[1] Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Germany
[2] Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Germany

Composition Modulation over Three-Way Catalysts

D. Hodonj[1], P. Lott[1], S. Tischer[2], O. Deutschmann[1,2*]

Introduction

- Composition modulation increases low temperature TWC performance [1]
- Optimal period decreases with increasing temperature [1]
- Optimal period decreases with increasing amplitude [2]

Scope of our present study:
Systematic numerical and experimental studies on the influence of period τ, amplitude A, temperature T on composition modulation

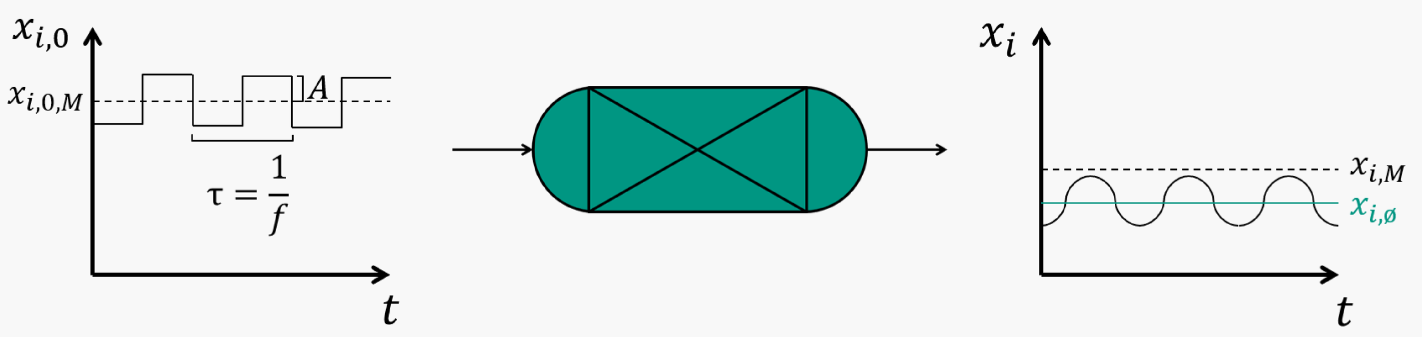

Fig. 1: Concept of composition modulation. Period τ : Time between repetitions of the change in the input condition. Amplitude A: Change in the value of the input condition compared to its mean value M.

Experiments

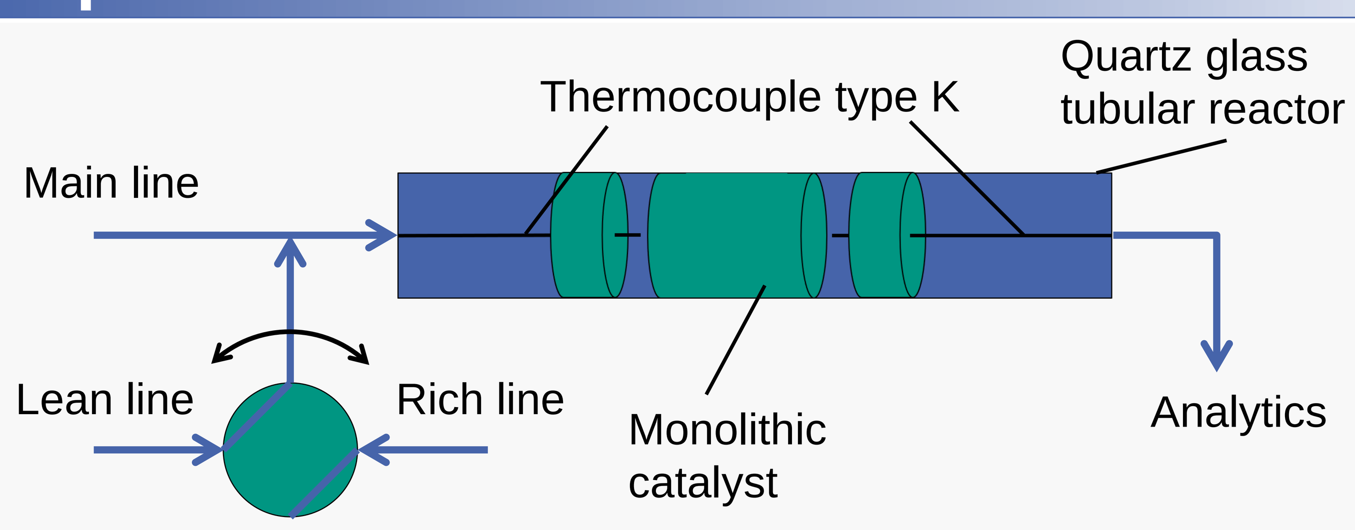

Fig. 2: Scheme of experimental setup for composition modulation.

