

Control of the surface chemistry and selectivity of a CO oxidation catalyst by changing the shape of its oxide support nanoparticles

J. C. Conesa, D. Gamarra, A. Martínez-Arias, A. López-Cámara, D. Olea, M. Monte
Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, 28049 Madrid, Spain
jcconesa@icp.csic.es

In previous works of our laboratory¹, the active species in CuO/CeO₂ catalysts used for mild temperature preferential oxidation of CO by O₂ in presence of H₂ (PROX process) have been found by several experimental techniques to be formed by partially reduced CuO nanoclusters dispersed on the ceria surface. Trying to influence the catalytic properties by tuning the CuO-CeO₂ interfacial interaction, CuO (1% by weight) has been deposited on different high surface area nanocrystalline ceria supports made by hydrothermal or precipitation methods, which display specific morphologies exposing different crystal planes of the CeO₂ lattice (Fig. 1).

The ceria material alone shows already different surface chemistry depending on the surface crystal planes exposed. Thus CeO₂ nanocubes exposing mostly (100) faces display in the CO + O₂ reaction higher specific rate per surface area than other ceria preparations, while stabilizing a different type of surface carbonates and higher amounts of acidic OH groups as shown by *in situ* IR spectra (Fig. 2).

In the case of the CuO/CeO₂ catalysts made by impregnation on these different ceria materials, different chemistry in the PROX process is also evidenced both by the *in situ* IR spectra and the reaction products analysis. Those spectra display different carbonate groups on the different samples, similarly to what is observed for pure CeO₂ in the CO + O₂ reaction; furthermore, they show Cu⁺-CO carbonyls in higher amounts on the ceria nanocube-supported sample, in spite of the lower CuO dispersion that could be expected in this sample if one considers simply its lower specific surface area (Fig. 3). It seems thus that the ceria (100) surface stabilizes a higher CuO dispersion or/and a higher surface density of the Cu⁺ species that produce these carbonyls.

This nanocube-based sample provides lower reaction rate than the other catalysts in the PROX reaction (Fig. 4a); this may be due to its lower surface area, although if compared with the intensity of the IR peak due Cu⁺-CO species (Fig. 4b) it questions previous interpretations about the direct relationship between the amount of these carbonyls and the catalytic activity. However, if reaction contact times are adjusted to give at the same temperature (130 °C and above) a similar overall CO conversion degree (90% and above), the product analysis shows that the nanocube-supported catalyst gives, for the same conversion level, clearly better selectivities (i.e. it oxidizes less H₂) than the other more active catalysts (Fig. 4). This evidences again that different chemical reactivity patterns are displayed when the type of crystal plane exposed at the surface by the ceria support is different. Efforts to characterize with AFM the CuO species dispersed on nanocube-shaped ceria, as well as DFT quantum modeling of the different situations, have been started to better understand the features of these catalysts.

References

[1] D. Gamarra *et al.*, J. Phys. Chem. C **111** (2007) 11026; and refs. therein

Figures

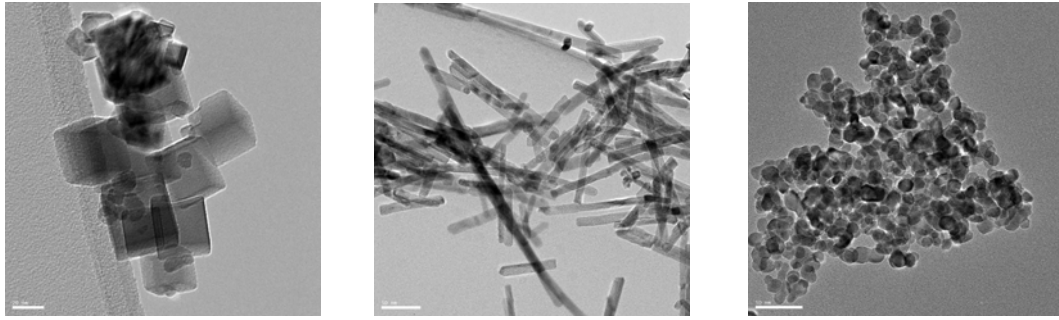


Fig. 1 TEM images of different CeO_2 preparations: nanocubes, nanorods and microspheres

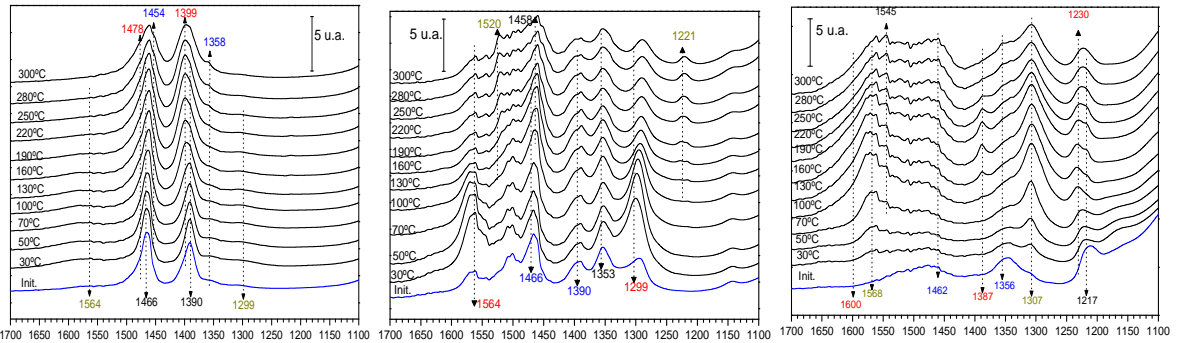


Fig. 2 IR spectra (carbonate range) of differently shaped CeO_2 particles under T -programmed $\text{CO} + \text{O}_2$ reaction

