Karlsruhe Institute of Technology

[1] Institute of Chemical Technology and Polymer Chemistry
[2] Institute for Nuclear and Energy Technologies

Development of a Combined Surface Reaction Mechanism for Steam- and Dry Reforming of Methane over Nickel

***Karla Herrera Delgado*[1], *Lubow Maier*[2], *Olaf Deutschmann*[1, 2]** **karla.herrera@kit.edu**

Background

Steam reforming and dry reforming of methane play a key role in the production of syngas (H_2/CO), used in synthesis of chemicals and fuels (gas-to-liquids) [1]

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

Dry reforming of methane with carbon dioxide has special interest due to the increasing concern of global warming and oil depletion since offers the opportunity to convert greenhouse gases into syngas with low H_2/CO ratio [2].
Nickel catalyst is widely used due to fast turnover rates, good availability and low cost, although it is more sensitive to coke formation and growth of carbon filaments than noble metals [3].

Mechanistic Model (mean field aproximation)

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

Adsorption rate

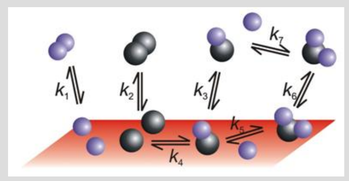
$$\dot{s}_i = s_i^{eff}\sqrt{\frac{RT}{2\pi M_i}}c_i$$

Surface reaction rate

$$\dot{s}_i = \sum_k^{K_s} \nu_{ik} k_{f_k} \prod_j^{N_g+N_s} c_j^{\nu'_{jk}}$$

Sticking coefficient

$$s_{eff}^i = s_i^0 \prod_{i=1}^{Ns} \Theta_j^{\nu'_{jk}+\mu_{jk}}$$



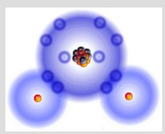
Surface coverage

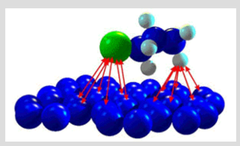
$$\Theta_i = \frac{c_i\sigma_i}{\Gamma} \qquad \frac{\partial\Theta_i}{\partial t} = \frac{\dot{s}_i\sigma_i}{\Gamma}$$

Rate expression

$$k_{f_k} = A_k T^{\beta_k} \exp\left[\frac{-E_{a_k}}{RT}\right] \prod_{i=1}^{N_s} \Theta_i^{\mu_{ik}} \exp\left[\frac{\varepsilon_{i_k}\Theta_i}{RT}\right]$$

Modeling and Simulation





Surface science
(TPD, XPS, AES, BET, IR)

Theory
(DFT, MC, Collision)

Initial Mechanism

Modeling of lab reactors
(including appropriate models for gas phase kinetics and heat & mass transport

Lab experiments
(conversion, selectivity, Light-of temperatures, coverage)

Sensitivity analysis & Evaluation of crucial parameters

Comparison of measured experiments and Simulation

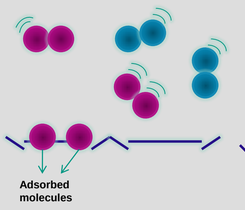
Reliable mechanism

-datailed multi-step reaction mechanism was developed to model steam reforming

- it include
  - Adsorption- desorption reactions of reactants and products
  - Gas phase and surface species
  - Partial and total oxidation reactions
  - Thermodynamically consistent