- Cordierite monoliths coated with 2 wt.-% Pd/Al_2O_3 powder catalyst
  - 400 cpsi
  - d = 16 mm, l = 30 mm
  - L_{WC} = 100 g/l_{cat}
- Main line: N_2, CO_2, C_3H_6, C_3H_8, NO
  Lean/ Rich line: CO, H_2, O_2, N_2
- Analytics: FTIR (5 Hz), Lambda sensor (10 Hz)
- Setup characteristics: f_{max} = 2.5 Hz, λ = 0.93 – 1.07, T = 100 – 600 °C, GHSV = 50,000 – 100,000 h^{-1}

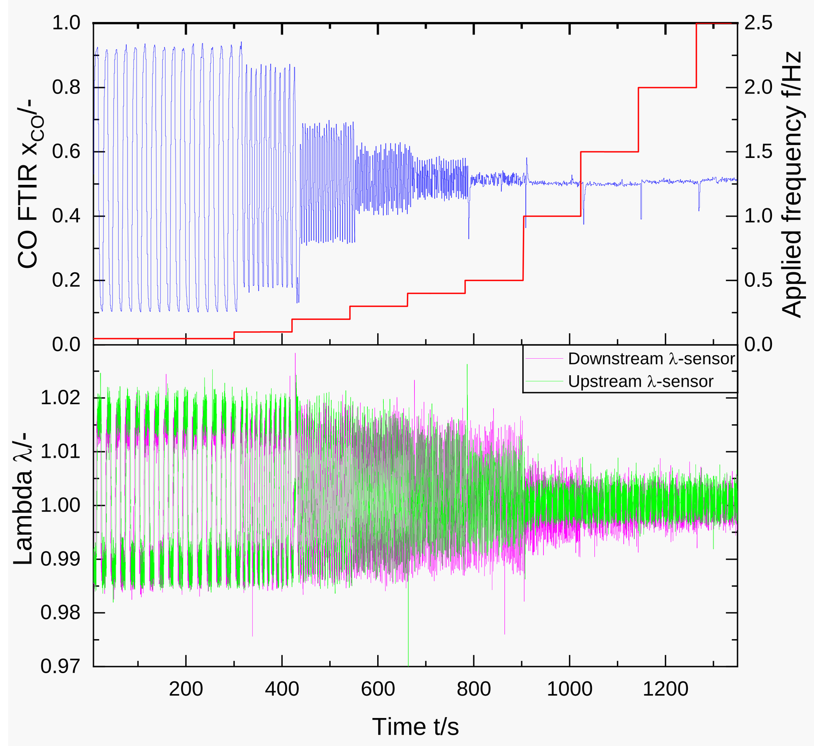

Fig. 3: CO FTIR signal and lambda sensor respond to different frequencies with inert monolith. $x_{CO,Rich}$ = 0.9 %, $x_{CO,Lean}$ =0.1 %.

- Signal smoothing in the FTIR due to low-pass dynamics [4].
  - Average concentration can be determined.
- The analysis of the lambda sensors shows that up to a frequency of 0.2 Hz the amplitude arrives at the catalytic converter.

Modelling

- CSTR Reactor Model:

$$\frac{dc_i}{dt} = \frac{\dot{V}_0}{V} c_{i,0} - \frac{\dot{V}}{V} c_i + \frac{S}{V} \dot{s}_i \qquad i \triangleq gas$$

$$\frac{d\theta_k}{dt} = \frac{\dot{s}_k}{\Gamma} \qquad k \triangleq adsorbate$$

- Mikrokinetic Model (CO oxidation part) [3]:

1) $O_2 + 2^* \rightleftarrows 2O^*$
2) $CO + * \rightleftarrows CO^*$
3) $CO_2 + * \rightleftarrows CO_2^*$
4) $CO^* + O^* \rightleftarrows CO_2^*$

