MICROKINETIC MODELING OF THE WATER-GAS SHIFT REACTION OVER COBALT CATALYSTS SUPPORTED ON MULTI-WALLED CARBON NANOTUBES

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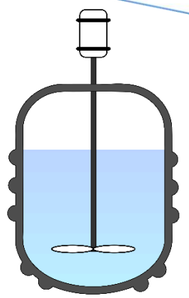
Kinetic modelling

***Macrokinetic* approach**

Lower computational cost

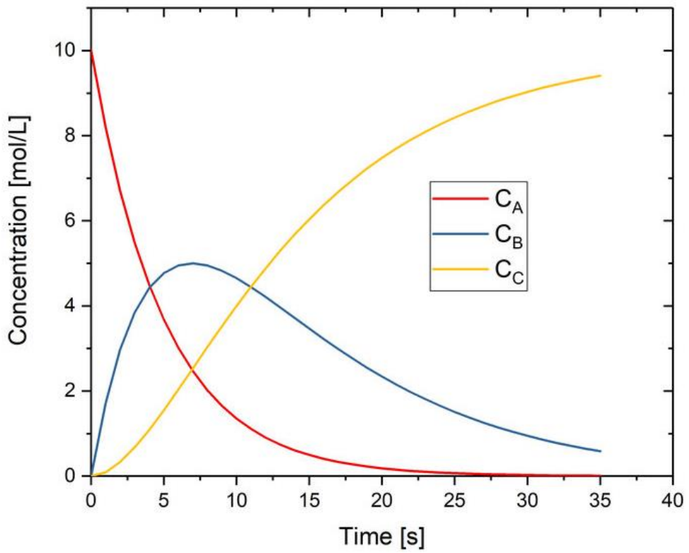
Widely used for reactor design

Specific for a certain catalyst



$$r_A = k\, P_A^a P_B^b$$

$$r_A = \frac{k K_A P_A}{1 + K_A P_A}$$



***Microkinetic* approach**

Reaction mechanism understanding

Sprung et al. 2015

It provides information for catalyst design

