Doped ceria nanostructures for the oxidation of pollutants: investigations into the role of defect sites

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Summary

Air pollution is a worldwide phenomenon strictly connected to severe risks to human health. Among the anthropic activities linked to the production of noxious compounds, road transport is one of the most impacting, especially in highly populated urban areas. In order to preserve air quality and the environment, strict regulations in terms of emission limits have been adopted by several nations. As a consequence, most vehicles are today equipped with a complex aftertreatment line in which the pollutants can be converted into harmless substances.

To this end, oxidation catalysts are needed to convert CO and unburned hydrocarbons into CO_2; moreover, proper catalysts can also be deposited inside particulate filters to promote soot oxidation at lower temperature, reducing the fuel consumption and thermal shock during regeneration. Among the attractive alternatives to expensive noble metals, ceria-based materials have exhibited promising oxidative performances. Ceria activity is linked to its unique redox behavior and oxygen storage capacity, but several other factors, such as morphology, reducibility or defectiveness, concur in determining the final catalytic properties. All these features can be tuned by adjusting the synthesis conditions or by doping.

In this thesis, different ceria-based nanostructured catalysts have been examined, with the intent of shedding light on the relevant structural and physico-chemical properties defining the catalytic activity and on the reaction pathways involved. The materials, prepared via hydrothermal synthesis, were extensively characterized and tested following the procedures reported in Chapter 2.

A first set of catalysts was obtained by doping ceria with Cu and Mn. The defect sites formed in ceria structure upon doping were investigated via in situ Raman spectroscopy, monitoring their behavior throughout thermal cycles and during soot oxidation (Chapter 3) and CO oxidation (Chapter 4). Three different types of structural defects were recognized, namely oxygen vacancies, Frenkel

interstitial-vacancy pairs and vacancy-free substitutional sites. The defectiveness was correlated with catalytic activity towards CO oxidation, while an increase of vacancy-free sites after soot oxidation suggested that peroxides and superoxides deactivation can occur on catalysts presenting excessive oxygen vacancy concentration. Hence, Cu-doped ceria was characterized by the best CO oxidation activity, thanks to its high specific surface area, reducibility and amount of defects; however, it featured poor soot oxidation activity; conversely, Mn-doped ceria exhibited the best soot oxidation activity, thanks to an intermediate density of oxygen vacancies and to its well-defined morphology. Spectral evolution also suggested that CO dissociative adsorption may occur at ceria surface. Moreover, oxygen vacancy clusters can form in reducing atmosphere, which could reorganize not only in the presence of O_2 but also upon a temperature decrease, forming isolated vacancies and then evolving into Frenkel and extrinsic oxidized dopant-containing sites when exposed to oxygen.

In Chapter 5, equimolar ceria-praseodymia was compared to pure CeO_2 in view of the possible application of this mixed oxide in a gasoline particulate filter. The weakening of the Ce – O bonds associated to Pr addition resulted in a high reducibility, promoting the catalytic activity towards CO, VOCs and soot oxidation. Thanks to its ability to release active oxygen, ceria-praseodymia exhibited a greater activity and CO_2-selectivity with respect to pure ceria also at low O_2 concentration, proving to be a promising catalyst for coated filters.

Rare earth-doped ceria samples containing different quantities of La and Nd were also prepared and analyzed in Chapter 6. La and Nd ions were well incorporated in ceria structure, but the final morphology was significantly altered: in fact, doping fostered the formation of smaller nanocubes and elongated particles, resulting in a higher specific surface area. The introduction of trivalent cations was also associated with a higher abundance of defects and oxygen vacancies, but a too high oxygen deficiency detrimentally affected the material reducibility and catalytic activity for CO and NO oxidation. Conversely, soot oxidation generally benefited from La and Nd addition. In particular, the Ce-La equimolar oxide exhibited outstanding performances in all the tested conditions, thanks to its optimal morphology and surface acidity. The presence of NO_x promoted soot oxidation in loose contact while it had detrimental effects in tight contact, giving insights on the active species and reaction mechanisms involved.

In conclusion, CO oxidation is highly promoted by the presence of active oxygen vacancies, like those associated to Cu doping. However, a high density of these sites favors reactive oxygen species deactivation. Hence, rare earths-doped CeO_2 exhibits better soot oxidation activity thanks to its less dynamic vacancies.