

Towards a fundamental understanding of the catalytic soot oxidation on Fe₂O₃: Coupling the catalytic kinetics with the fluid dynamics

Steffen Wagloehner, Sven Kureti *

Karlsruhe Institute of Technology, Technical Chemistry and Polymer Chemistry, D-76131 Karlsruhe, Germany
*Corresponding author. Phone: +49 721 608 8090, Fax: +49 721 608 2816, E-mail: sven.kureti@kit.edu

Introduction

Diesel particulate filters (DPF) represent a state-of-the-art technology for the removal of soot from diesel exhaust. However, the continuous regeneration of these filter systems remains a considerable challenge, as the trapped soot causes backpressure effects potentially decreasing the engine efficiency [1]. While the so-called CRT technique using NO₂ is already established for heavy duty vehicles, the catalytic soot oxidation by O₂ is considered to be a promising procedure for passenger cars, ships and work machines. Therefore, the present paper aims to provide a fundamental understanding of the oxidation of soot employing an effective Fe₂O₃ model catalyst [2,3]. For this purpose, we report on mechanistic and kinetic investigations as well as a resulting global-kinetic model implemented into computational fluid dynamics (CFD).

Experimental

The experimental studies were performed by using a α -Fe₂O₃ model catalyst as well as a home-made C₃H₆ model soot [2]. The solids were mixed establishing loose and tight contact modes. Kinetic investigations were carried out by using various reactor concepts. The reaction mechanism was elucidated by HRTEM, DRIFTS and isotopic labelling as well as a series of BET and TPD studies. For validation of the fluid dynamics computations, some experiments were made in a special reactor allowing gas-phase and local temperature analysis (IR camera).

Results and discussion

Based upon the mechanistic and kinetic studies a global-kinetic model of the soot oxidation on Fe₂O₃ catalyst was developed, which was validated by simulations [2,3]. For CFD, the reaction system was described by using the conservation equations of mass, heat and momentum (Fig. 1), wherein the momentum transport through the packed bed of soot/Fe₂O₃ was expressed by the Brinkman equation. The resulting model, which includes the coupling of the chemical kinetics and fluid dynamics, was validated by comparing simulated and experimental temperature distributions showing very good accordance. As a consequence of the modelling, some insights into the local heat and CO₂ evolution in the soot/catalyst bed were obtained (Fig. 1). For example, the existence of hot spots was excluded under the adjusted conditions being important for the assessment of the high-temperature stability of the catalysts used. However, it has to be stated that the model exclusively implies tight contact of soot and Fe₂O₃ and therefore our approach is currently extended to other realistic contact states as well, e.g. loose contact mode.

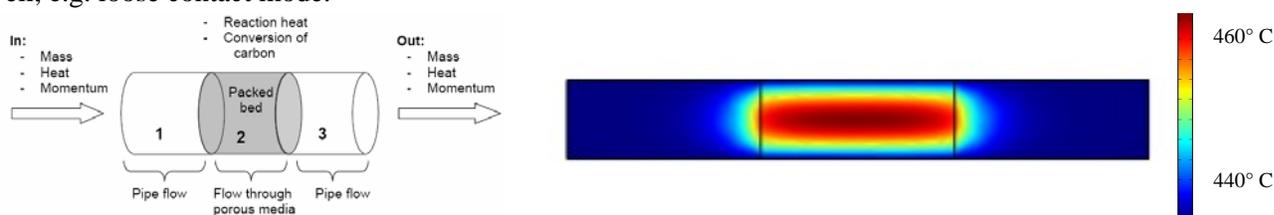


Figure 1: Scheme of the model structure (left) and simulated temperature distribution (right) upon soot oxidation on Fe₂O₃.

Conclusions

This paper concerns the fundamentals of the soot oxidation in diesel exhaust using Fe₂O₃ catalysts. Based upon mechanistic and kinetic studies we constructed a global-kinetic model which was implemented into computational fluid dynamics. The relevance of this comprehensive approach was demonstrated by predicting experimental features.

References

- [1] B. van Setten, *Cat. Rev.* 43 (2001) 489.
- [2] D. Reichert, H. Bockhorn, S. Kureti, *Appl. Catal. B* 80 (2008) 248.
- [3] D. Reichert, T. Finke, N. Atanassova, H. Bockhorn, S. Kureti, *Appl. Catal. B* 84 (2008) 803.