Thybaut et al., 2011

Without *a priori* defining a RDS

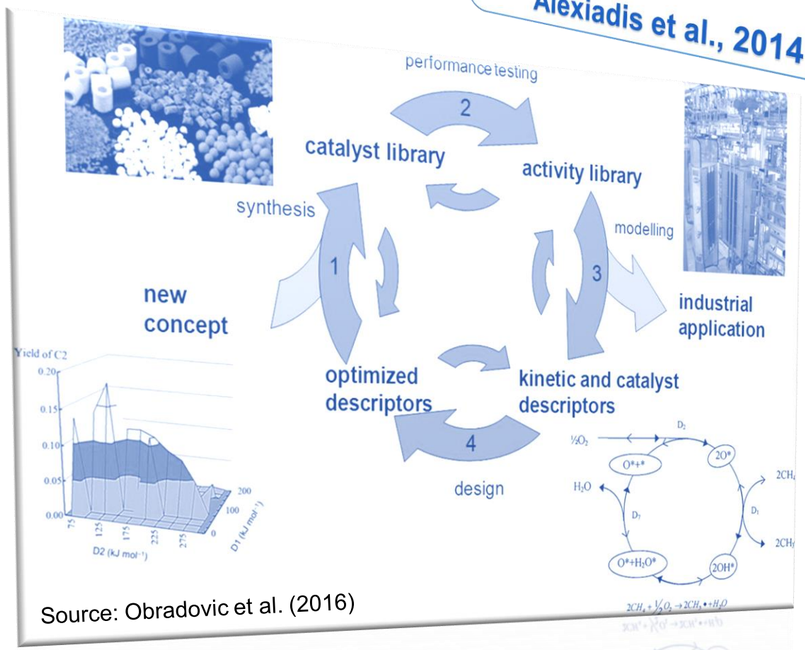
Metaxas et al., 2009

Catalytic Behavior Assessment

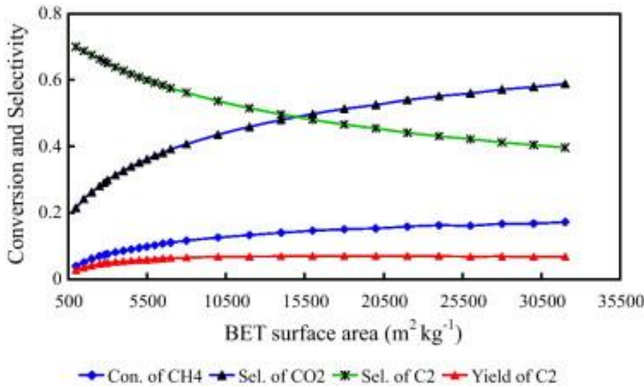
Alexiadis et al., 2014

Determination of more detailed kinetics

Sun et al., 2008

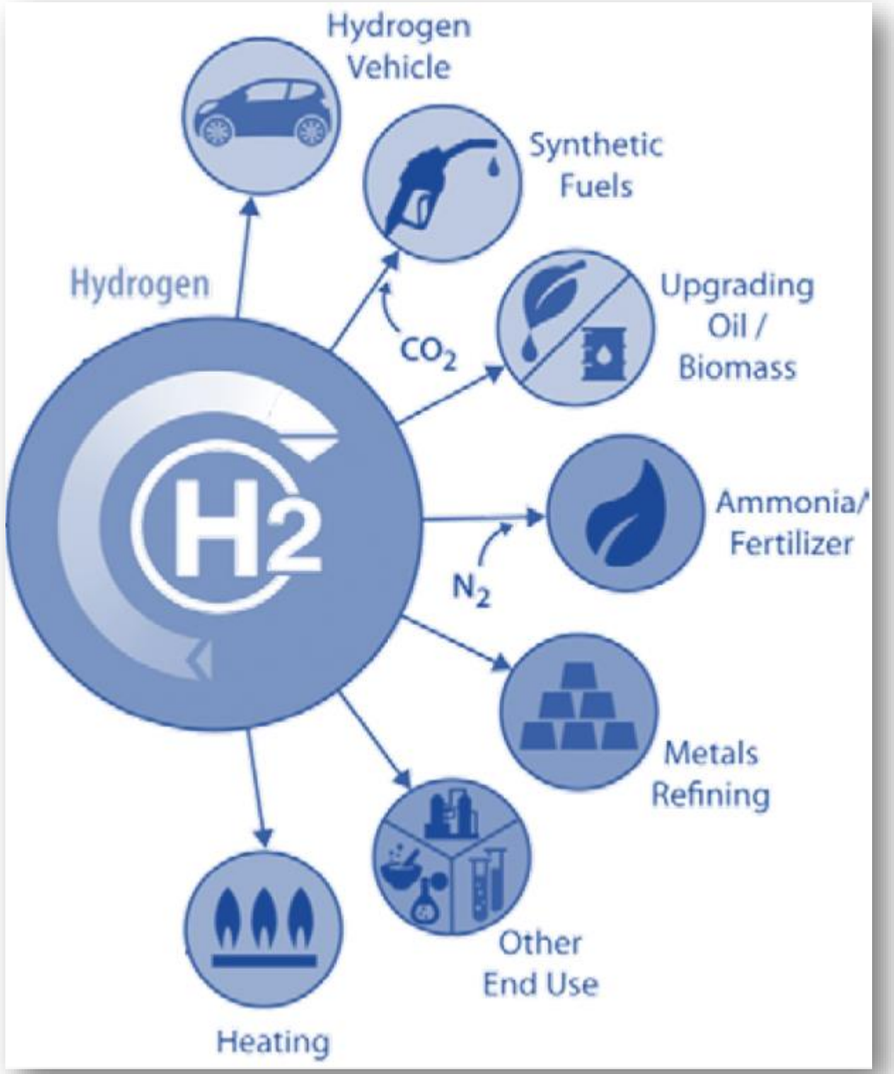


Source: Obradovic et al. (2016)



Source: Thybaut et al. (2011)

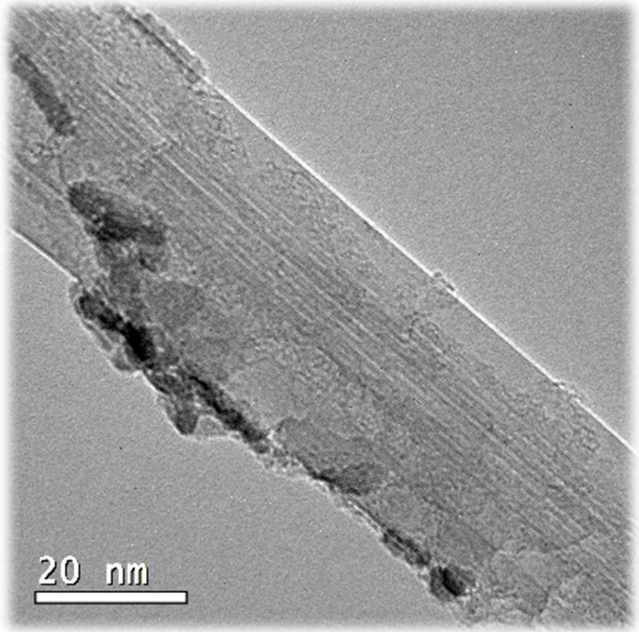
Water-Gas Shift (WGS) reaction and the Co-MWCNT catalyst



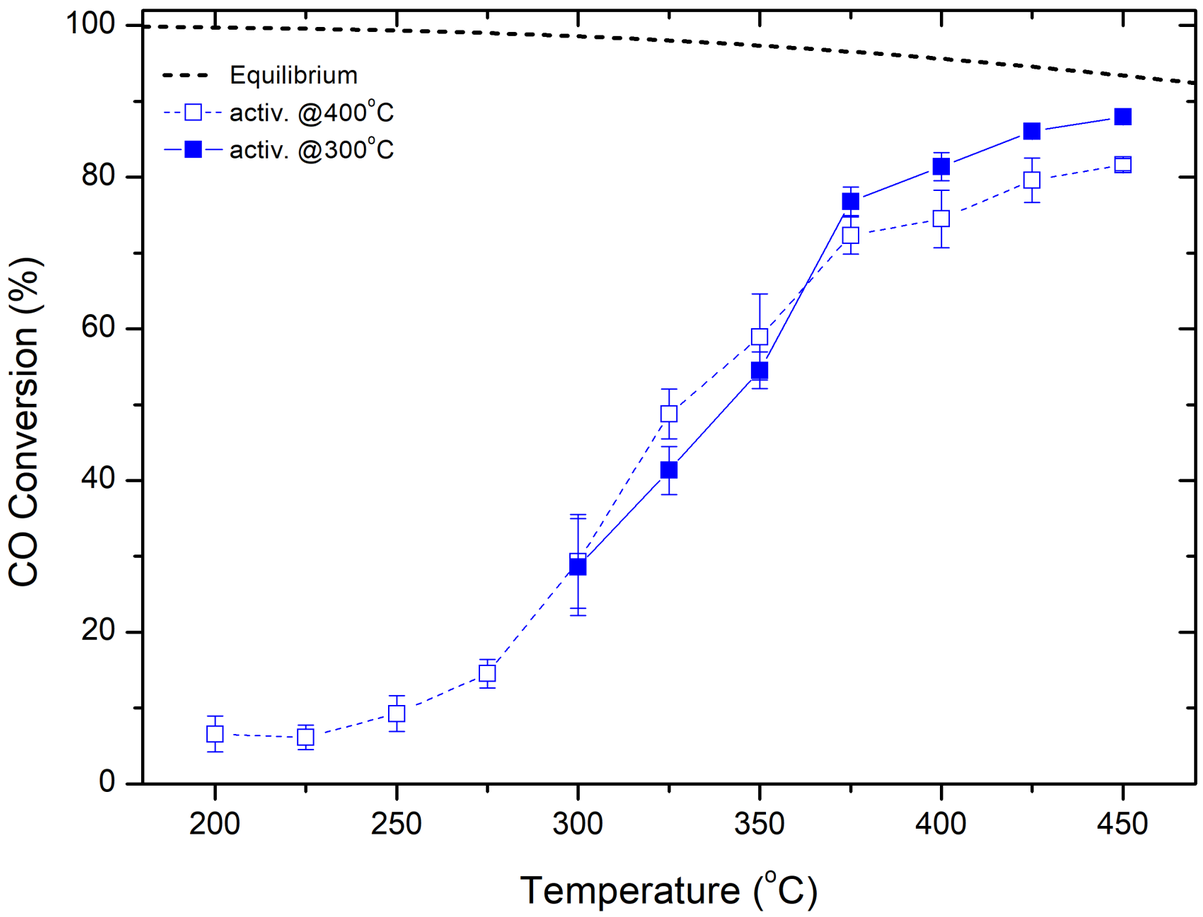
Source: US Department of Energy (2018)