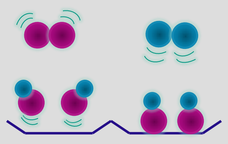
	Reaction	A^*	n	E^*
1.	$H_2 + Ni(s) + Ni(s) \rightarrow H(s) + H(s)$	$1.000 \cdot 10^{-02\dagger}$	0.0	0.00
2.	$H(s) + H(s) \rightarrow Ni(s) + Ni(s) + H_2$	$5.593 \cdot 10^{+19}$	0.0	88.12
3.	$O_2 + Ni(s) + Ni(s) \rightarrow O(s) + O(s)$	$1.000 \cdot 10^{-02\dagger}$	0.0	0.00
4.	$O(s) + O(s) \rightarrow Ni(s) + Ni(s) + O_2$	$2.508 \cdot 10^{+23}$	0.0	470.39
5.	$CH_4 + Ni(s) \rightarrow CH_4(s)$	$8.000 \cdot 10^{-03\dagger}$	0.0	0.00
6.	$CH_4(s) \rightarrow Ni(s) + CH_4$	$5.302 \cdot 10^{+15}$	0.0	33.15
7.	$H_2O + Ni(s) \rightarrow H_2O(s)$	$1.000 \cdot 10^{-01\dagger}$	0.0	0.00
8.	$H_2O(s) \rightarrow Ni(s) + H_2O$	$4.579 \cdot 10^{+12}$	0.0	62.68
9.	$CO_2 + Ni(s) \rightarrow CO_2(s)$	$1.000 \cdot 10^{-05\dagger}$	0.0	0.00
10.	$CO_2(s) \rightarrow Ni(s) + CO_2$	$9.334 \cdot 10^{+07}$	0.0	28.80
11.	$CO + Ni(s) \rightarrow CO(s)$	$5.000 \cdot 10^{-01\dagger}$	0.0	0.00
12.	$CO(s) \rightarrow Ni(s) + CO$	$4.041 \cdot 10^{+11}$	0.0	112.85
		$\epsilon_{CO(s)}$		-50.0‡
13.	$O(s) + H(s) \rightarrow OH(s) + Ni(s)$	$5.000 \cdot 10^{+22}$	0.0	97.90
14.	$OH(s) + Ni(s) \rightarrow O(s) + H(s)$	$2.005 \cdot 10^{+21}$	0.0	37.19
15.	$OH(s) + H(s) \rightarrow H_2O(s) + Ni(s)$	$3.000 \cdot 10^{+20}$	0.0	42.70
16.	$H_2O(s) + Ni(s) \rightarrow OH(s) + H(s)$	$2.175 \cdot 10^{+21}$	0.0	91.36
17.	$OH(s) + OH(s) \rightarrow O(s) + H_2O(s)$	$3.000 \cdot 10^{+21}$	0.0	100.00
18.	$O(s) + H_2O(s) \rightarrow OH(s) + OH(s)$	$5.423 \cdot 10^{+23}$	0.0	209.37
19.	$O(s) + C(s) \rightarrow CO(s) + Ni(s)$	$5.200 \cdot 10^{+23}$	0.0	148.10
20.	$CO(s) + Ni(s) \rightarrow O(s) + C(s)$	$1.418 \cdot 10^{+22}$	-3.0	115.97
		$\epsilon_{CO(s)}$		-50.0‡
25.	$HCO(s) + Ni(s) \rightarrow O(s) + CH(s)$	$3.700 \cdot 10^{+24}$	−3.0	95.80
26.	$O(s) + CH(s) \rightarrow HCO(s) + Ni(s)$	$7.914 \cdot 10^{+20}$	0.0	114.22
27.	$CH_4(s) + Ni(s) \rightarrow CH_3(s) + H(s)$	$3.700 \cdot 10^{+21}$	0.0	57.70
28.	$CH_3(s) + H(s) \rightarrow CH_4(s) + Ni(s)$	$4.438 \cdot 10^{+21}$	0.0	58.83
29.	$CH_3(s) + Ni(s) \rightarrow CH_2(s) + H(s)$	$3.700 \cdot 10^{+24}$	0.0	100.00
30.	$CH_2(s) + H(s) \rightarrow CH_3(s) + Ni(s)$	$9.513 \cdot 10^{+22}$	0.0	52.58
31.	$CH_2(s) + Ni(s) \rightarrow CH(s) + H(s)$	$3.700 \cdot 10^{+24}$	0.0	97.10
32.	$CH(s) + H(s) \rightarrow CH_2(s) + Ni(s)$	$3.008 \cdot 10^{+24}$	0.0	76.43
33.	$CH(s) + Ni(s) \rightarrow C(s) + H(s)$	$3.700 \cdot 10^{+21}$	0.0	18.80
34.	$C(s) + H(s) \rightarrow CH(s) + Ni(s)$	$4.400 \cdot 10^{+22}$	0.0	160.49
35.	$O(s) + CH_4(s) \rightarrow CH_3(s) + OH(s)$	$1.700 \cdot 10^{+24}$	0.0	88.30
36.	$CH_3(s) + OH(s) \rightarrow O(s) + CH_4(s)$	$8.178 \cdot 10^{+22}$	0.0	28.72
37.	$O(s) + CH_3(s) \rightarrow CH_2(s) + OH(s)$	$3.700 \cdot 10^{+24}$	0.0	130.10
38.	$CH_2(s) + OH(s) \rightarrow O(s) + CH_3(s)$	$3.815 \cdot 10^{+21}$	0.0	21.97
39.	$O(s) + CH_2(s) \rightarrow CH(s) + OH(s)$	$3.700 \cdot 10^{+24}$	0.0	126.80
40.	$CH(s) + OH(s) \rightarrow O(s) + CH_2(s)$	$1.206 \cdot 10^{+23}$	0.0	45.42
	$\ldots H(s)$	$3.700 \cdot 10^{+21}$	0.0	48.10
	$\ldots H(s)$	$1.764 \cdot 10^{+21}$	0.0	129.08

* Arrhenius parameters for the rate constants written in the form: $k = AT^n \exp(-E/RT)$. The units of A are given in terms of moles, centimeters, and seconds. E is in kJ/mol.
† Sticking coefficient.
‡ Coverage-dependent activation energy (see Eq. 10).
Total available surface site density is $\Gamma = 2.60 \times 10^{-9}$ mol/cm^2.



