DFT MODELING OF CuO CATALYST NANOPARTICLES

José C. Conesa
Instituto de Catálisis y Petroleoquímica, CSIC
Marie Curie 2, Cantoblanco, 28049 Madrid, Spain
jcconesa@icp.csic.es

Copper oxide is an active component of different catalysts, especially of those promoting reactions of CO at mild temperatures. In particular, cerium dioxide-supported copper oxide facilitates the preferential oxidation of CO (PROX reaction) by O_2 at T<375 K in presence of a large excess of H_2, a process of large industrial interest as it is needed to purify from CO the H_2 gas used by polymer membrane fuel cells. Although this type of catalyst has been subjected to many studies using different techniques, the structure and characteristics of the CuO_x active phase are not known in detail. Within a study trying to correlate catalytic activity with the size and shape of the constituent nanoparticles, previous work from our laboratory using HR-TEM, XPS, ESR, IR and XANES [1] has indicated that the catalytically relevant species exists, at least in the initial catalyst state, as small ill-crystallized or amorphous CuO nanoparticles dispersed on the CeO_2 surface, that become partially reduced during the reaction. A DFT-based modeling of such dispersed nano-entities is undertaken here.

The theoretical approach uses DFT at the GGA level (PBE functional) supplemented with an on-site Coulomb interaction (Hubbard term U) to correct for the known inadequacy of standard DFT when describing partially filled d or f shells of transition or lanthanide elements. Effective U_{eff}=U-J terms are used, with values equal to 4.5 and 7 eV for Ce and Cu respectively. The plane wave code VASP, with PAW potentials to describe the core region, was used; the calculations used high plane wave cutoff values (400 eV) and gamma point-centred Monkhorst-Plank samplings of the reciprocal space dense enough to ensure convergence to within <3% of the energy differences of interest.

First the structure and energetics of standalone CuO and its surfaces were modelled. CuO has a centred monoclinic lattice, with four formula units per unit cell; the latter is derived from a fcc packing of Cu atoms in which 50% of the tetrahedral interstices are filled with O atoms ordered in a specific way, so that distorted tetrahedral and near-square planar coordinations result for O and Cu atoms respectively. An antiferromagnetic ordering of the spins at the copper ions (that have a $3d^9$ configuration) occurs at low temperature ($T_c \approx 220$ K), with up and down spins forming alternating double layers parallel to the (1 0 -1) planes so that a superstructure magnetic cell with double volume appears [2]. This structure, that cannot be reproduced using standard DFT theory but does appear if self-interaction or Hubbard corrections are used, was obtained also here. To model its surfaces periodic slab models were constructed from the magnetic cell, with symmetric slabs of 9-10 Å thickness parallel to all non-equivalent low index Miller planes of the crystallographic unit cell. Some of the surfaces ((1 0 1), (1 0 -1), (0 1 1), (1 1 1) and (1 1 -1)) are non polar and have all surface atoms 3-fold coordinated; surface (0 1 0) is nonpolar but contains 2-fold coordinated atoms, and the others ((1 0 0), (1 0 0) and (1 1 0)) besides having 2-coordinated atoms are polar and can become stable only upon reconstruction (with elimination of 50% of the atoms in the outer plane).

After relaxation of the atomic positions, the surface energy of each surface was obtained. The values lie in the range 0.74-1.7 J/m^2, increasing in the order (1 1 1)<(1 1 -1)≈(0 1 1)<(1 0 -1) ≈(1 1 0)<(1 0 1)<(0 1 0)<(1 0 1). With these energies the nanocrystallite equilibrium shape at low temperature predicted by a Wulff construction is as given in Fig. 1. However, shapes of very varied types (plates, rods, spindles, spheres, etc) have been found experimentally, as they are affected by the temperature and molecular environment present during crystal growth.

The energy necessary to create an anion vacancy at the surface (a basic elementary step in most redox reactions catalyzed by CuO) was then evaluated for all the lowest energy surfaces, and found to be relatively similar (between 2.0 eV for (1 1 0) and 2.7 eV for (1 1 1)), the values being lower than for a bulk vacancy (ca. 3.0 eV). Thus one finds energies similar to or lower than those necessary to form vacancies on the most stable ceria surface [3]. Formation of the vacancy leads to the formation of Cu^+ ions (in some cases with partial delocalization of the added electron over nearby cations) that appear located at sites neighbour to the vacancy.