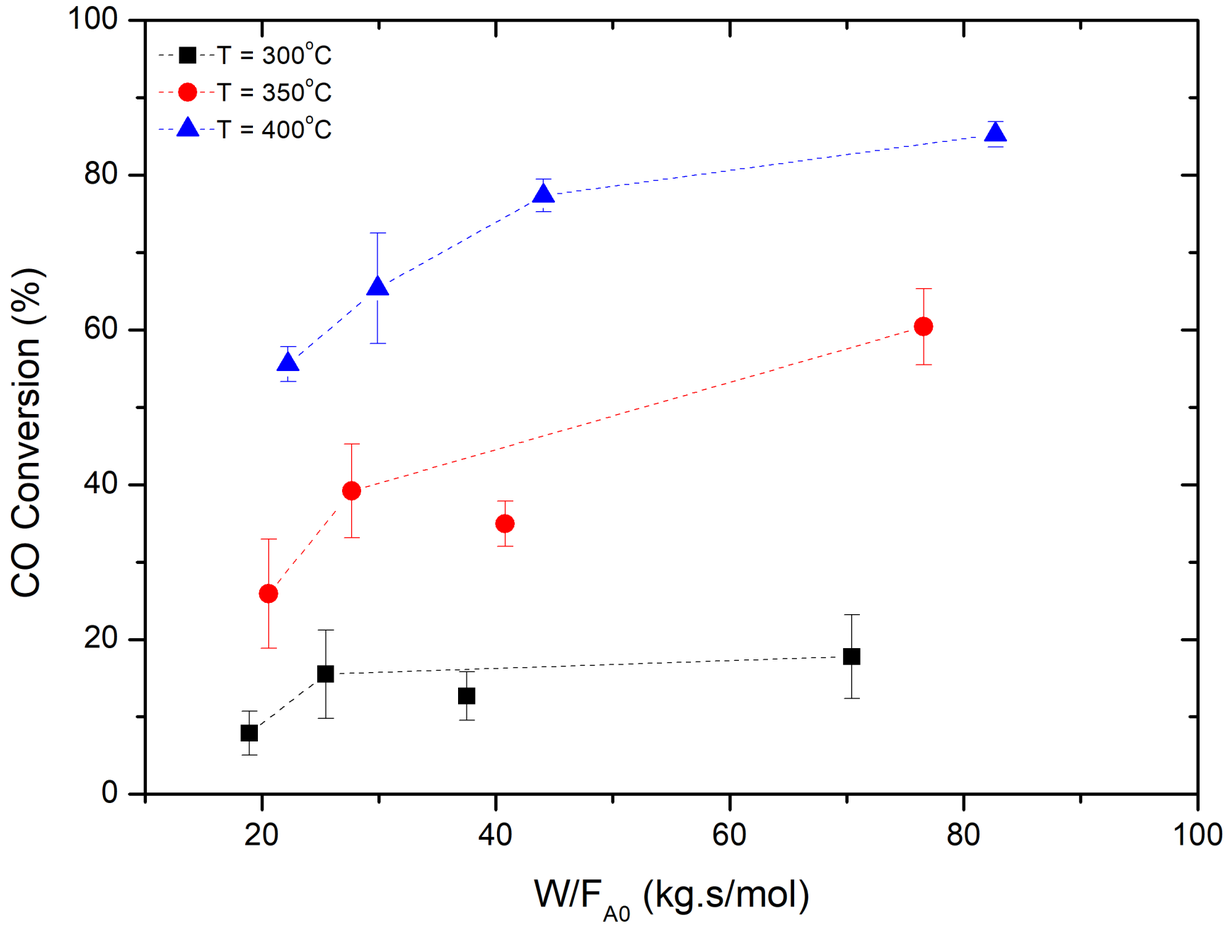
$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

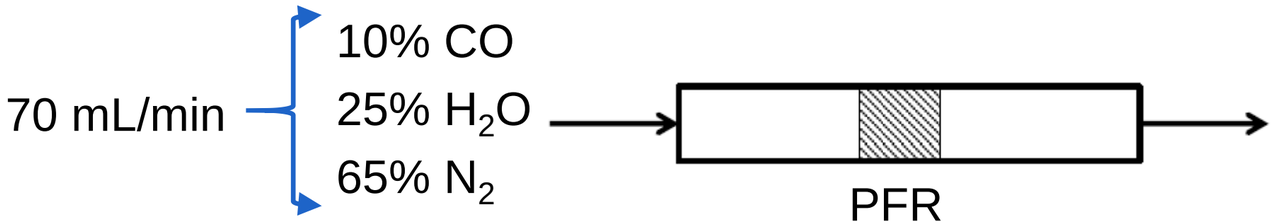
Catalyst: Co-Ce,Sr**/MWCNT** (impregnation)



