water

$MMO + MH \leftrightarrow MOH + 2M$

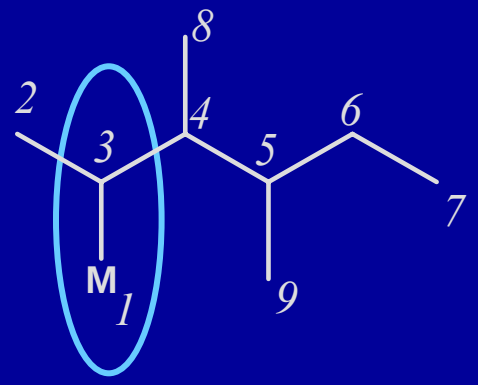
$MOH + MH \leftrightarrow H_2O + 2M$



Reaction network

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)*

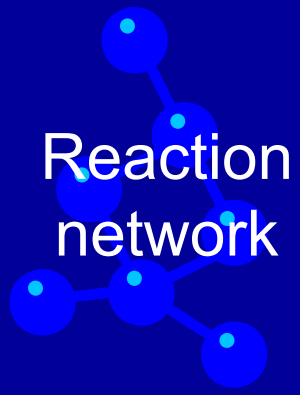


		1	2	3	4	5	6	7	8	9
1	M	0	0	1	0	0	0	0	0	0
2	C	0	0	1	0	0	0	0	0	0
3	C	1	1	0	1	0	0	0	0	0
4	C	0	0	1	0	1	0	0	1	0
5	C	0	0	0	1	0	1	0	0	1
6	C	0	0	0	0	1	0	1	0	0
7	C	0	0	0	0	0	1	0	0	0
8	C	0	0	0	1	0	0	0	0	0
9	C	0	0	0	0	1	0	0	0	0

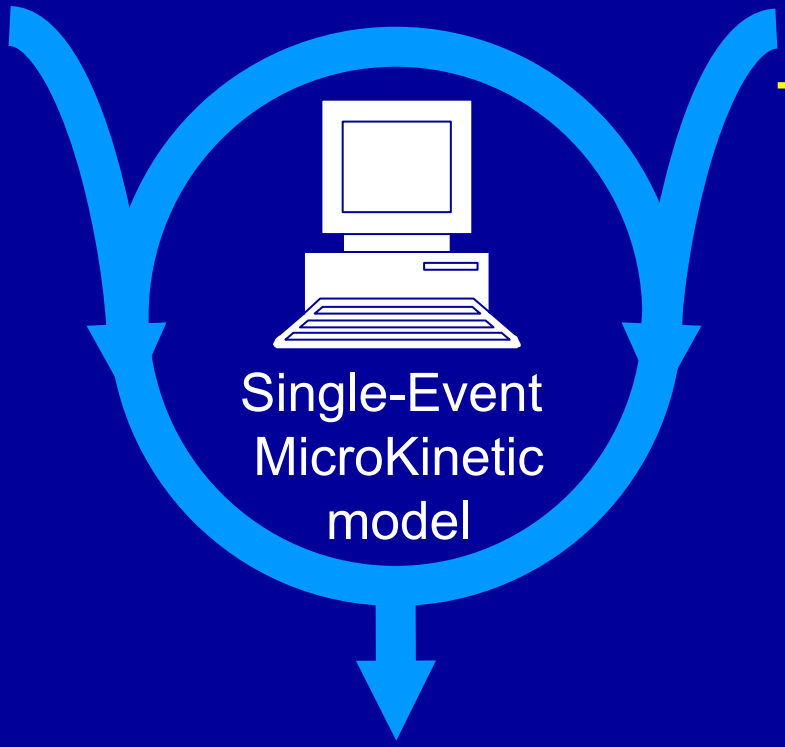
  - Standardized labels *(storage)*

$$\begin{bmatrix} 1 & 1 & 3 & 3 & 3 & 2 & 1 & 1 & 1 \\ 25 & 28 & 26 & 28 & 28 & 28 & 28 & 28 & 28 \end{bmatrix}$$

