In situ Raman analysis of the CO oxidation reaction over ceria nanocatalysts

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In situ Raman analysis is emerging as a valuable tool to elucidate the role and the evolution of the defect sites in solid oxides during heterogeneous catalytic processes [1]. In this work, pure and Cu/Mn doped ceria nanocatalysts [2] were studied during the CO oxidation reaction. Raman spectroscopy performed at room temperature (RT) evidenced the presence of different defect bands, ascribed to oxygen vacancies (D3), Frenkel anion pairs (D1) and dopant-containing oxidized sites (D2) [1]. The evolution of the Raman spectrum of the catalysts was then compared during thermal cycles in air and throughout the CO oxidation reaction. The in situ analyses allowed to detect the formation of polyene-like chains via the dissociative adsorption of CO, whose maximum accumulation marked the catalysts light-off temperature. Moreover, at the end of the process, an intensity increase of the defect Raman bands was observed on all the doped samples at RT, in particular for the most catalytically active Cu-containing ones (Fig.1a). Cycles of reduction (CO/N_2) and oxidation (O_2) at 400°C revealed a reversible oxygen vacancies (O_v) clustering at the catalyst surface (Fig. 1b) induced by CO conversion and pointed out the dependence of the increase of the oxidized defect Raman bands contribution on such previous structural rearrangements. The close correlation between these phenomena, the reducibility of the dopants and the catalytic activity of the investigated materials was highlighted and carefully discussed.

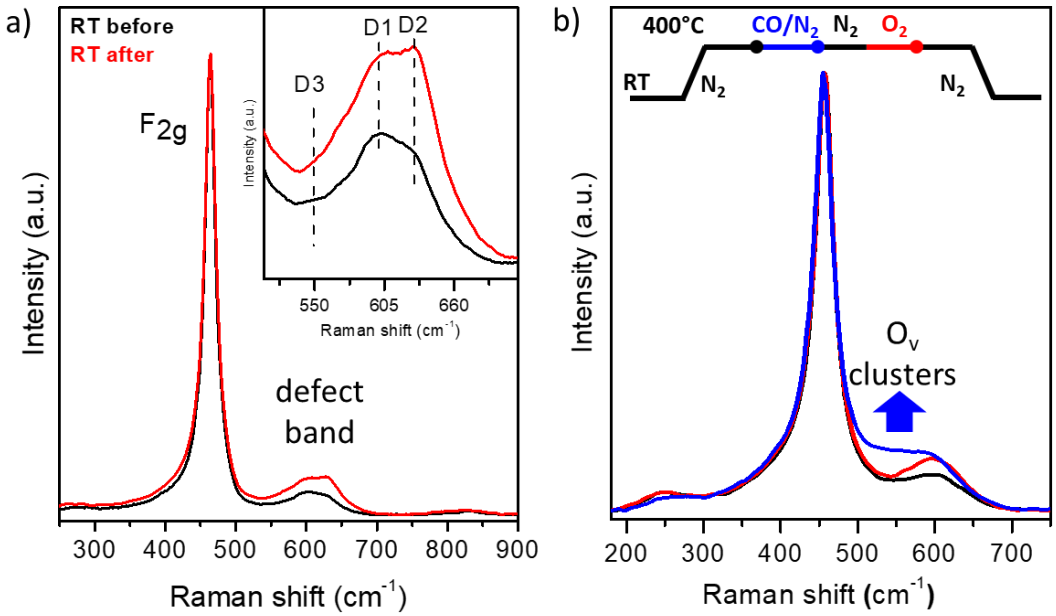

Figure 1: a) Raman spectra of the 5% Cu doped ceria catalyst at RT before (black curve) and after (red curve) CO oxidation. The defects band region is magnified in the inset; b) In situ Raman analysis of the 5% Cu doped sample during cycles of reduction and oxidation (according to the top scheme) performed in different atmospheres at 400°C.

[1] E. Sartoretti, C. Novara, F. Giorgis, M. Piumetti, S. Bensaid, N. Russo, D. Fino, Sci. Rep. 9, 2019, 3875.

[2] M. Dosa, M. Piumetti, S. Bensaid, T. Andana, C. Novara, F. Giorgis, D. Fino, N. Russo, Catal. Lett. 148, 2018, 298.