Abstract

An increasing human population, social development and ongoing globalization increases the number of fuel-driven vehicles accordingly and, thus, increases the pollution based on exhaust gas emissions. Constantly more strict regulations are passed by the government, which demands research to constantly improve catalysts for gasoline and diesel vehicles. The implementation of ceria in the three-way catalyst (TWC) as an active component to lower the emission of hazardous CO and hydrocarbons and to decrease the use of noble metals is still seen as a breakthrough for the automotive catalysis in the 80’s of the last century. Especially the unique properties of ceria like the suitably high specific surface area and the good redox properties point out that ceria is an ideal candidate for the reduction of exhaust gas emissions. Furthermore, its capacity to facilitate and store oxygen is a key issue as it helps to compensate oscillations between lean and rich exhaust gas compositions.

Ceria can easily be doped with many different transitions- and rare earth metals enhancing the thermal stability, the oxygen storage capacity (OSC) and the catalytic activity. Doping metals like Zr$^{4+}$, Y$^{3+}$, Pr$^{3+}$, La$^{3+}$, Hf$^{4+}$, Cu$^{2+}$ and many more are studied thoroughly in different ratios and stoichiometries, and the ceria-based catalysts are applied as support or as active phase on alumina, silica or other support materials. Their surface and bulk characteristics, including the defect structure of the samples, yield important information about the capacity to activate oxygen on the surface for the reaction with CO and soot. However, strong trends are ambiguous. While a correlation between redox properties and CO oxidation activity is often demonstrated, no correlation between the capacity to activate oxygen on the surface under oxygen excess conditions and the redox properties like high OSC values are reported for soot oxidation. To address this problem, different ceria-based catalysts were prepared by different synthesis procedures and tested for their catalytic activity in CO and soot oxidation. Thereby, structure-activity correlations were investigated for oxygen excess conditions. Fur-
thermore, the relation between powder catalysts and catalytic thin coatings is studied with the help of a newly developed plate reactor, which was first studied by means of pure and Li-doped zirconia catalysts.

The surface characteristics are the pivotal aspects in soot oxidation for the oxygen activation process under oxidizing conditions. Secondly, when the gradient of reduction between surface and bulk is sufficiently large, the redox properties including several lattice layers become important. While oxygen transport through the first surface layer is fast, the limiting reaction step seems to be the spill-over of activated surface oxygen to the soot particle. In contrast, results from CO oxidation show that a high catalytic activity correlates with enhanced redox properties based on the mobility of oxygen and CO and, especially, due to the high reducing property of CO.

The Li-doped zirconia samples are highly active as both powder and thin-film catalysts in soot oxidation due to the high ion mobility of Li through the zirconia matrix. In contrast, pure zirconia is not active in soot oxidation. Although Li ion doping enhances the thermal stability of zirconia and favors the formation of the monoclinic phase, which is more active in CO oxidation than the tetragonal phase, it does not act as an active site in CO oxidation.

The investigation of low-calcined, pure ceria samples revealed that the precursor used to synthesize the ceria catalyst influences both surface and bulk characteristics. Similarly, different preparation techniques applied to obtain Ce$_{0.7}$Zr$_{0.3}$O$_2$ catalysts influenced the structure and, thus, the activity of the catalysts in CO and soot oxidation. The addition of a low molar amount of Y$^{3+}$ enhanced the redox properties and thermal stability of ceria-zirconia catalysts. The doping amount had an impact on the soot oxidation activity based on the substitution of active surface ceria by the Y ions. In contrast, the low doping amounts did not show an impact on the catalytic activity in CO oxidation.