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Contact: Sven.Kureti@KIT.edu

Introduction

Diesel particulate filters (DPF) represent a state-of-the-art technology for the removal of soot from diesel exhaust. However, the continuous regeneration of these filter systems remains a considerable challenge, as the trapped soot causes backpressure effects potentially decreasing the engine efficiency [1]. While the so-called CRT technique using NO₂ is already established for heavy duty vehicles, the catalytic soot oxidation by O₂ is considered to be a promising procedure for passenger cars, ships and work machines. To provide a fundamental understanding of the catalytic soot oxidation the Temperature Programmed Oxidation (TPO) was chosen as basic experiment using α-Fe₂O₃ as model catalyst. In these investigations, the catalyst/soot mixture is present in the form of a packed bed. Based on these experiments a reaction mechanism implying a global kinetic model was set up. For the determination of unknown kinetic parameters, a tanks-in-series model was used. Furthermore, fluid dynamics of this system were established. Finally, the chemical kinetics were coupled with fluid dynamics resulting in a full model being able to simulate the soot TPO with α-Fe₂O₃ catalyst.

Chemical kinetics

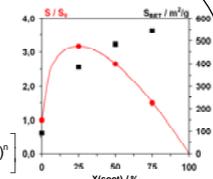
Global-kinetic approach [2]:

$$r(\text{CO}_2) = k_{\text{CO}_2} \cdot n(\text{C}_T) \cdot c(\text{O}_2)^n \quad \text{with } k_{\text{CO}_2} = A \cdot \exp\left(\frac{E_A}{RT}\right)$$

$$n(\text{C}_T) = \lambda \cdot S(X)$$

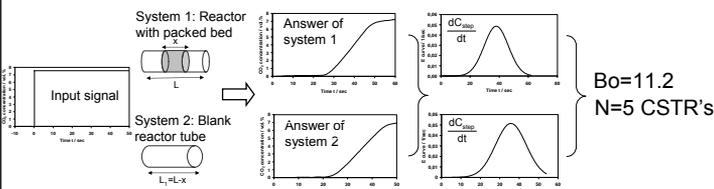
$$S(X) = S_0 \cdot m_0 \cdot (1-X) \cdot (1+60 \cdot X)^{1/2}$$

$$\Rightarrow r(\text{CO}_2) = \frac{1}{V_{\text{packed bed}}} \left[A \cdot \exp\left(\frac{E_A}{RT}\right) \cdot \lambda \cdot S_0 \cdot m_0 \cdot (1-X) \cdot \sqrt{(1+60 \cdot X)} \cdot c(\text{O}_2)^n \right]$$



Tanks-in-series model

Determination of the Bo number of the packed bed: Step experiment



Setting up the model: Heat and Mass balance for ideal CSTR

Heat balance:

$$m_{\text{cat}} \cdot c_{\text{p,cat}} \frac{dT_{\text{N}}}{dt} = \dot{V} \cdot c_{\text{p,gas}} \cdot (T_{\text{furnace}} - T_{\text{N}}) - r \cdot V_{\text{CSTR}} \cdot \Delta H_r - k \cdot A \cdot (T_{\text{N}} - T_{\text{furnace}})$$

Mass balance:

$$\frac{dC_A}{dt} = \frac{1}{T_i} (C_{A,N-1} - C_A) - r_{A,N}$$

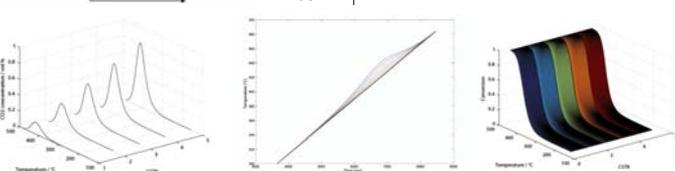
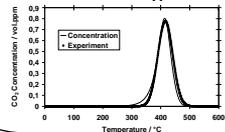


Fig.1: Results of the tank-in-series Model (5 CTR's): CO₂ profile, Temperature and Conversion for each CSTR.

