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In situ Raman analyses of nanostructured ceria-based catalysts during the soot oxidation

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Introduction

In the recent years, ceria-based catalysts have been widely investigated, since they can be fruitfully employed in several applications. In the automotive field, they can be used to promote the oxidation of particulate matter during the Diesel Particulate Filters regeneration, exploiting ceria good redox properties and high oxygen storage capacity. Recently, novel synthesis procedures allowed to obtain nanostructured ceria particles with well-defined shapes, and the morphology has been proved to affect the properties of these materials [1]: indeed, ceria nanocubes and nanorods exposing reactive crystal planes on their surface showed a higher catalytic activity, which was ascribed to a better catalyst-soot contact but also to their higher defect abundance [2]. In fact, different types of defects can be found in the ceria lattice and they play a role during the soot oxidation, which is believed to occur via a Mars-van Krevelen mechanism involving oxygen vacancies.

Raman spectroscopy is a useful technique to investigate the properties of solid materials, and it was employed here to study the defect sites in four nanostructured ceria-based catalysts, consisting of pure and Cu/Mn doped ceria. In situ Raman analyses were performed to monitor the changes in defectivity through thermal cycles and also during the soot oxidation reaction, revealing different effects of Cu and Mn addition into the ceria lattice.

Materials and Methods

The four samples, consisting of pure ceria (CeO₂) and ceria doped with 5% Cu (Ce95Cu5), 5% Mn (Ce95Mn5) and 2.5% Cu together with 2.5% Mn (Ce95Cu2.5Mn2.5), were prepared via the hydrothermal synthesis procedure reported elsewhere [3]. All the Raman measurements were performed in a Renishaw InVia Reflex micro-Raman spectrometer, equipped with a 100-mW power solid-state laser emitting monochromatic light at a wavelength of 514.5 nm. In situ Raman analyses were carried out in a Linkam TS1500 cell, heating the catalyst up to 700 °C in air and then cooling it down to room temperature. In situ analyses of the soot oxidation were performed on tablets of catalyst and soot (40:1 weight ratio) prepared by mixing the two solids in a ball mill.

Results and Discussion

Doped ceria samples showed smaller particles and a higher specific surface area than pure ceria nanocubes. In the Raman spectrum of CeO₂ a single defect peak located at 596 cm⁻¹ (D1) was present, assigned to Frenkel anion pairs. A second band related to the presence of extrinsic defects (D2) appeared at higher Raman shifts only in the spectra of the doped samples. In the Cu-doped catalysts, also a less intense peak at lower shifts (D3) was detected, pointing out the presence of oxygen vacancies. The ratios between the areas of the defect peaks and of the main ceria F_{2g} vibrational feature indicated a higher defect abundance in the doped

samples, especially in the Cu-containing ones. In situ Raman measurements carried out during thermal cycles in oxygen-rich atmosphere highlighted an increase in the D2 component for the Ce95Cu5 sample at the end of the test (see Fig. 1a), suggesting the assignment of this peak to oxidized sites not containing oxygen vacancies. In situ Raman analyses were performed also during the soot oxidation, allowing to directly observe the reaction progress through the disappearance of the soot bands and the increase of the ceria peaks intensity, due to the reduced light absorption by soot (see Fig. 1b); in this case, a higher increase in the D/F_{2g} area ratio was observed after the test for Ce95Cu5, suggesting that this reaction fosters the formation of defects. A higher initial defect abundance was correlated with an improved activity for CO oxidation; conversely, for soot oxidation the Cu-doped samples exhibited the worst activities, suggesting that a high content of oxygen vacancies may have a detrimental effect, in agreement with a recently proposed mechanism about reactive oxygen species - vacancy annihilation [4].

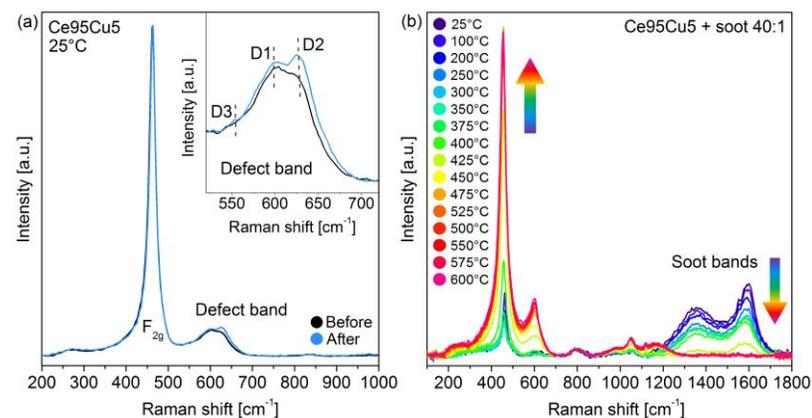


Figure 1. (a) Normalized Raman spectra collected at 25°C on the Ce95Cu5 catalyst before and after the in situ analysis, in which it was heated up to 700 °C and then cooled down in air flow (in the inset a magnification of the defect band is shown); (b) in situ Raman spectra recorded at different temperatures during the analysis of soot oxidation on the Ce95Cu5 sample.

Significance

Cu and Mn doping allows to create new intrinsic and extrinsic defects in the ceria lattice, improving the activity towards the CO oxidation. Mn-doped ceria exhibited the best performance in soot oxidation, thanks to its morphology and intermediate density of defects.

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