

Effect of Cu clustering on activity and selectivity of CuO_x/CeO₂ catalysts for preferential oxidation of CO in H₂ streams

J. C. Conesa, D. Gamarra, A. Martínez-Arias, G. Munuera[#], A.B. Hungria[@], M. Fernández-García, P.A. Midgley[@]

Inst. de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, Cantoblanco, 28049 Madrid, Spain

[#]Dep. de Química Inorgánica e Inst. de Ciencia de Materiales (Centro Mixto Universidad de Sevilla-CSIC), 41092 Sevilla (Spain)

@Dept. of Materials Science, University of Cambridge, Cambridge CB23QZ (UK)

jcconesa@icp.csic.es

Polymer membrane fuel cells (PEMFC) require that H₂ fed to them be free of CO. Since nowadays the processes generating H₂ (via fossil fuel or biomass reforming followed by water gas shift) leave in the gas some CO, the latter must be eliminated, this being normally done through preferential catalytic oxidation (PROX) with O₂ where the reaction must proceed with as low simultaneous H₂ consumption as possible. Among the catalysts used for this, those based on ceria-supported copper have the advantage of being active, selective and stable enough while avoiding the use of an expensive precious metal. The structure at the nano-scale that leads in these catalysts to optimum performances is still, however, a matter of debate. This issue is studied here by comparing different preparations and examining with nanostructure-sensitive probes the characteristics of the most interesting specimens.

Two series of catalysts have been prepared. One of them, labeled as Ce_{1-x}Cu_xO_{2-z} (x = 0.05, 0.1, 0.2), was made by alkaline coprecipitation from aqueous nitrate solutions within microemulsion droplets. The other, labeled yCuO/CeO₂ (y= 0.5, 1 and 5, y being the final weight % of Cu in the solid), was made by incipient wetness impregnation with copper nitrate aqueous solution on a pure ceria sample prepared by precipitation in microemulsion as said above. For all samples final calcination temperature (in air) was 773 K.

XRD data revealed formation of CuO_x phases separate from CeO₂ (which was always dominant, with crystallite sizes in the 6-8 nm range consistent with the TEM data and high surface areas found) only for sample 5CuO/CeO₂. Raman spectra showed that Ce_{1-x}Cu_xO_{2-z} samples, but not yCuO/CeO₂ samples, had incorporated Cu ions in the ceria lattice, consistent with microstrain data provided by XRD linewidths. However, Cu in the Ce_{1-x}Cu_xO_{2-z} samples was partially surface-segregated (consistent with a limited solubility of oxidized copper in ceria), as revealed by ion-sputtering results in XPS experiments. These (Fig. 1) showed distinct features for short sputtering times, which correspond to surface CuO_x domains with sizes around 3-4 nm (producing the shoulder at ca. 3 min. sputtering time) besides a thin layer of highly dispersed entities (clusters of ca. 0.6 nm size, responsible for the sharp decay at sputtering times < 0.5 min). The impregnated sample with 1% load, on the contrary, only showed the latter feature, implying that very high dispersion of Cu is achieved in this case.

These size effects are reflected in the peak energies found in the XPS spectra and in their evolution under chemical treatments; the corresponding XPS and Auger energies for copper are summarized in Fig. 2. The point corresponding to sample 1CuO/CeO₂, well down along the line with slope=3 characteristic of the Cu²⁺ state, indicates a small cluster size, which is kept during treatments of reduction (to Cu⁺) and reoxidation; sample 5CuO/CeO₂, appears closer to bulk Cu oxides, confirming the larger particle size involved. The data for samples Ce_{1-x}Cu_xO_{2-z} are consistent with a relatively large but intermediate particle size; the behavior reflects the mixed contribution of segregated small particles and ceria-dissolved species.

TEM images show clearly the sizes and shapes of the ceria nanoparticles, but cannot discern the Cu-rich particles due to the dominance of contrast by ceria. Space-resolved EDX data

(Fig. 3) allow to discern occasionally Cu-rich areas; for sample $Ce_{0.8}Cu_{0.2}O_{2-z}$, line profiles show that the surface segregated entities have in this sample sizes around the 2-3 nm range.

Data of catalytic activity and selectivity (Fig. 4) indicate that samples with higher Cu content, prepared by coprecipitation in microemulsion, have higher CO oxidation activity, but also catalyze more efficiently the undesired oxidation of H_2 . The best selectivity (lowest ratio of H_2 and CO oxidation) is found for sample $1CuO/CeO_2$, evidencing the importance of a strict control of the nuclearity of surface CuO_x clusters, with optimal sizes around 1 nm, to achieve the desired PROX selectivity.

Figures:

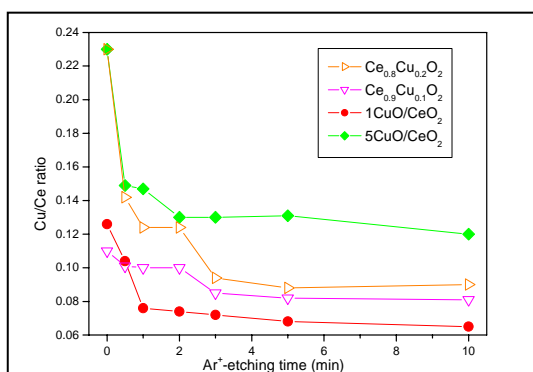


Fig. 1. Evolution of the XPS-detected Cu/Ce ratio as a function of the Ar^+ -sputtering time for the indicated samples.