General scheme

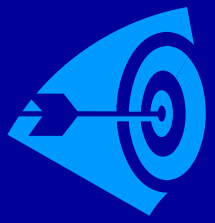


Reaction network



Single-Event MicroKinetic model

Thermochemistry

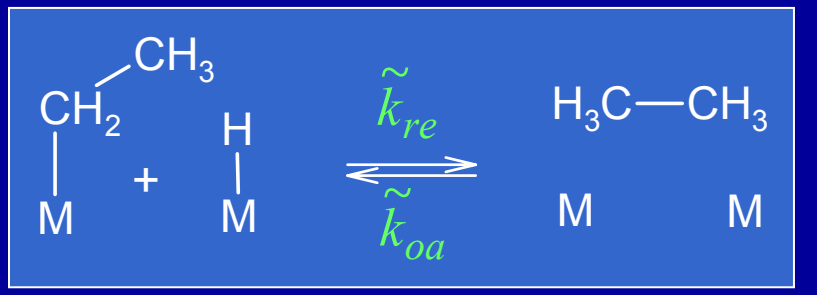


Validation

Model equations

Gas-phase compounds $\dfrac{dx_i}{d\left(W/F_{CO,ini}\right)} = R_i$

Surface intermediates $R_i = 0$



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

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

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

Pre-exponential factors

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

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

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

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

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

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

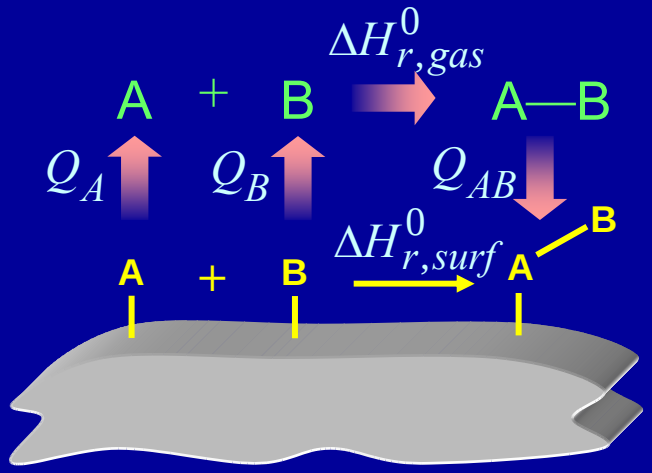
Thermochemistry

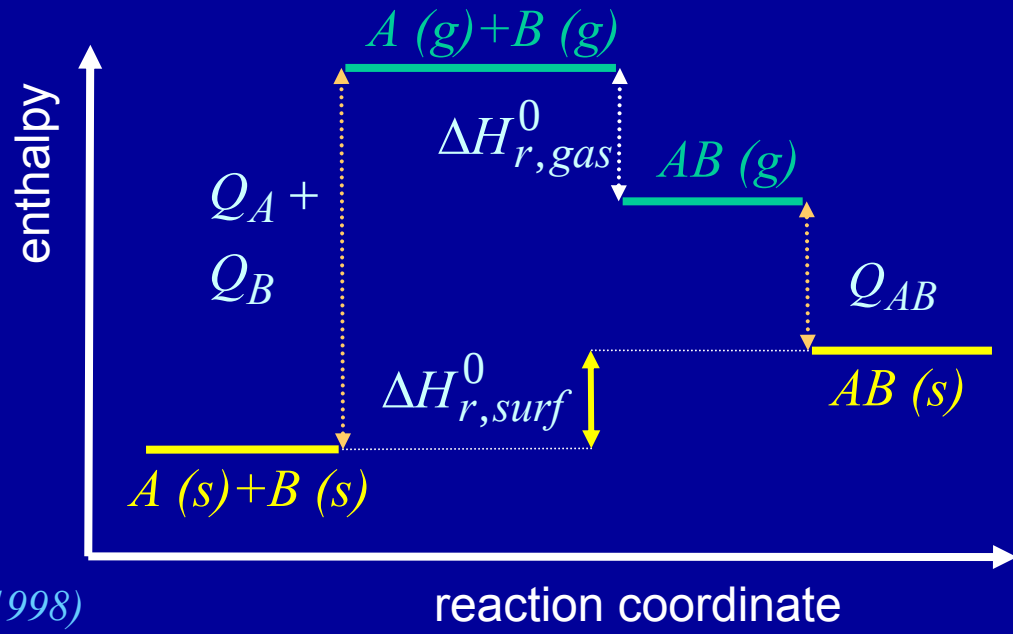
- Calculated by phenomenological method (UBI/QEP)

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

$$Q_{AB} = \frac{Q_A}{Q_A + D_{AB}} \qquad (\text{“strong” chem. enthalpy})$$

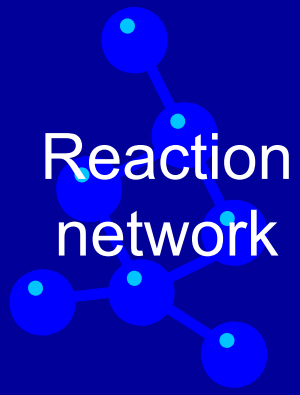
- Adjustable parameters: $Q_A = (Q_C, Q_H, Q_O, ..)$



