

Soot oxidation on manganese oxide catalysts in gasoline exhaust

Maria Nitzer-Noski, Sven Kureti*

Motivation

Diesel and gasoline engines with direct fuel injection are due to their efficiency the state of the art technology. However, a critical issue is the output of soot particles, which are carcinogenic and contribute to the greenhouse effect. To reduce soot emissions, particulate filters are widely employed, which have to be regenerated periodically to remove the soot deposits. Otherwise the counter pressure increases, which consequently reduces the motor performance. The regeneration of the filter is performed by oxidation of the soot at temperatures higher than 600°C, which exceed the common exhaust gas temperature. For this reason, catalytically coated particulate filters aiming the activation of the soot/O₂ reaction are developed since many years. In order to fulfil the European regulations concerning exhaust gas treatment, a particulate filter is also needed in gasoline engines with direct fuel injection. To overcome this issue this paper addresses the development of highly active manganese oxide catalysts which achieve the regeneration of diesel as well as gasoline particulate filters.

Results and Discussion

The design of new catalysts for the soot oxidation is a knowledge-based approach in which the understanding of structure-activity relations plays a crucial role [1]. With this purpose, several bare manganese oxide samples have been systematically evaluated towards soot oxidation activity in diesel and gasoline model exhaust gas.

The catalytic tests were performed by temperature programmed oxidation (TPO). Tight contact catalyst/soot powder mixtures were investigated, while soot originated from C₃H₈ combustion was employed. The tight contact was achieved by mixing the catalyst powder and the model-soot in a ball mill for 15 min. The TPO tests demonstrated that the manganese oxide catalyst synthesized by flame-spray-pyrolysis (FSP) is able to oxidize the soot at much lower temperatures than a reference α -iron oxide (Figure 1).

Based on previous experiments and comparisons with published studies, the manganese oxide has shown up as the most efficient soot oxidation catalyst [1-3].

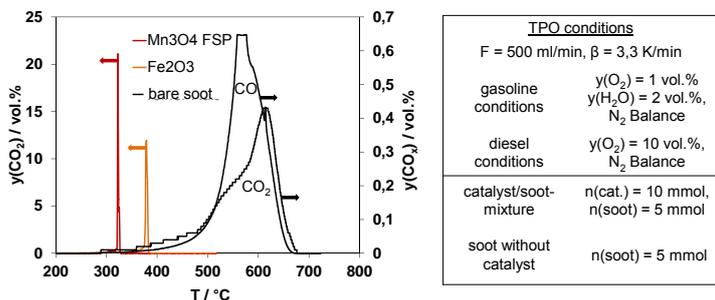


Figure 1: Oxidation of bare soot and mixtures of soot and α -iron oxide reference catalyst and the FSP-synthesized manganese oxide catalyst under diesel model exhaust gas.

Catalysts were thoroughly characterized by powder X-ray diffraction, N₂ physisorption, scanning electron microscopy, temperature programmed reduction by H₂ and temperature programmed desorption of NH₃. The correlation of the physical-chemical properties and the soot oxidation activity of the catalysts showed that high amount of surface oxygen vacancies and small particle sizes are crucial for the oxidation of soot (Figure 2).

These findings agree with the mechanistic studies of FSP-Mn₃O₄/soot suggesting that the supply of oxygen occurs from the gas-phase and catalyst bulk via the surface of the catalyst to the contact points of the soot. The contribution of the bulk is very pronounced indicating strong mobility of inner oxygen, particularly when comparing with other catalysts, e.g. iron oxides [1].

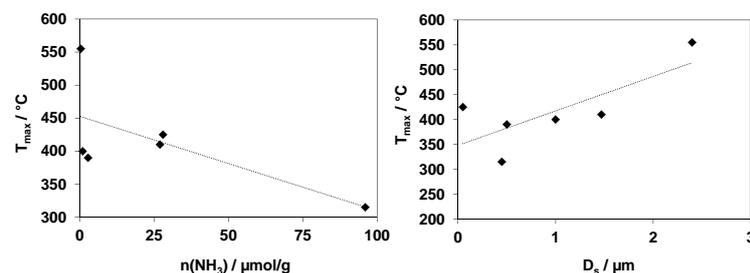


Figure 2: Correlation of the number of oxygen vacancies (left; expressed as molar NH₃ equivalents) and the particle diameter (right) with the activity of a systematic series of manganese oxide catalysts evaluated under gasoline-type exhaust gas.

Furthermore, the soot oxidation activity of the systematic series of MnO_x full catalysts corresponding to Figure 2 is shown in Figure 3, whereas the samples were evaluated under both diesel- as well as gasoline-type conditions (Figure 3). As reference, bare soot was taken indicating start of oxidation at around 650°C. The soot oxidation on the manganese oxide catalyst prepared by FSP provides soot combustion already at 300°C under diesel and gasoline exhaust conditions. Moreover, the FSP-Mn₃O₄ catalyst reveals high thermal stability. After hydrothermal exposure at 750°C and thermal treatment in static air at 1050°C its activity does not vary significantly, although the particle size, crystallinity and morphology drastically changed [1].

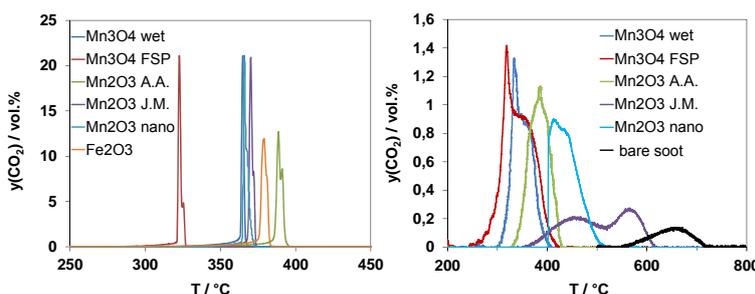


Figure 3: Comparison of the soot oxidation activity of different catalysts under diesel (left) and gasoline conditions (right).

Summary

Bare manganese oxide catalysts for soot oxidation were evaluated. The best catalyst was FSP-Mn₃O₄ implying high activity in diesel as well as gasoline model exhaust gas. FSP-Mn₃O₄ only slightly changed its performance after hydrothermal and thermal treatment. The correlation of physical-chemical properties and soot oxidation activity showed that high amount of surface oxygen vacancies and small particle sizes are crucial for soot oxidation of catalysts. These findings coincide with the mechanistic studies suggesting that the supply of oxygen occurs from the gas-phase and catalyst bulk via the surface of the catalyst to the contact points of the soot. The contribution of the bulk is very pronounced indicating strong mobility of inner oxygen.

Literature

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- [3] S. Wagloehner, J. N. Baer, S. Kureti, Structure-activity relation of iron oxide catalysts in soot oxidation, Applied Catalysis B: Environmental 147 (2014) 1000-1008.

Acknowledgments

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