

## On the kinetic modeling of soot oxidation in diesel particulate filters

Soheil Soltani<sup>1</sup>, Ronnie Andersson<sup>1\*</sup>, Bengt Andersson<sup>1</sup>

<sup>1</sup> Department of Chemistry and Chemical Engineering, Competence Centre for Catalysis,  
Chalmers University of Technology, SE-412 96 Gothenburg, Sweden.

\*Corresponding author: ronnie.andersson@chalmers.se

### Highlights

- Synergistic effect of NO<sub>2</sub>, O<sub>2</sub>, and water vapor revealed.
- Changes in micro-structure of soot effecting reaction rate revealed.
- Kinetic model for the entire conversion interval developed.

### 1. Introduction

Diesel particulate filter (DPF) has been proven to be a viable solution for mitigating particulate emissions of diesel exhaust. Regular regeneration periods are required through which the accumulated soot cake is oxidized in order to keep the engine back pressure below the required limits. This study concerns non-catalytic oxidation of a soot (Printex-U) with NO<sub>2</sub> in the presence of water vapor and O<sub>2</sub>. The aims are to investigate the promoting effect of those compounds experimentally and to develop a global kinetic model that can explain the observed rate of reaction as a function of temperature, concentration of the oxidizers. This model must also account for changes in morphological structure of the soot during the conversion. Furthermore, an alternative mechanism based on interactions with oxygen-containing complexes is proposed that can be a viable explanation for the observed promoting effect of water.

### 2. Methods

A set of isothermal experiments was designed and conducted with four effects: i) concentration of NO<sub>2</sub> (300-500 ppm), ii) concentration of water (0-5 vol. %), iii) concentration of O<sub>2</sub> (0-3 vol. %), and iv) temperature (350-450 °C). The design of experiments is based on a full-factorial analysis with replicated experiments and the statistical analysis was done following classical non-linear regression analysis. Flow-reactor experiments were conducted using argon as the carrier gas. Randomly chosen, replicated experiments were used to ensure reproducibility. In each experiment, the sample was initially heated up to about 600 °C under a flow of argon to strip pre-adsorbed species off the surface. The gas-phase composition was then switched to the reactive mixture to commence the oxidation reaction. Towards the later stages of conversion (after about 5 hr) temperature was ramped up to about 600 °C to finalize oxidation and thus to allow carbon balance to be closed. A computational model was formulated in the MATLAB environment to solve the non-linear parameter estimation problem. The differential, mass-balance equations of the model were numerically integrated using MATLAB's stiff solver ode15s. The parameters of the kinetic model were identified through non-linear regression analysis using MATLAB's gradient-based optimization subroutine, lsqnonlin. To speed-up simulations, the system of differential equations were vectorized and implemented through MEX-files, which are dynamically loaded after being compiled. Thereby, computational time was reduced by more than 80%.

### 3. Results and discussion

The analysis reveals a strong conversion dependency for the reaction order of carbon with its initially negative values being attributed to increasing porosity and thereby increasing surface concentration of carbon active sites. This indicates parallel, competing steps of gradual increase in porosity and thus oxygen access versus the removal of active sites with progressive conversion. A random pore model can resolve gradual changes in the porous structure of carbon. It has been considered as a viable approach for approximating the dynamics of active surface area of carbon [1]. As shown in Figure 1, the kinetic model

can be successfully fitted to the experimental observations with minimal number of adjustable parameters. The model was fitted to a subset of experiments where both water vapor and oxygen were present alongside NO<sub>2</sub> because of the significance of taking realistic exhaust conditions into consideration.

The conversion intervals of 0-1%, and 99-100% were not included in the regression analysis. Exclusion of the latter was due to the start of temperature ramp to complete oxidation. Nevertheless, Figure 1 shows that the predictions of the model can safely be extrapolated to 100% conversion. The very early phase of the reaction was excluded because of the artifacts arising from exposure of the sample to ambient air, which has been observed to cause quite different kinetics identified as overshoots in the reaction rate [2]. This effect lasts for a short period of time, and the fitted model is considered to predict conservative results over the 0-1% conversion interval. Consequently, the model can, with a very good degree of accuracy, cover the entire range of conversion.

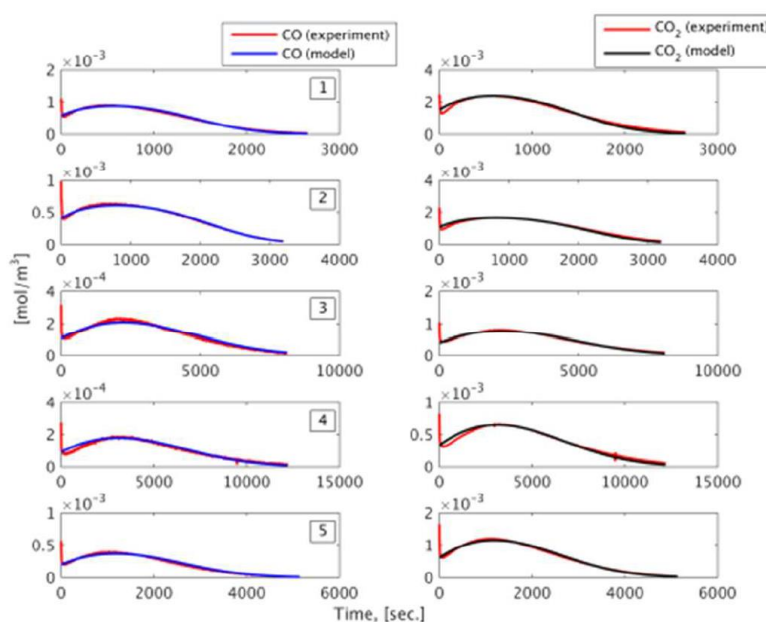


Figure 1. Kinetic model fitted to the experimentally measured concentrations of the oxidation products.

#### 4. Conclusions

Synergistic effect on the rate of soot oxidation was observed when NO<sub>2</sub>, water and oxygen were all present in the gas phase. Evidences have been found suggesting that the promoting effect of water proceeds via an interaction with surface oxygen complexes. Kinetic analysis shows that, the reaction order in carbon is initially negative, which increases with conversion to a value between 2/3 and unity at the final stages of burn-off. A global kinetic model was developed that can successfully fit the observed reaction rates over 1-99% conversion, which can be safely extrapolated to cover the entire range of carbon conversion. The results of this study can help develop models for controlling and optimizing the diesel particulate filter regeneration by predicting the required exhaust condition for maintaining a balance between soot accumulation and burn-off.

#### References

- [1] B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, Catal. Rev. 43 (2001) 489–564.
- [2] C. Wang-Hansen, C.J. Kamp, M. Skoglundh, B. Andersson, P.A. Carlsson, J. Phys. Chem. C. 115 (2011) 16098–16108.

#### Keywords

Soot oxidation; NO<sub>2</sub>; O<sub>2</sub>; H<sub>2</sub>O; Kinetics.