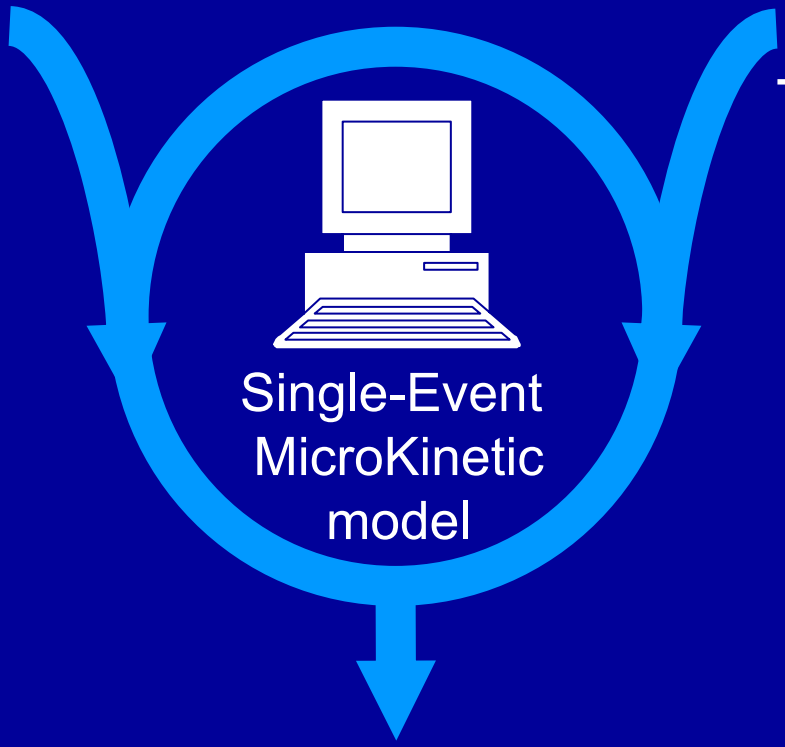


Shustorovich et al., Surface Science Reports 31 (1998)

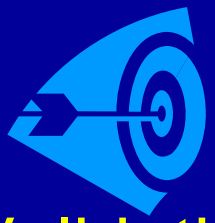
General scheme



Reaction network



Thermochemistry



Validation

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

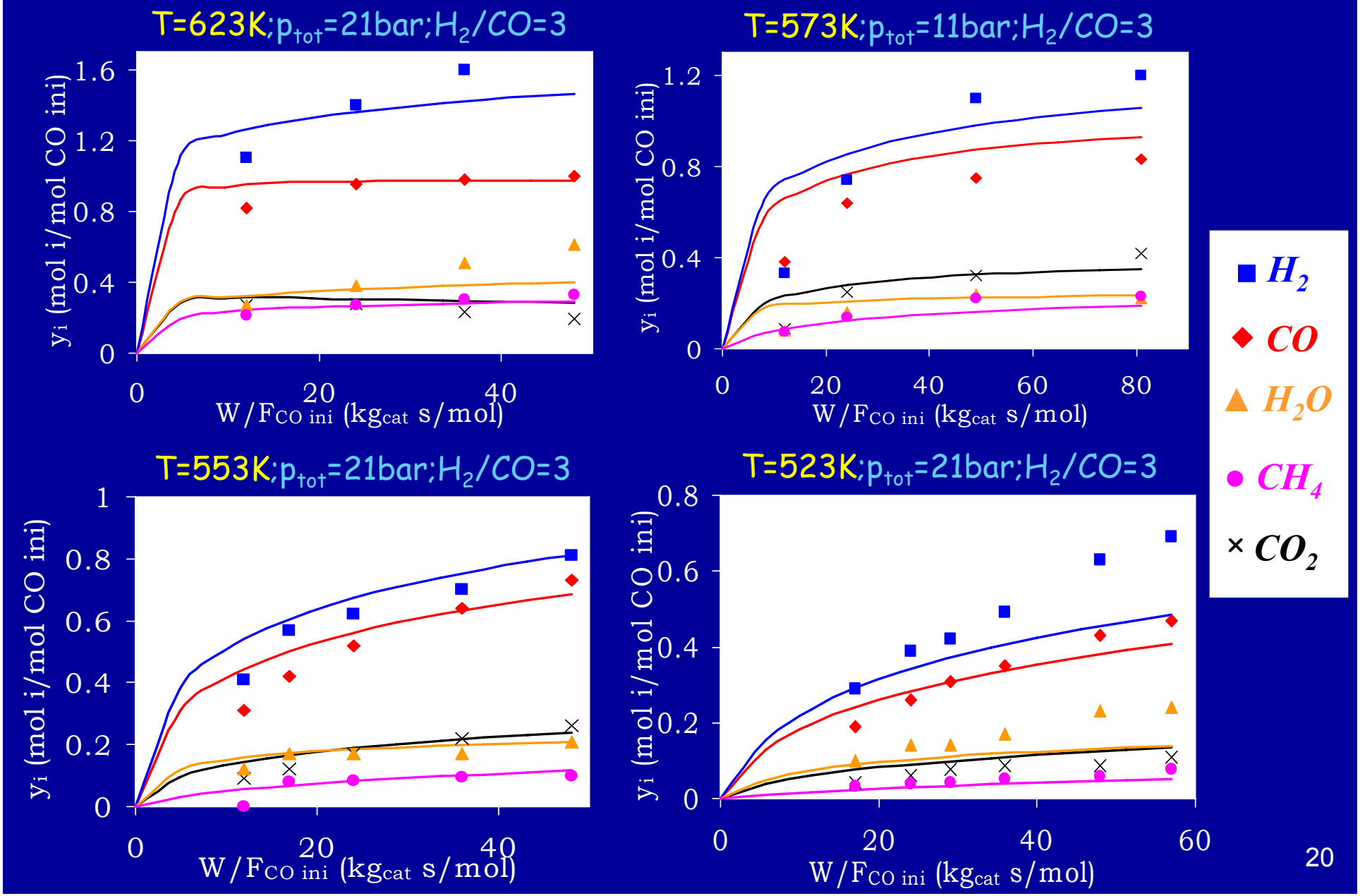
Reaction family/ elem. reaction	$\tilde{A}_{for}$ ($bar^{-1}s^{-1}$ or s^{-1})	$E_{a,for}$ / Q (kJ/mol)	
		Fe	Co
$H_2 + 2M \leftrightarrow 2MH$	$3.1\ 10^{8}$	0.0	0.0
$CO + 2M \leftrightarrow MMCO$	$2.2\ 10^{7}$	0.0	0.0
$MMCO + 3M \leftrightarrow MMMC + MMO$	$1.3\ 10^{13}$	56.8±0.5	52.8±6.2
$MMMC + MH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