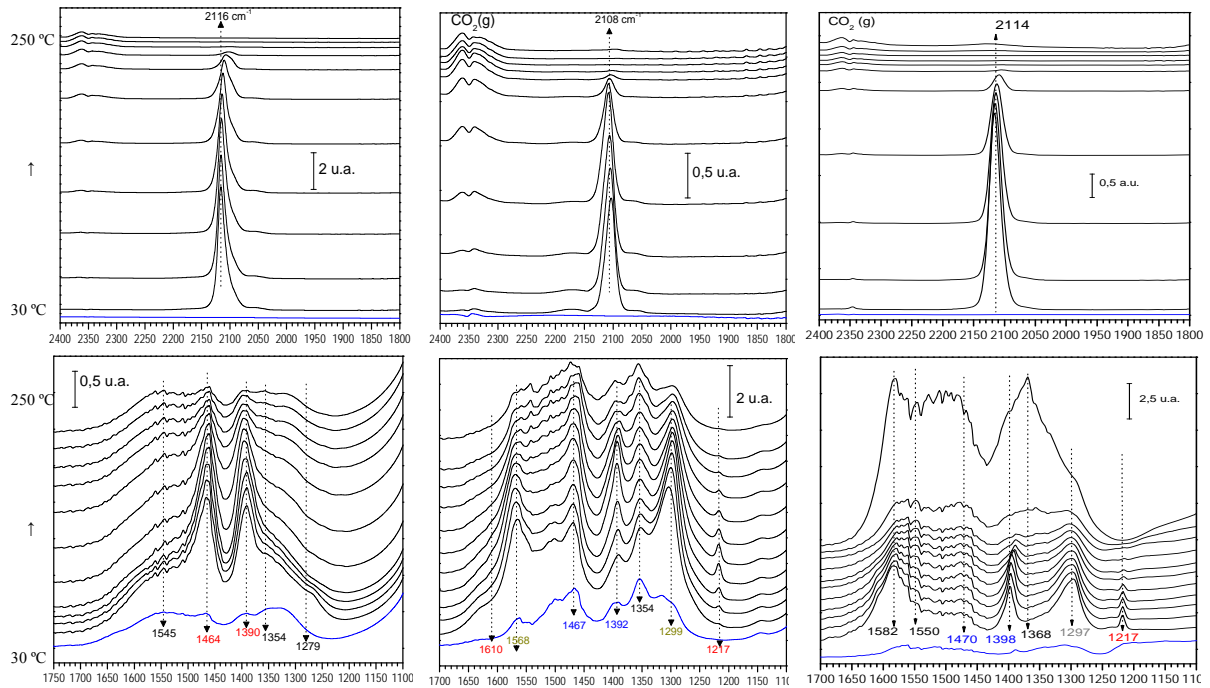


Fig. 3 IR spectra of different CuO/CeO_2 samples under the $\text{CO} + \text{O}_2 + \text{H}_2$ reaction at increasing temperatures

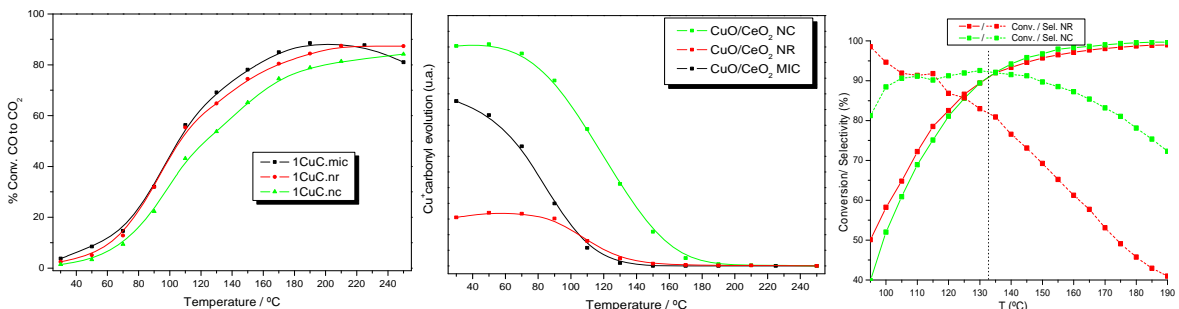


Fig. 4 Data obtained on different CuO/CeO_2 samples under $\text{CO} + \text{O}_2 + \text{H}_2$ reaction: evolution of a) products and b) Cu^+ -CO IR band; c) activity and selectivity of nanocube- and nanorod-based samples at tuned contact times