Co-MWCNT Catalyst Activity







Agenda

- Microkinetic Modeling and Parameter Estimation 
- Catalyst Descriptors 
- Results: kinetic parameters, parity plots, performance curves, and energy diagram 
- Conclusions 

Microkinetic Modeling and Parameter Estimation

Initial Estimates

$\alpha^{k=0} = [k_o^0, E^0, \dots]$

→ **Calculate F's** from the model

DDAPLUS

→ **Maximum Likelihood Method**

$$\min_{\alpha} \sum_{i=1}^{NE} \sum_{j=1}^{NY} \frac{\left(F_{ij_{exp}} - F_{ij_{calc}}\right)^2}{\sigma_j^2}$$

GREGPLUS

→ **Parameters**

$\alpha^{opt} = [k_o, E, \dots]$

Proposed Mechanism for the WGS reaction ($CO + H_2O \rightleftharpoons H_2 + CO_2$)

1) **CO** + * ⇌ CO*
2) **H_2O** + * ⇌ H_2O*
3) H_2O* + * ⇌ OH* + H*
4) CO* + OH* ⇌ COOH* + *
5) COOH* + * ⇌ CO_2* + H*
6) 2 H* ⇌ **H_2** + 2 *
7) CO_2* ⇌ **CO_2** + *

$$\frac{dF_i}{dW} = R_i$$

$$R_{interm} = 0$$

$$C_* + \sum C_{int} = C_{tot}$$

System of Differential-Algebraic Equations (DAEs)

The **law of mass action** is applied to each elementary step

Kinetic Data

60 experimental points

2^{6-1} factorial design

+ activity test data

CO (10-17%)

H_2O (10-30%)

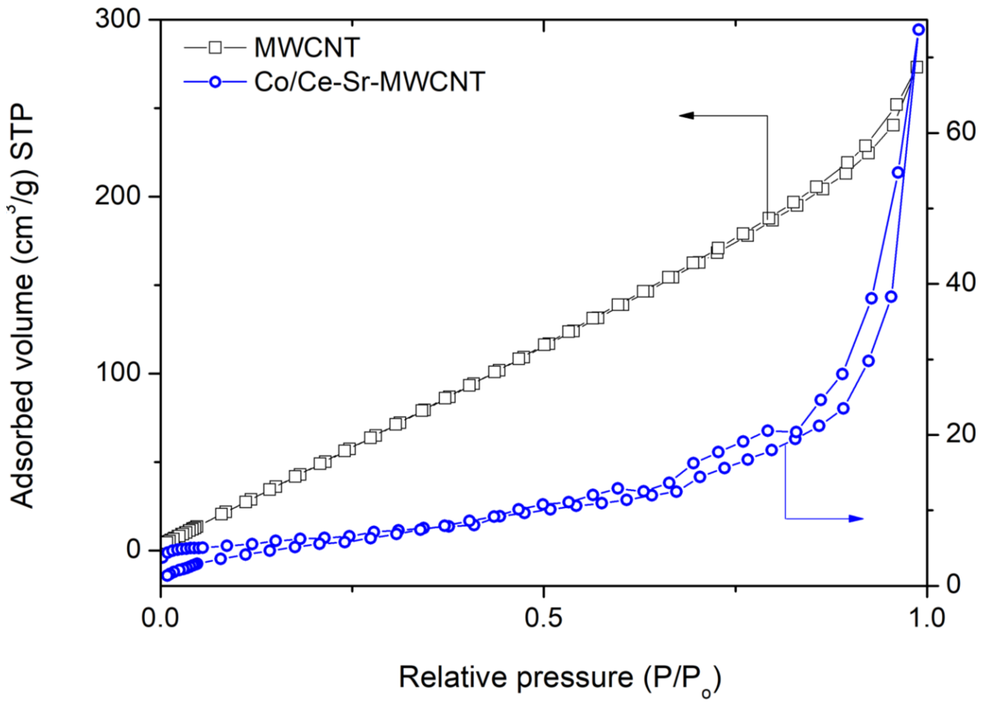
H_2 (0-36%)

CO_2 (0-18%)

T (300-400ºC)

GHSV (50-150 mL/min)