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

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

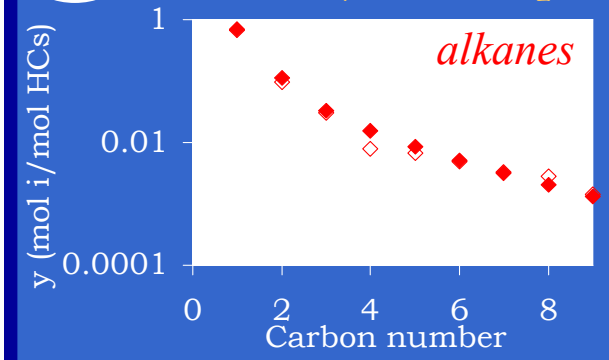
Model validation on Fe

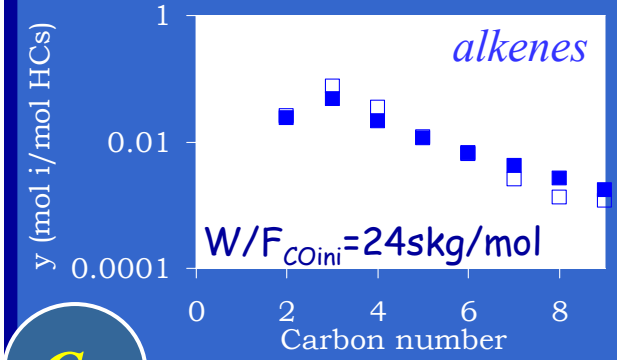


Model validation on Fe and Co

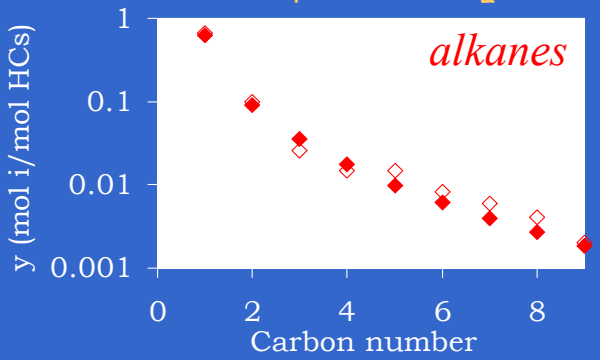
Fe

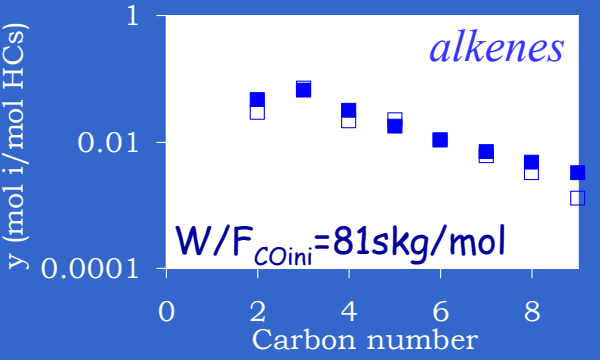
T=623K;P_T=21bar;H_2/CO=3