Catalyst Surface Adsorption

Catalyst Surface Reaction



Catalyst Surface Desoption

Numerical Simulation - DETCHEM Software

- modelig and simulation of reacting flows field.
- coupled with the detailed surface chemistry model and transport phenomena.
- transport coefficients depend on mixture composition and temperature [4]

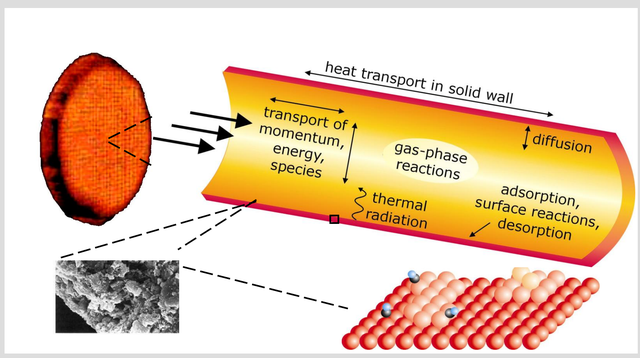
MONOLITH
Transient temperature profile of the solid structure → CHANNEL or PLUG

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

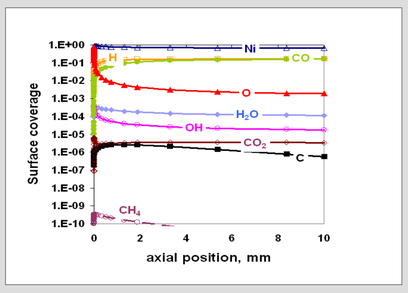
BATCH + CSTR
Batch and stirred tank → SENSITIVITY TEST

PACKEDBED
1D Bed Reactor

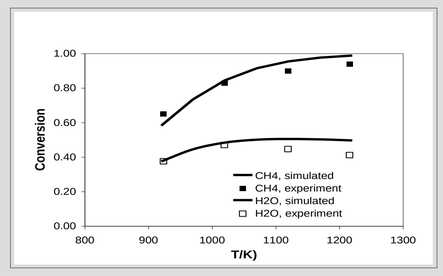
DETCHEM- Library
Detailed Reaction Mechanisms
Thermodynamic and Transport Data
Mol Data
Species



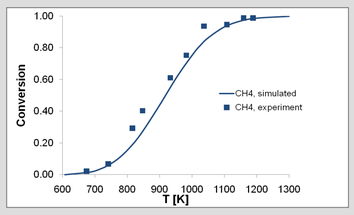
Simulation Results



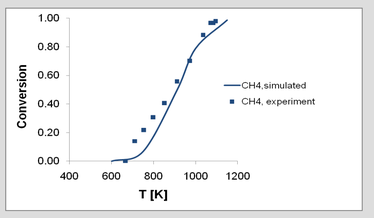
Computed surface coverage of adsorbed species along the catalytic channel wall in methane steam reforming at 1120K, S/C=2.77



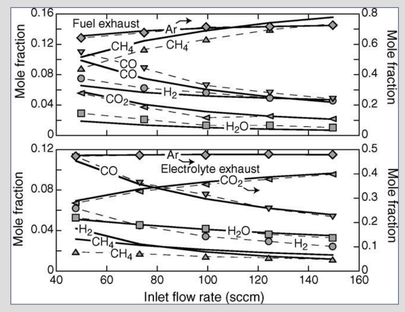
CH4 and H2O conversion as a funcion of tempreature in CH4 SR: S/C=2.77, 75%Ar



Steam reforming (metal monolith) [5]



Steam reforming (packed-bed) [5]



Dry Reforming of CO2 over Ni/YSZ anodes in Solid-oxide fuel cells (SOFC) [6]

The model developed is able to properly describe steam reforming of methane for wide ranges of experimental conditions, simulation results of the mechanism are in good agreement with experiments .

References:
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Contact: K. Herrera Delgado, O. Deutschmann, Institute for Chemical Technology and Polymer Chemistry, Engesserstraße 20, 76131 Karlsruhe, Germany. karla.herrera@kit.edu, deutschmann@kit.edu

Presented at 44. Jahrestreffen Deutscher Katalytiker, Weimar/Germany, März 16.-18., 2011