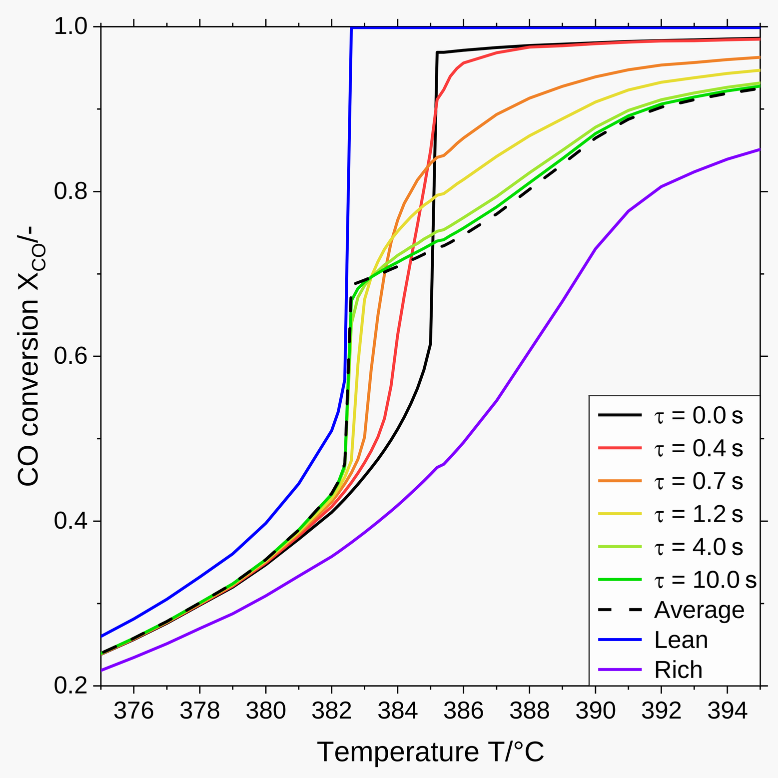

Fig. 4: CO conversion versus temperature for different periods τ. GHSV = 60,000 h^{-1}, A_{O2} = 5 %, $x_{CO,0}$ = 0.02, $x_{O_2,0}$ = 0.01.

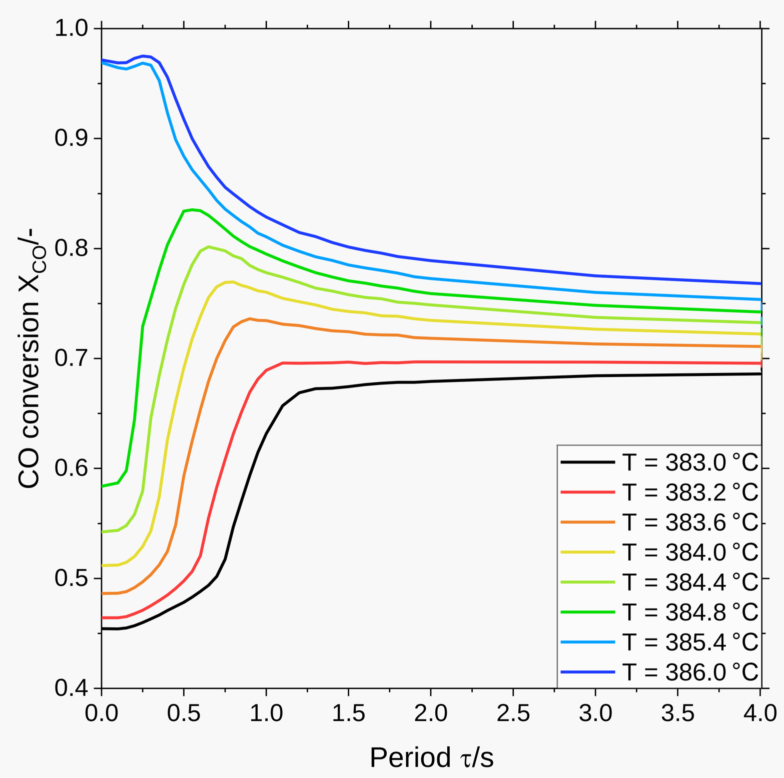

Fig. 5: CO conversion versus periods for different temperatures T. GHSV = 60,000 h^{-1}, A_{O2} = 5 %, $x_{CO,0}$ = 0.02, $x_{O_2,0}$ = 0.01.