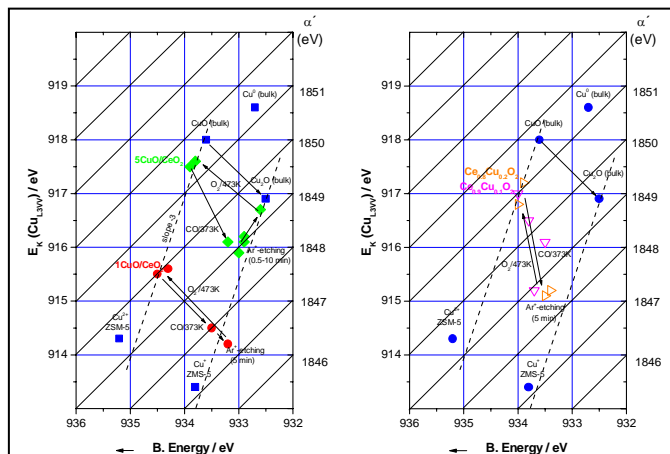


Fig. 2. Wagner diagrams showing the evolution of Cu (2p and AES) XP parameters during redox treatments performed over the indicated catalysts. Left: $yCuO/CeO_2$ catalysts. Right: $Ce_{1-x}Cu_xO_{2-z}$ catalysts.

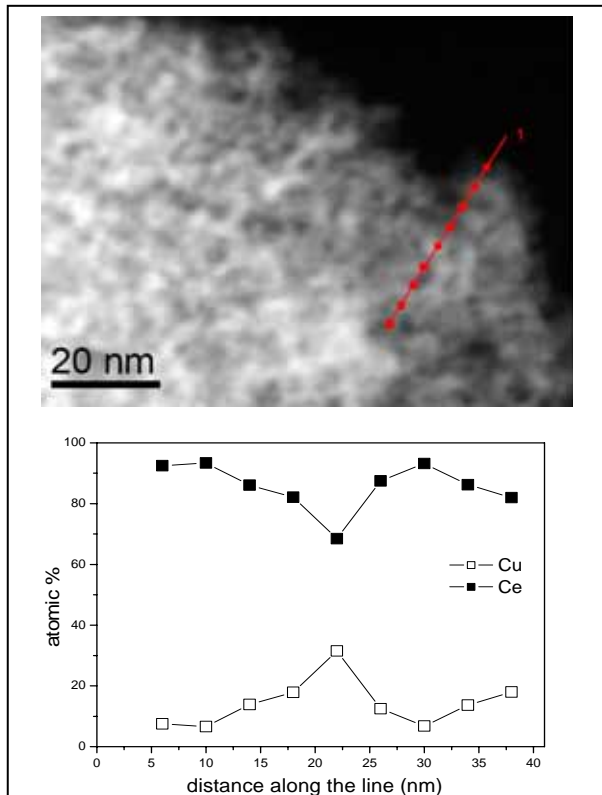


Fig. 3. Results of XEDS analysis in the points marked along the line depicted over the STEM HAADF image of $Ce_{0.8}Cu_{0.2}O_{2-z}$ displayed on top.

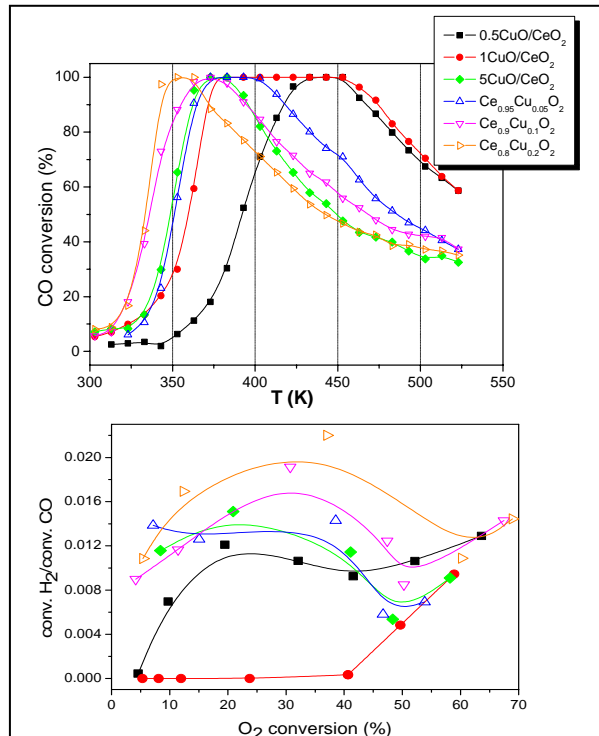


Fig. 4. Catalytic activity data obtained under 1 % CO, 1.25 % O_2 and 50 % H_2 (Ar balance) for the indicated catalysts. Top: CO conversion vs. temperature. Bottom: Ratio between H_2 and CO conversions vs. O_2 conversion.