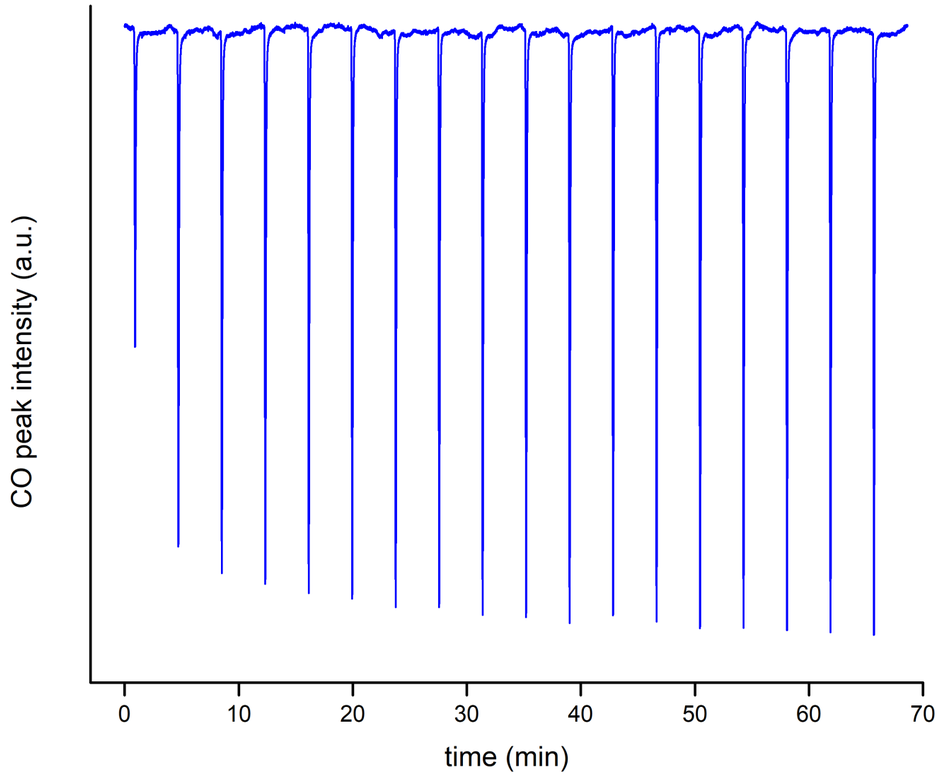
Catalyst Descriptors



N_2 Physisorption Analysis:

S_P → specific surface area

22,000 $m^2\ kg_{cat}^{-1}$



CO Pulsed Chemisorption Analysis:

σ → density of active sites

0.012 $mol_{Act.Surf.}\ m_{cat}^{-2}$

Rate Coefficients:

Collision Theory:

$$k_{io} = \frac{S_P}{\sigma}\frac{1}{\sqrt{2\pi MRT}} \qquad [Pa^{-1}s^{-1}]$$

Transition-State Theory:

$$k_{io} = \frac{N_A}{S_P}\frac{k_B T}{h}\frac{Q''_{AB\ddagger}}{Q''_{A*}Q''_{B*}} \qquad [kg.mol^{-1}s^{-1}]$$

Kinetic Parameters

5

parameters estimated from the experimental data ($k_{o,5}$, $k_{o,-6}$, E_4, E_{-4}, E_6)

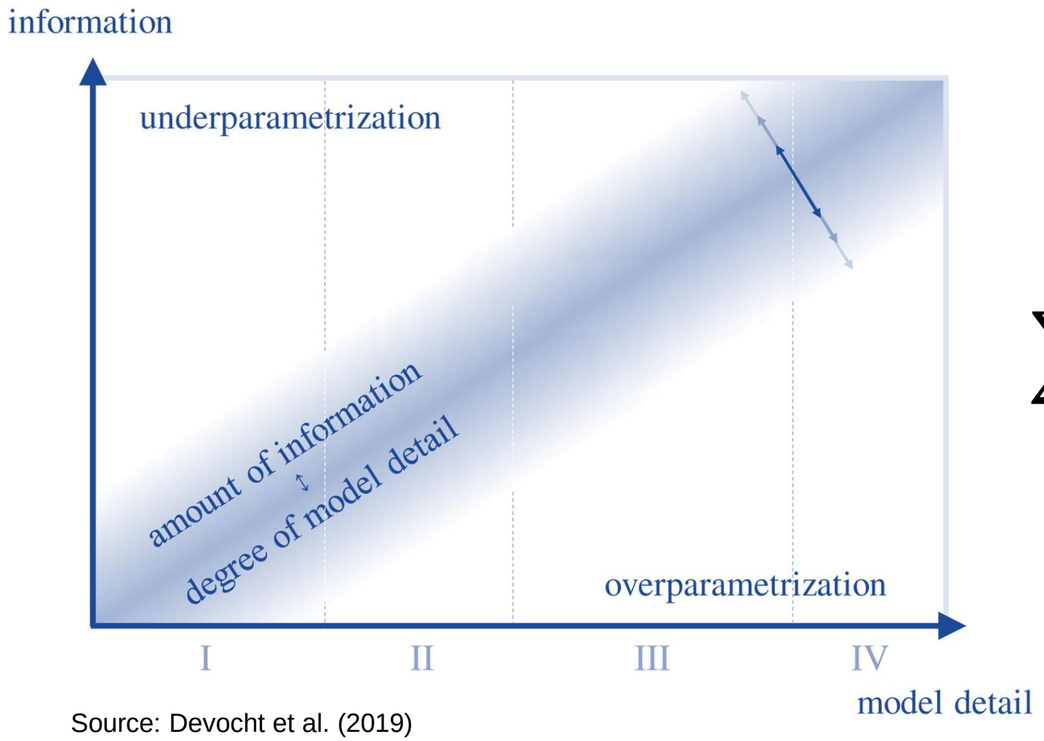
23

parameters computed from chemistry theories, the literature, and a thermodynamic constraint (E_5)

lowest t_{calc} (7.74) > t_{tab} (1.98)
⇒ **all parameters are statistically significant**