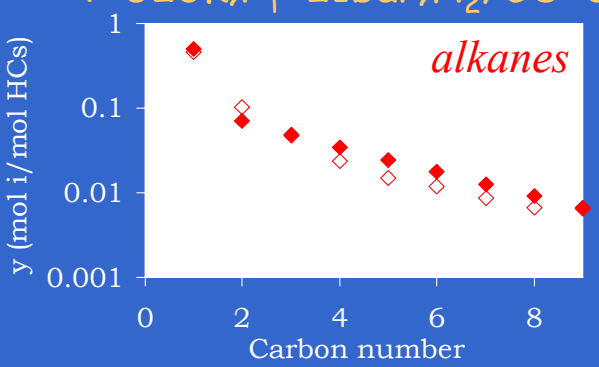


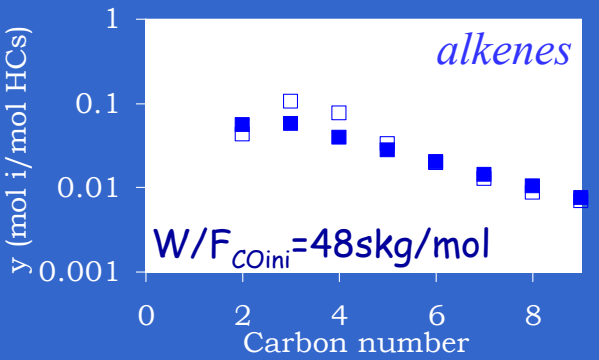
T=573K;P_T=11bar;H_2/CO=3





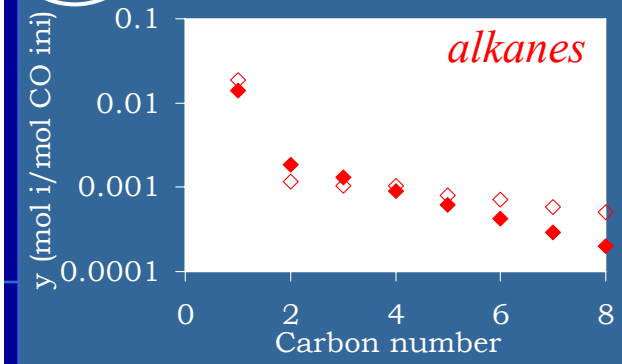
T=523K;P_T=21bar;H_2/CO=3

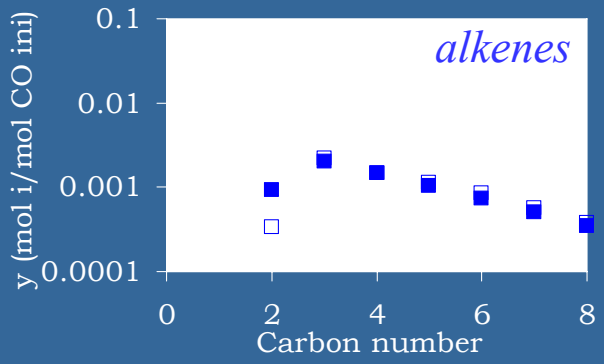


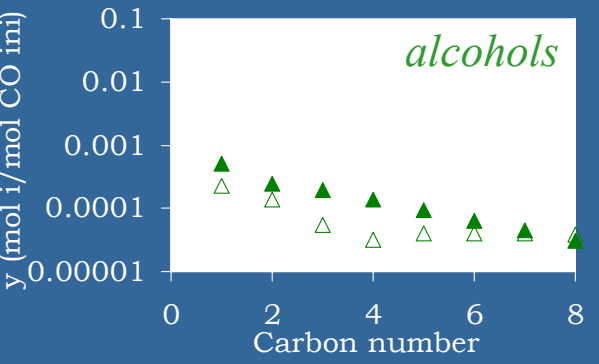


Co

T=493K;P_T=20bar;H_2/CO=1.6;W/F_{COini}=48skg/mol

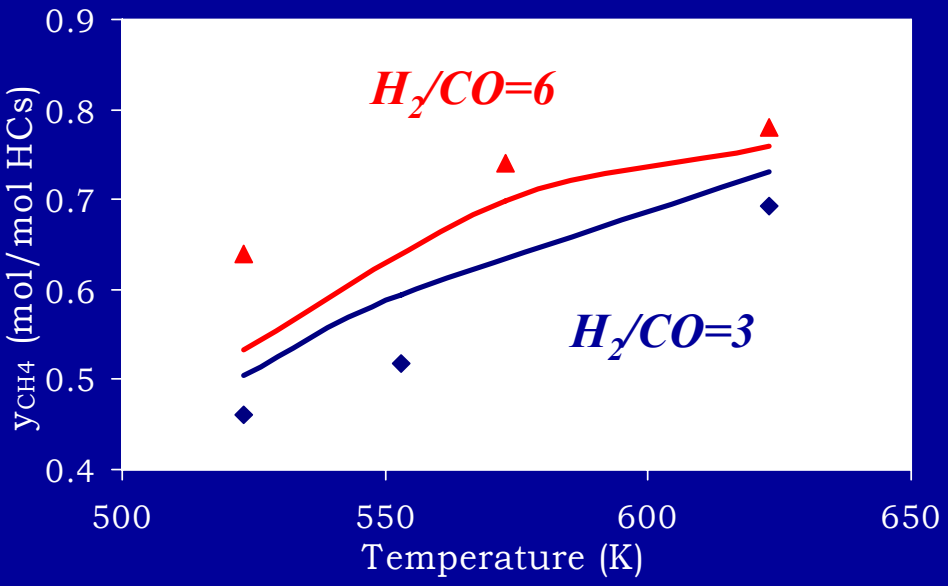