The situation of a CuO nanoparticle on a CeO_2 surface was modeled also with a periodic slab model (Fig. 2), containing a slab of the CeO_2 fluorite structure in (1 1 1) orientation (that provides the most stable surface), with 20 Ce atoms per unit cell, and a rod of CuO in contact with the slab, with 12 Cu atoms per unit cell and having its structure and faces oriented so that there is a good epitaxy (achieved through a (1 0 1) face) with the underlying CeO_2 and low energy CuO surfaces (in particular, (2 1 0) and its symmetry equivalent (-2 1 0)) are exposed. This allows to keep minimal the distortions of the Cu-O distances. Then the formation of vacancies in the surface of this composite material was modeled, testing for them all relevant nonequivalent oxygen positions.

It was found here that the lowest energy for vacancy formation corresponded to sites in the middle of the exposed (2 1 0) surface of CuO, where this energy was somewhat lower than for the same surface in pure CuO; again, reduced Cu ions appeared in the neighbourhood. It was followed in energy by sites of the CuO rod at the borderline with the CeO_2 surface; here either two Cu^+ ions or one Cu^+ and one Ce^{3+} appeared, depending on the exact location at the bordeline. Forming the vacancy at the bare CeO_2 surface, which led to the generation of two Ce^{3+} ions at nearest-neighbour positions as shown previously [3], was the least favourable option. These energy differences are ascribed to the higher strength of the Ce-O bond compared to the Cu-O bonds, due to the higher cationic charge of the Ce ions. The need to have in real catalysts very small CuO entities over the ceria surface, in order to maximize the ratio between borderline sites and bare CuO surface sites, is thus explained. Studies to model the adsorption of O_2 and CO on the partially reduced catalyst surface have been undertaken.

References:

[1] D. Gamarra *et al*., J. Phys. Chem. C **111** (2007) 11026.
[2] B. X. Yang *et al.*, Phys. Rev. B **38** (1988) 174.
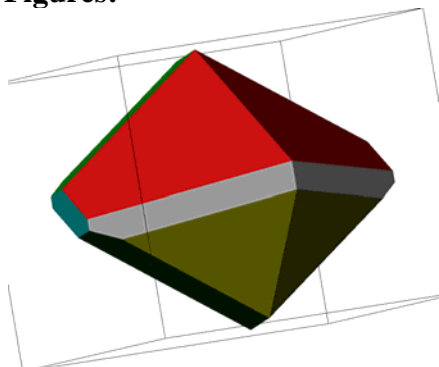[3] J. C. Conesa, Catalysis Today, accepted (doi:10.1016/j.cattod.2008.11.005)

Figures:

Fig. 1- CuO particle shape according to a Wulff construction based on the surface energies computed for the different faces.
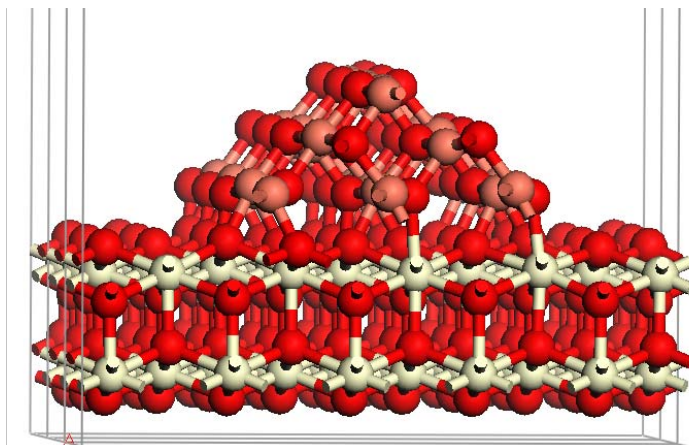

Fig. 2-Periodic model of the CuO/CeO_2 catalyst used in the calculations. Red: O; white: Ce; pink-beige: Cu.