

The impacts of fluorine doping of ceria are studied by means of surface science experimental methods. Fluorine-doped and fluorine-free ceria layers are epitaxially grown on rhodium single crystals and their properties are compared in regular and inverse catalyst configurations. A procedure for epitaxial growth of $\text{CeO}_2(110)$ and $\text{CeO}_x\text{F}_y(110)$ layers on $\text{Rh}(110)$ single crystal is developed and described in detail. Shape alterations of Ce $3d$ spectrum brought about by fluorine doping are explained and a suitable deconvolution method is proposed. Special attention is focused towards stability of fluorine in ceria. Presented data show that fluorine incorporation in ceria lattice causes stable reduction of ceria, which withstands up to 200°C in near-ambient pressure conditions. Morphological changes are observed due to elongation of surface lattice constant of reduced ceria. Oxygen storage capacities and hydrogen oxidation reaction rates of four different studied systems are compared and discussed. The twofold nature of oxygen exposure of fluorinated ceria is discovered and explained. Oxygen repels fluorine from the surface, while the remaining part of fluorine is expelled to adsorbate positions, where its electronic state is altered. Moreover, such fluorine is prone to interact with atomic hydrogen. This reaction is put forward as the main fluorine removal mechanism.