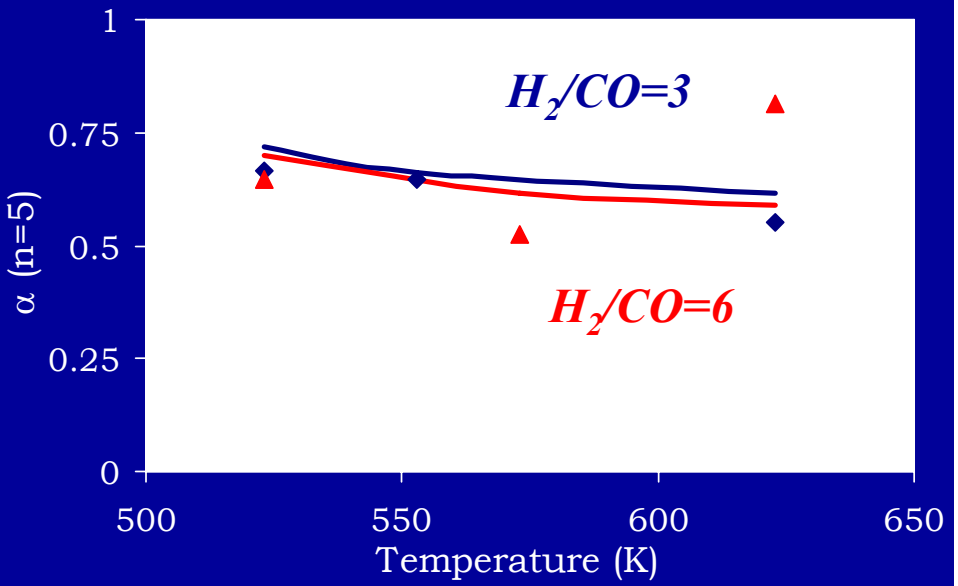




General trends (Fe)

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

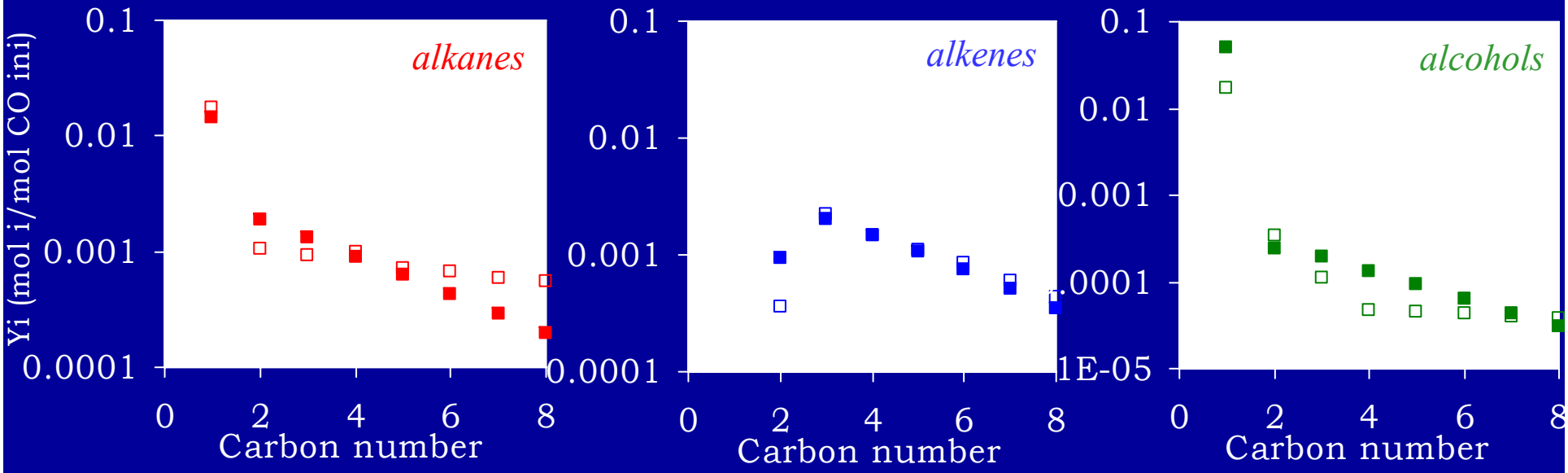




- Chain growth probability: $$\alpha_n = \frac{r_{prop,n}}{r_{prop,n} + r_{term,n}}$$
- At higher temperatures more hydrogenated products and lower molecular mass hydrocarbons

