

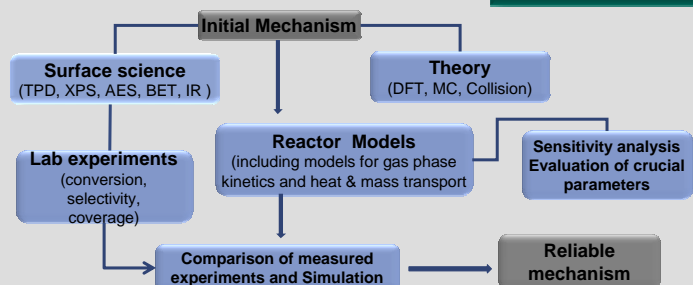
# Modeling oxidation and reforming of hydrogen, carbon monoxide, and methane over nickel catalysts

Karla Herrera Delgado<sup>1</sup>, Lubow Maier<sup>2</sup>, Olaf Deutschmann<sup>1, 3</sup>

## Introduction

During the last years, there has been an increased interest in catalytic reforming of light hydrocarbons such as steam reforming (SR) and dry reforming (DR). The increasing concern of global warming and oil depletion offers the opportunity to convert greenhouse gases into synthesis gas (H<sub>2</sub>/CO), which is used in the manufacturing of valuable basic chemicals and synthetic fuels, as first shown by Fischer and Tropsch [1]. Industrial practice relies on Ni catalysts due to fast turnover rates, good availability and low costs, although it is more sensitive to carbon formation than noble metals [2]. The objective of this work is the development of a surface reaction mechanism applicable for catalytic conversion of hydrogen, carbon monoxide, and light hydrocarbons under oxidative, reforming, and pyrolysis conditions at a wide range of temperature, pressure, and residence time

## Modeling Approach



## Numerical Simulation - DETCHEM Software

DETCHEM- Library  
Reaction Mechanisms  
Thermodynamic and Transport Data  
Mol Data  
Species

MONOLITH  
Transient temperature profile  
of the solid structure  
  
CHANNEL or PLUG

BATCH + CSTR  
Batch and stirred tank  
  
SENSITIVITY ANALYSIS

PACKEDBED  
1D Bed Reactor

1D or 2D-flow field simulations for a representative number of channels using a boundary layer or plug flow equations [3]

## Mechanistic Model (mean field approximation)

- The molecules are randomly distributed on the catalytic surface
- Surface is viewed as being uniform

Adsorption rate

$$\dot{s}_i = S_i^{eff} \sqrt{\frac{RT}{2\pi M_i}} c_i$$

Surface coverage

$$\Theta_i = \frac{c_i \sigma_i}{\Gamma} \quad \frac{\partial \Theta_i}{\partial t} = \frac{\dot{s}_i \sigma_i}{\Gamma}$$

Surface reaction rate

$$\dot{S}_i = \sum_k v_{ik} k_{f_k} \prod_j c_j^{N_{j,k}} \prod_l c_l^{N_{l,k}}$$

Rate expression

$$k_{f_k} = A_k T^{\beta_k} \exp\left[-\frac{E_{a_k}}{RT}\right] \prod_{i=1}^{N_i} \Theta_i^{\nu_{i,k}} \exp\left[\frac{\varepsilon_{i,k} \Theta_i}{RT}\right]$$

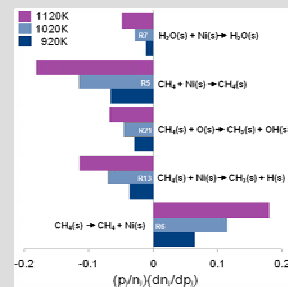


Figure 1. Sensitivity coefficients for CH<sub>4</sub> mole fraction as function of temperature for CH<sub>4</sub> steam reforming, S/C = 1.9 (75% Ar) [4]

## Simulation Results

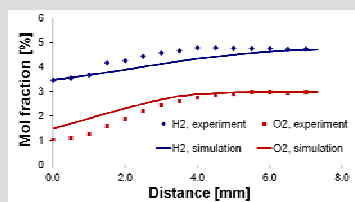


Figure 2. H<sub>2</sub> oxidation in a stagnation flow reactor over nickel cat. Inlet mol fractions: x<sub>H<sub>2</sub></sub> = 4.78%, x<sub>O<sub>2</sub></sub> = 2.89% in Ar, total flow = 15 L/min, T<sub>inlet</sub> = 350°C, p = 0.5 bar

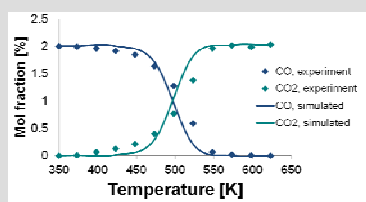


Figure 3. CO oxidation in a packed-bed over nickel cat. Inlet composition of CO/O<sub>2</sub> = 1: 2 in Ar, total flow = 2 SL/min, T<sub>inlet</sub> = 100°C, p = 1 bar

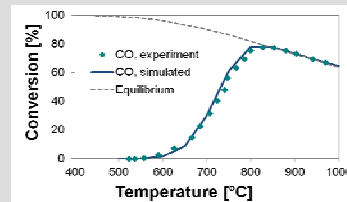


Figure 4. CO conversion in Water-gas-shift reaction on Ni supported on alumina foam monolith [5]

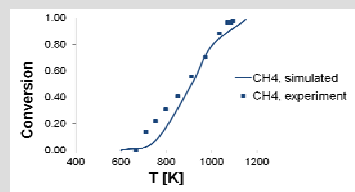


Figure 5. CH<sub>4</sub> conversion in Steam reforming in a (packed-bed) [6]

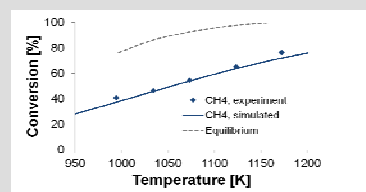


Figure 6. CH<sub>4</sub> conversion in Dry Reforming of CH<sub>4</sub>/CO<sub>2</sub> in a fixed-bed reactor over NiO/γ-Al<sub>2</sub>O<sub>3</sub> [7]

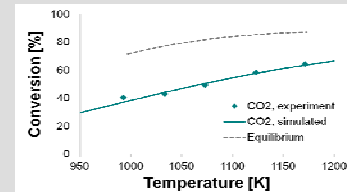


Figure 7. CO<sub>2</sub> conversion in Dry Reforming of CH<sub>4</sub>/CO<sub>2</sub> in a fixed-bed reactor over NiO/γ-Al<sub>2</sub>O<sub>3</sub> [7]

### References:

- V. F. Fischer, H. Tropsch, Brennstoff-Chemie, 3, 39 (1928)
- S. Wang, G. Q. M. Lu, Appl. Catal. B: Environ, 16, 269 (1998)
- O. Deutschmann, S. Tischer, et al, DETCHEM™ Software package, 2.3 ed., Karlsruhe (2010)
- L. Maier, B. Schädler, K. Herrera Delgado, S. Tischer, O. Deutschmann, Top Catal, 54, 845 (2011)
- C. Weeler, A. Jhalani, J. Catalysis, 223, 191 (2004)
- J.-H. Ryu, K.Y. Lee, J. Power Sources 171, 499 (2007)
- X. Chen, K. Honda, Z. Zhang, Appl. Catal. A: General, 288, 86 (2005)

<http://www.detchem.com>

<http://www.itcp.kit.edu/deutschmann>