Fluorine dopant promoted peroxide and superoxide groups on CeOxFy/Rh(111) and CeOxFy/Rh(110) catalyst supports

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Cerium ability to store oxygen when in oxygen rich environment and to release it during oxygen deficit makes it a suitable oxygen storage material [1]. As a catalyst support, cerium oxide (CeO_x) provides oxygen to the catalytically active particles and increases the reaction rate [2]. This process is widely exploited in three way catalysis (TWC) [3] or fuel cells [4].

In practice, fluorine is a common contaminant of CeO_x layers. It can be present either in the cerium base material [5] or incorporated from adjacent instrument parts [6]. Due to fluorine enthalpy, it segregates at the surface. Therefore, even a low fluorine bulk concentration results in a higher surface concentration [7].

Fluorine dopant incorporates itself into the ceria lattice instead of oxygen. The additional electron in fluorine valence shell causes changes in the electronic state of nearby Ce atom. As a result of charge transfer, oxygen adsorption sites change their energies and peroxide or superoxide species can be formed. Peroxides and superoxides are known for their high reactivity and their presence influences catalytic reactivity. Fluorine changes reaction mechanism on ceria and effects its oxygen storage capacity as well as overall catalyst reactivity.

In our research, peroxide and superoxide species formation is studied on oriented $CeO_xF_y(111)$ and $CeO_xF_y(110)$ layers prepared by fluorine doped Ce evaporation on Rh(111) and Rh(110) single crystals. Fluorine doped layers are compared with oriented cerium oxide $CeO_x(111)$ and $CeO_x(110)$ layers. Oxide species are studied in terms of stability at atmospheric pressure and elevated temperatures. Species are detected by means of FT-IR and electronic structure changes are observed by XPS.

References:

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