Secondary reactions (Co)

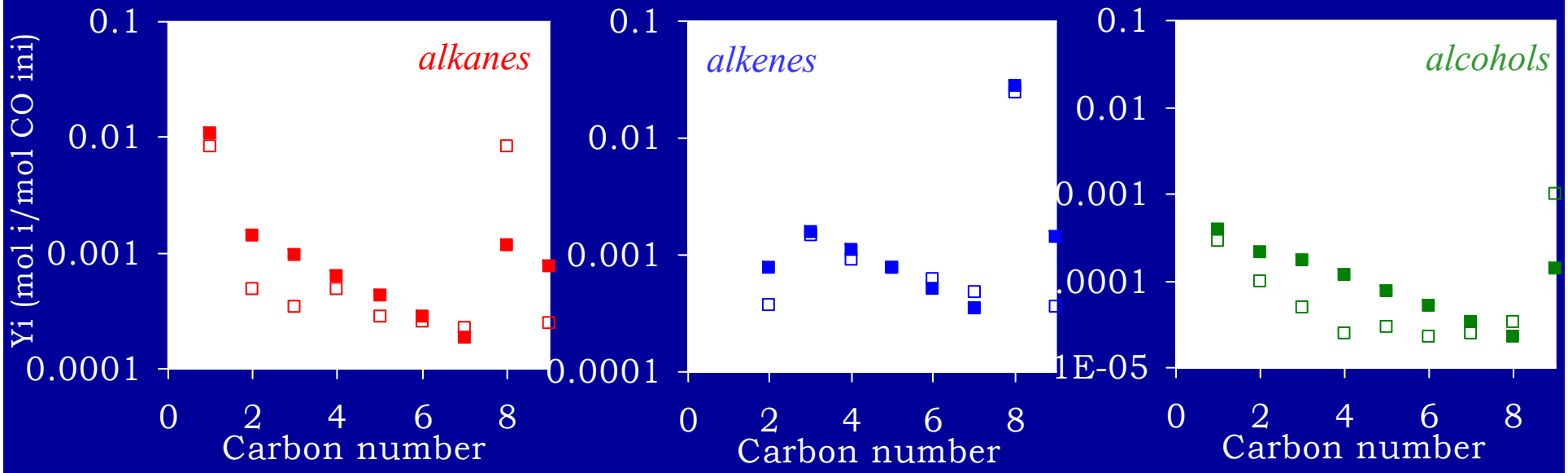
- Methanol addition
  - No effect on product distribution



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=493K ; p_{tot}=20bar ; H_2/CO=1.6 ; W/F_{COini}=48skg/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

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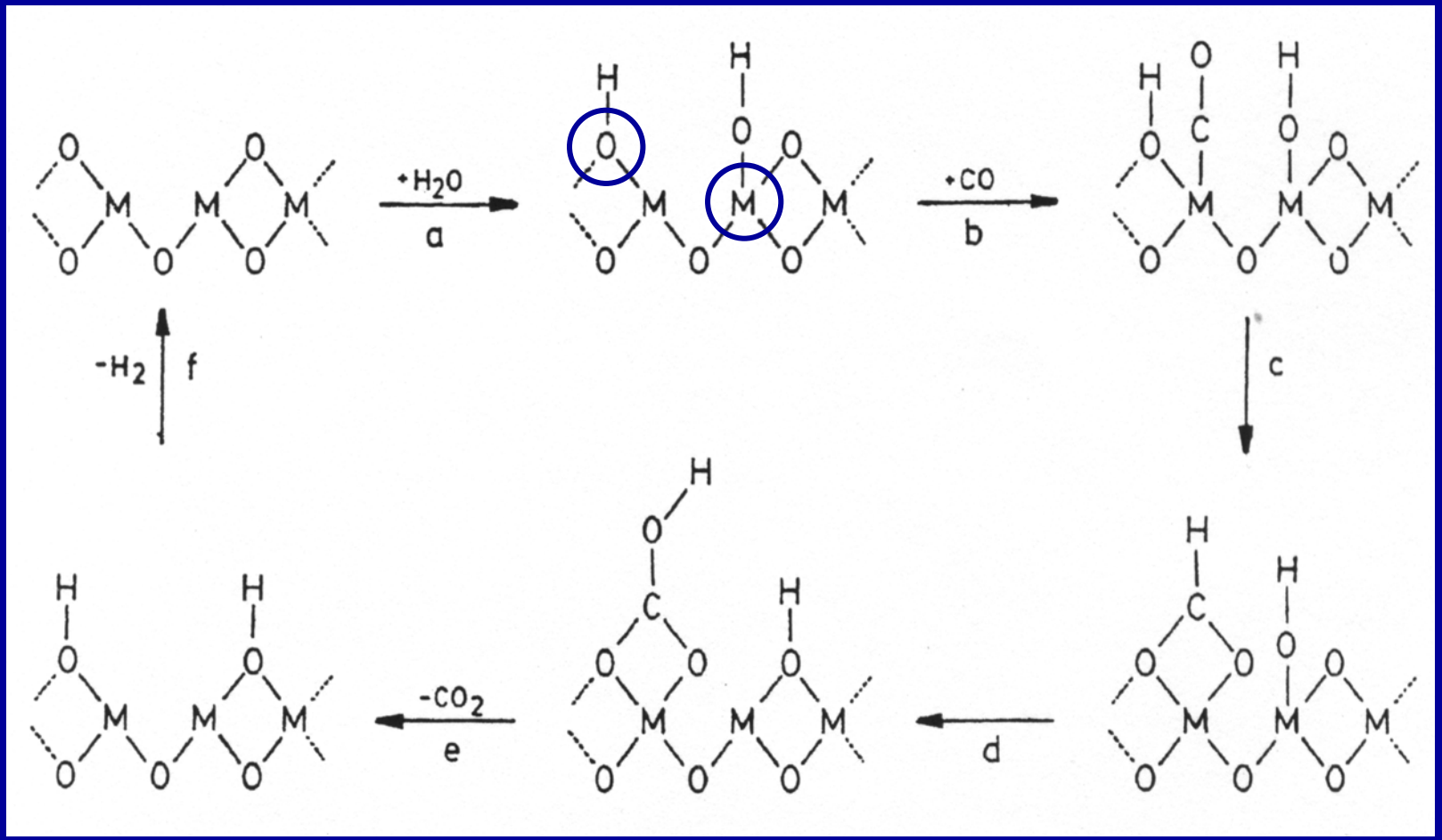
- PoliMi and EniTecnologie