$$t_{cal} = \frac{|b_k - 0|}{\sigma_{b_{kk}}}$$

$$t_{tab}\left(NE \cdot NY - NP; 1 - \frac{\alpha}{2}\right)$$

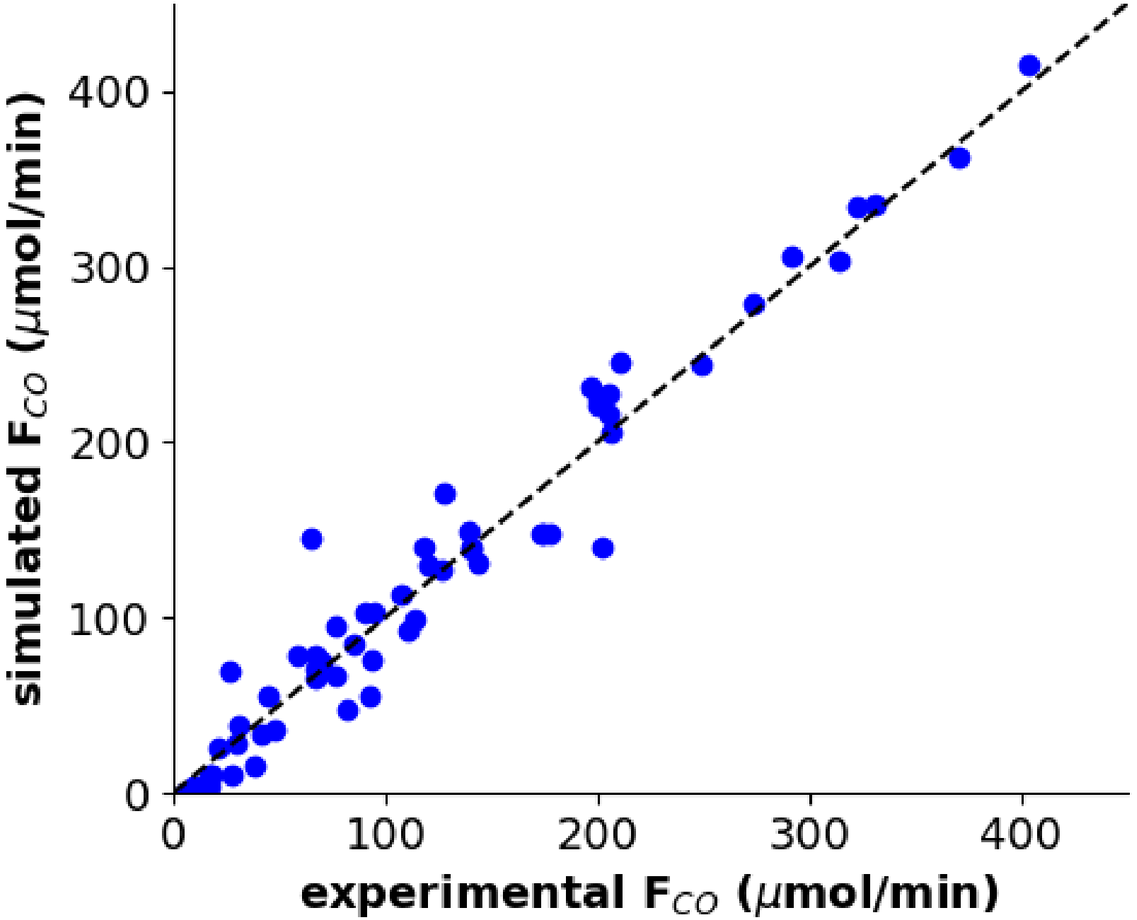


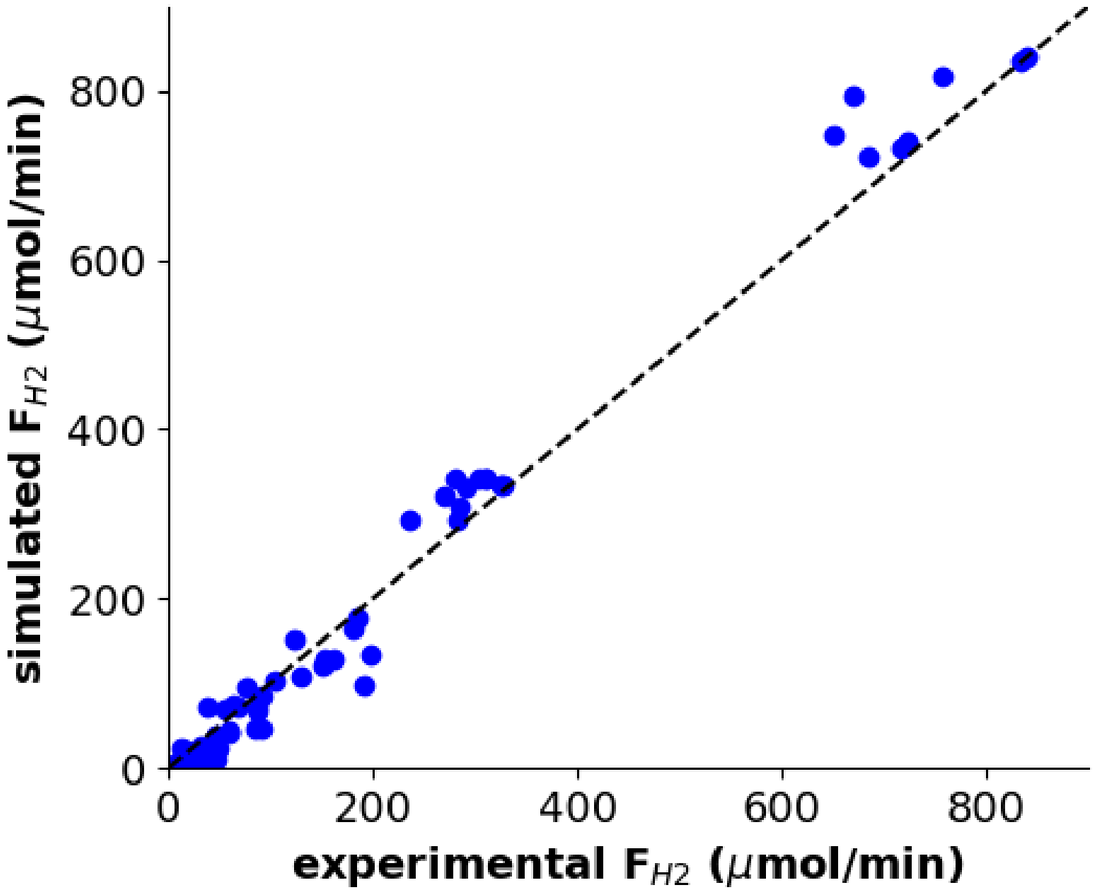
Source: Devocht et al. (2019)

Thermodynamic Consistency

$$\sum_j \nu_j\left(E_{j,for}\right) - \sum_j \nu_j\left(E_{j,rev}\right) = \Delta H^0_{WGS}$$

