On the catalytic conversion of soot and NO_x into N_2 and CO_2

D. Reichert [1], H. Bockhorn [1], S. Kureti [1], M. Sander [2], A. Raj [2], M. Kraft [2]

[1] University of Karlsruhe – Karlsruhe Institute of Technology, Institute of Technical Chemistry and Polymer Chemistry, 76128 Karlsruhe, Germany

[2] University of Cambridge, Department of Chemical Engineering, Pembroke Street, Cambridge CB2 3RA, UK

Corresponding author (S. Kureti): Kureti@ict.uni-karlsruhe.de

Diesel engines with direct fuel injection exhibit the highest efficiency for automotive applications. However, a crucial constraint is the emission of NO_x and soot. In the past, much attention has been concentrated on the removal of these pollutants mainly dealing with the diminution of either soot or NO_x. However, the direct catalytic conversion of soot and NO_x into N_2 and CO_2 has hardly been considered. The present contribution shows some experimental results substantiating the soot/NO_x reaction under practical conditions. Furthermore, the paper also deals with the fundamentals of the catalytic soot/NO_x/O_2 reaction to build up a base for a targeted catalyst development. For this purpose mechanistic and kinetic studies as well as kinetic modelling and quantum-mechanical calculations were made using Fe_2O_3 as a model catalyst.

To elucidate the mechanism of the soot/NO_x/O_2 reaction and particularly the role of the Fe_2O_3 catalyst a series of examinations was performed including TPO (Temperature Programmed Oxidation), transient experiments, carbothermal reaction, DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy), HRTEM (High Resolution Transmission Electron Micrography) and isotopic labelling. TPO and transient studies in which the soot/O_2 and soot/NO reaction are temporally separated showed that the NO reduction occurs on the soot surface without direct participation of the Fe_2O_3 catalyst. In agreement with the quantum-mechanical calculations, the first reaction step is assumed to be the formation of CC(O) groups being associated with the attack of oxygen on the soot surface. The decomposition of these complexes leads to active carbon sites on which NO is adsorbed. Furthermore, the oxidation of soot by oxygen provides a specific configuration of active carbon sites with suitable atomic orbital orientation that enables the chemisorption and dissociation of NO as well as the recombination of two adjacent N atoms to evolve N_2. Moreover, carbothermal reaction, DRIFTS, HRTEM and isotopic studies show that the Fe_2O_3 catalyst acts as an “oxygen pump” leading to a higher number of active carbon sites thus resulting in enhanced NO reduction. Pumping of oxygen includes dissociative O_2 adsorption on the catalyst, surface migration of oxygen to the contact points of soot and Fe_2O_3 and then final transfer of O to the soot. Moreover, the contact between both solids is maintained up to high conversion thus resulting in continuous oxygen transfer from catalyst to soot.

Based upon the above described mechanism a kinetic model was constructed. This model represents a global approach in which the NO reduction and soot oxidation are coupled. To obtain independent kinetic parameters additional kinetic studies were performed by using a gradient-free loop reactor. The comparison of the measured and calculated data shows that the experimental results of catalytic soot/NO_x/O_2 reaction are well described by the kinetic model. In accordance with our mechanism postulated the kinetic model involves same $E_{A,app}$ for catalytic and non-catalytic NO

reduction (56 kJ/mol), but different apparent activation energies for catalytic (85 kJ/mol) and non-catalytic soot/O_2 reaction (115 kJ/mol). Finally, the model was validated by some simulations as shown in Fig. 1.

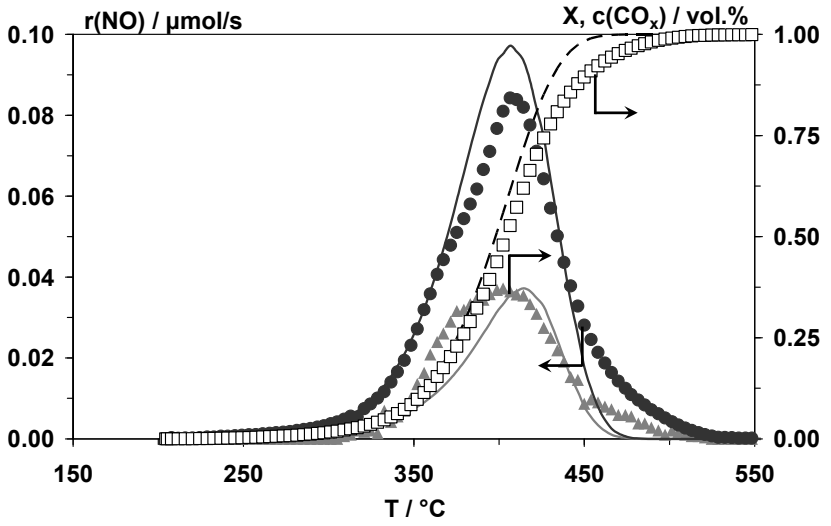

Fig. 1. Experimental and numerically modeled TPO data of the catalytic soot/NO_x/O_2 on Fe_2O_3 (20 mmol catalyst, 10 mmol soot, 500 ppm NO, 14 vol.% O_2, N_2 balance, 500 ml/min). CO_x concentration (●, —), soot conversion (□, – –) and rate of NO reduction (▲, —); symbols represent experimental data.