Water-Gas Shift

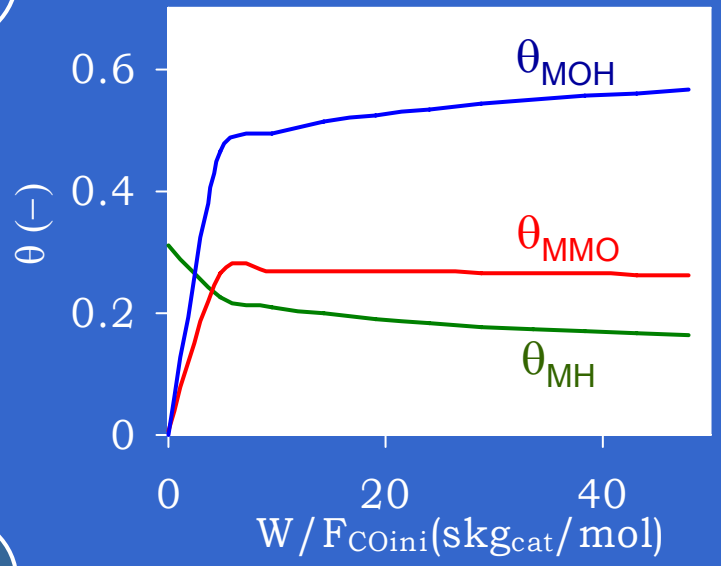
- Formate mechanism

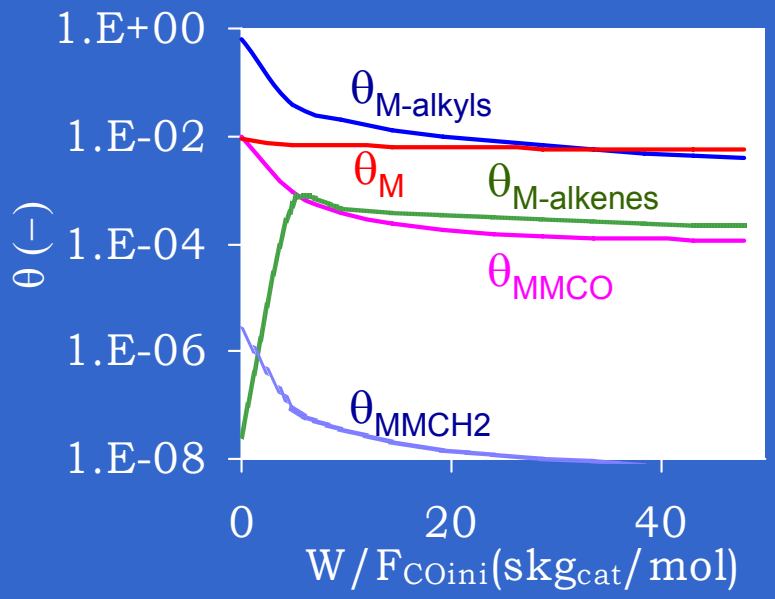


Rethwisch and Dumesic, J. Catal., 101, 35-42 (1986)

Surface species

Fe





Co