Parity Plots

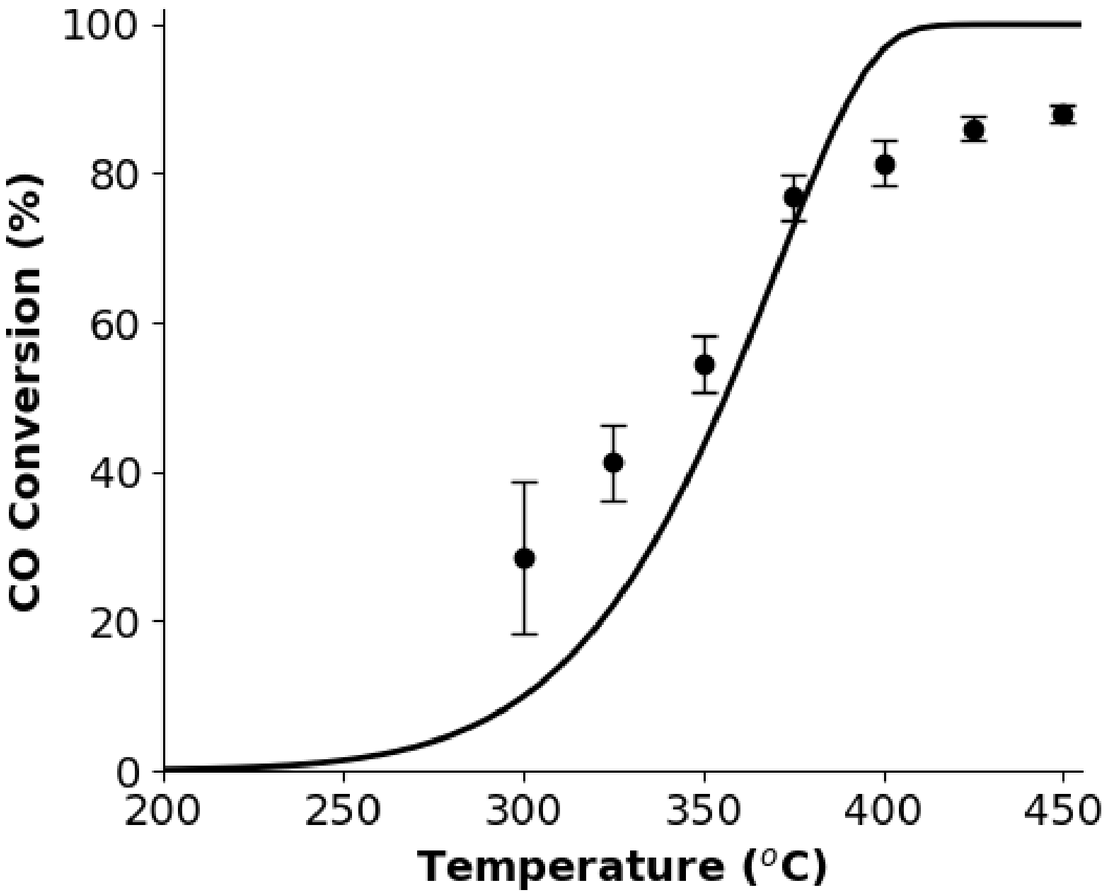


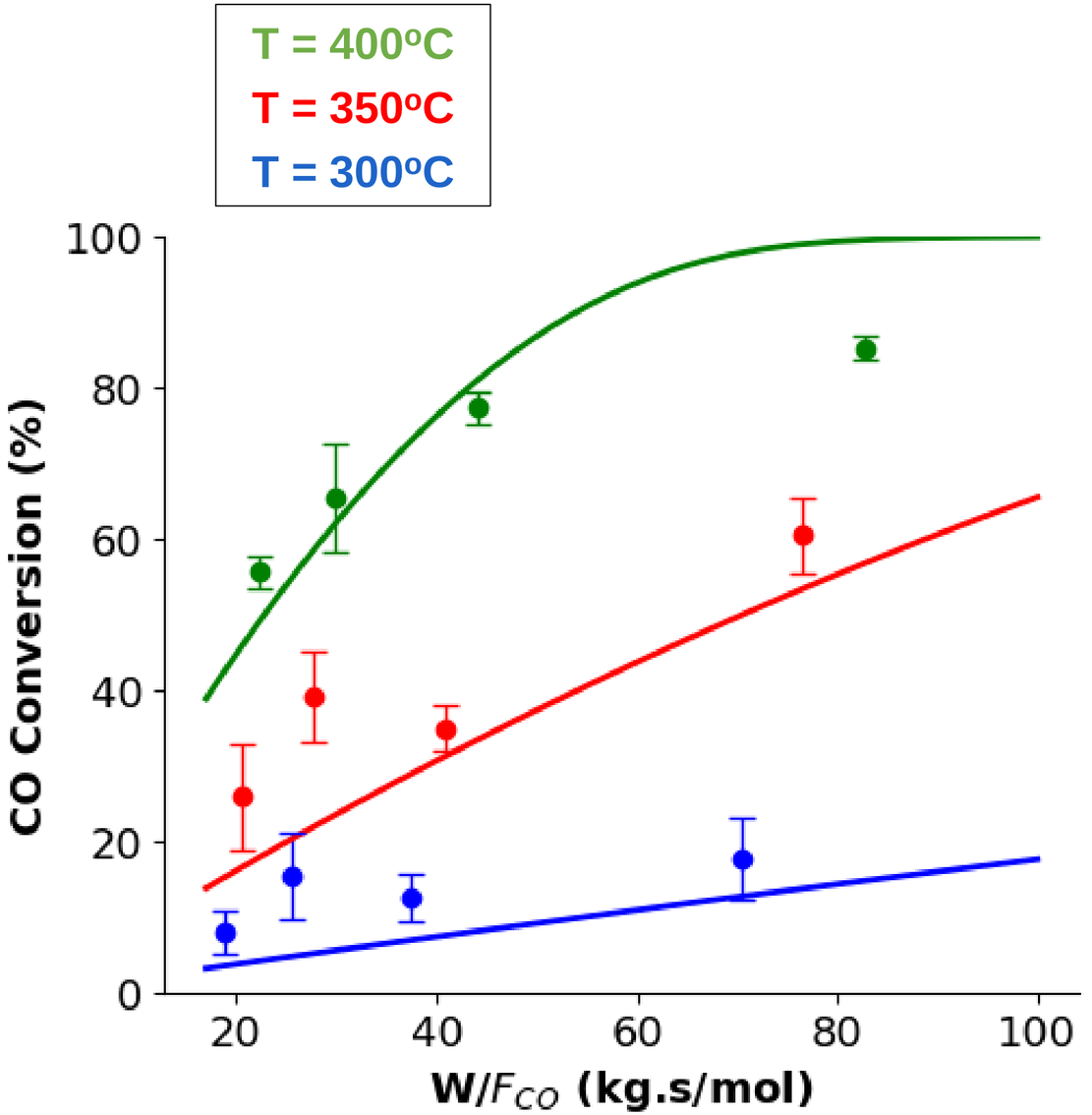


$R^2 = 0.97$

$F_{value} = 10^3 > F_{tab} = 4$

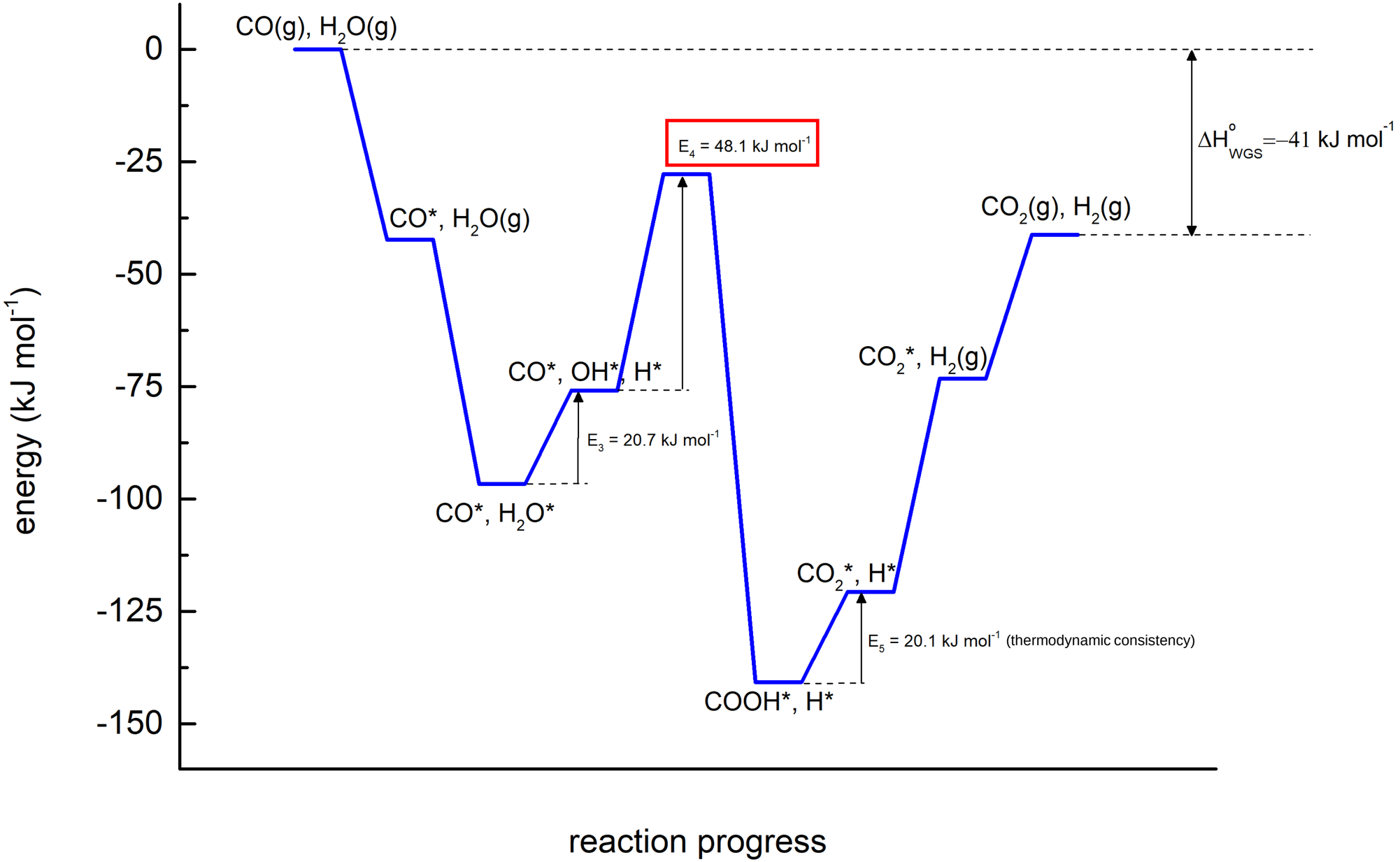
Performance Curves





The model seems to work well in **high temperature** regions, but far from equilibrium and at low CO conversion

Energy Diagram



Conclusions

- The incorporation of the **catalyst descriptors** (S_P and σ) into the developed **microkinetic model** confirmed:
  - that the COOH* formation reaction (CO* + OH* → COOH* + *) is the rate-determining step
  - the good predictive capability, describing the optimal catalyst performance at elevated temperatures (350-450^{o}C) and space times (70-80 kg.s/mol)

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