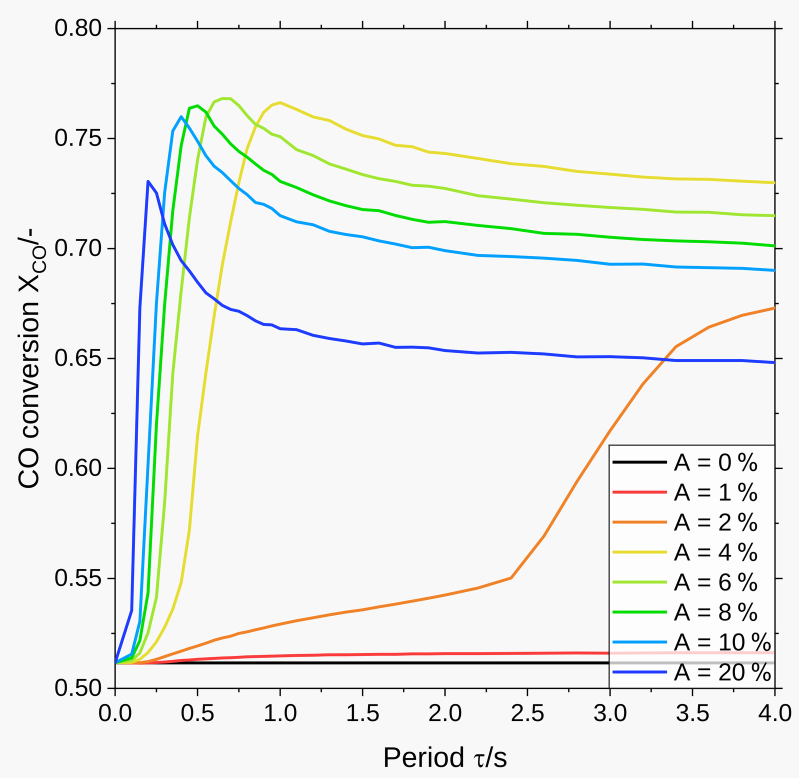

Fig. 6: CO conversion versus periods for different O_2-amplitudes A. GHSV = 60,000 h^{-1}, T = 384 °C, $x_{CO,0}$ = 0.02, $x_{O_2,0}$ = 0.01.

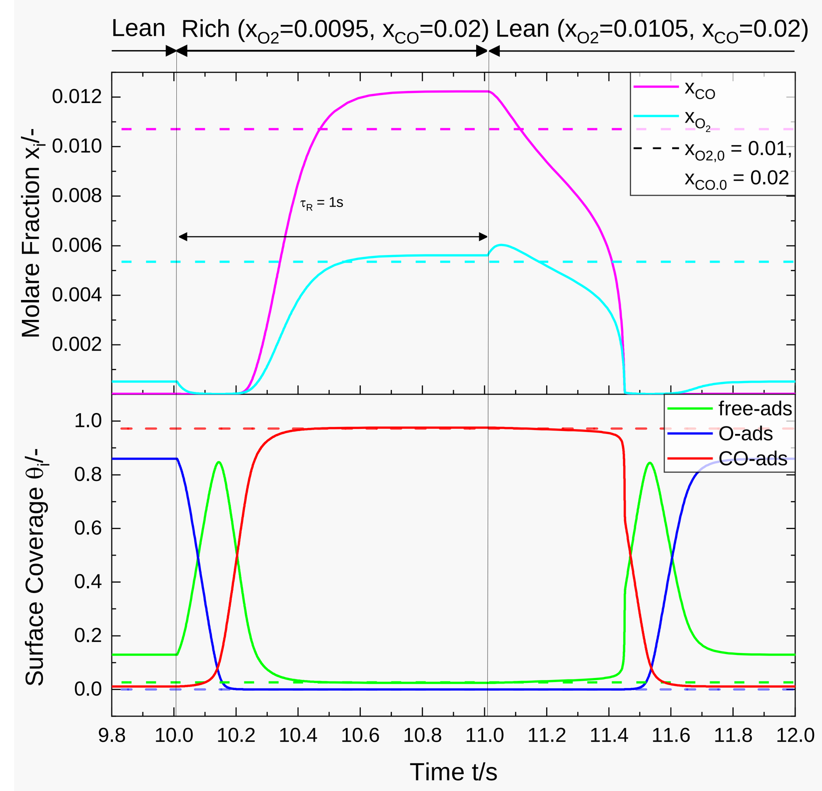

Fig. 7: Temporal concentration and surface coverage profiles during composition modulation. T = 377 °C GHSV = 38,000 h^{-1}

- Model predicts decreasing optimal period with increasing temperature and amplitude, respectively.
- Surface is covered by O-ads during the lean phase and poisoned by CO-ads during the rich phase.
- Free surface sites for reaction after switching conditions.

Conclusions

- Surface sites are poisoned by adsorbates during steady state operation.
- Switching conditions can increase free surface sites and improve catalytic performance.
- The use of detailed chemistry allows the description of composition modulation effects observed in literature.

Outlook

- Increase the frequency of pulses reaching the catalyst by reduction of dead volumes in the setup.
- Experimental parameter study on variation of temperature, period, amplitude and GHSV.
- Increasing the complexity of the model by adding other TWC reactions.

References and Acknowledgements

References

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Contact: daniel.hodonj@kit.edu, deutschmann@kit.edu

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