Determination of E_A and A: Fit model with experimental data



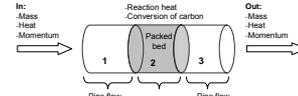
$$E_A = 89 \text{ kJ/mol}$$

$$A = 2.41 \cdot 10^4 \frac{\text{m}^3}{\text{mol} \cdot \text{sec}}$$

Fig.2: Experiment vs. simulation. Conditions: V=500mL/min, 10% O₂ in N₂, β=2K/min, tight contact.

Fluid dynamics

Conservation equations for packed bed in the PFR



Momentum transport: Brinkman (porous media) and Navier Stokes:

$$\left(\frac{\rho}{\epsilon_p} \right) \frac{\partial u}{\partial t} + \left(\frac{\rho}{k} + Q \right) u = \nabla \cdot \left[-pI + \left(\frac{1}{\epsilon_p} \right) \eta (\nabla u + (\nabla u)^T) - \left(\frac{2\eta}{3} - \kappa_{sv} \right) (\nabla \cdot u) \right] + F$$

Heat transfer: Convection and conduction:

$$\delta_u \rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = Q - \rho C_p u \cdot \nabla T$$

Mass transfer: Convection and diffusion:

$$\delta_s \frac{\partial c_i}{\partial t} + \nabla \cdot (-D_{\text{eff}} \nabla c_i) = R_i - u \cdot \nabla c_i$$

For chemical kinetics a simple analytical expression was used (derived from CO₂ profile upon a TPO run)

Verification of the system of equations on the basis of measurements with an IR camera (special reactor design): Experiment vs. simulation

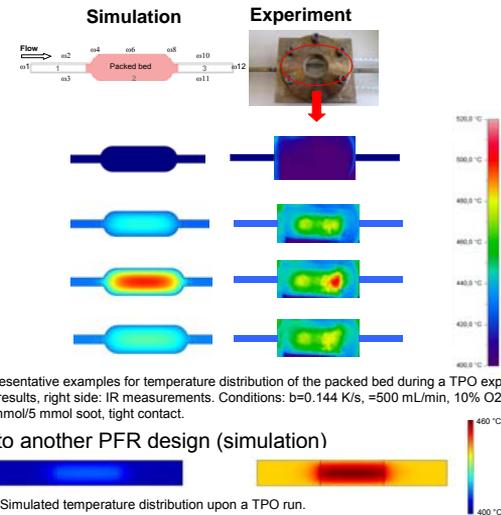


Fig.3: Four representative examples for temperature distribution of the packed bed during a TPO experiment. Left side: Modelling results, right side: IR measurements. Conditions: b=0.144 K/s, =500 mL/min, 10% O₂ in N₂, ncat/insoot=10 mmol/5 mmol soot, tight contact.

Transfer to another PFR design (simulation)

Fig.4: Simulated temperature distribution upon a TPO run.

Coupling of fluid dynamics and chemical kinetics

The coupling of fluid dynamics and catalytic kinetics results in a full model being able to describe the catalytic oxidation of soot by α-Fe₂O₃ upon a TPO run. This model provides fundamental insights into the catalytic soot oxidation as it can be seen on the exemplarily results below.

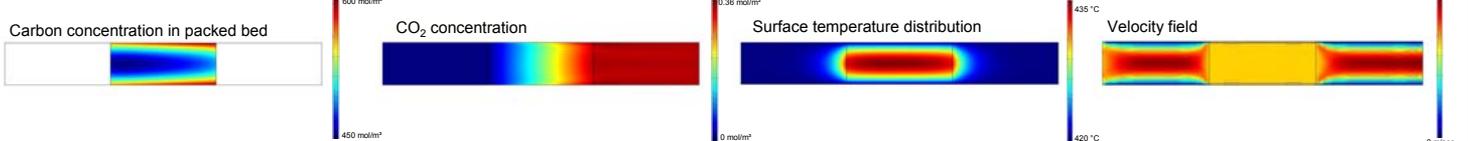


Fig.5: Simulated Carbon concentration, CO₂ concentration, temperature distribution and velocity field upon a catalytic TPO run at 420 °C.

Literature

- [1] B. van Setten, Cat. Rev. 43 (2001) 489.
[2] D. Reichert, H. Bockhorn, S. Kureti, Appl. Catal. B 80 (2008) 248.

Acknowledgements

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