Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The adsorption of Cu on the CeO_2(110) surface

Arunabhiram Chutia,*[1,2] Emma K. Gibson,[1,2] Matthew R. Farrow,[2] Peter P. Wells,[1,3,4] David O. Scanlon,[2,4] Nikos Dimitratos,[5] David J. Willock,[5] C. Richard A. Catlow*[1,2,5]

[1]*UK Catalysis Hub, RCaH, Rutherford Appleton Laboratory, Didcot, OX11 0FA, UK.*
[2]*UCL Chemistry, Gordon Street, London, WC1H 0AJ, UK.*
[3]*School of Chemistry, University of Southampton, Southampton, 50718J, UK.*
[4]*Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK.*
[5]*Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK.*

Email: a.chutia@ucl.ac.uk, c.r.a.catlow@ucl.ac.uk

To construct models of CeO_2 with Cu(II) incorporated, we substitute a Ce atom with a Cu^{2+} ion either on the surface using the CeO_2(110) slab representation or in the bulk material and create an oxygen vacancy for charge compensation. We refer to the Cu^{2+} ions replacing surface and bulk ceria as Cu_{srf} and Cu_{blk} respectively. On visualizing the calculated spin density of these systems we see that it is highly localized around the Cu centres and nearby O-atoms in both bulk and surface substitution positions, (Figure S1). The shape of this spin density indicates that there is bonding between Cu d and O p-orbitals.

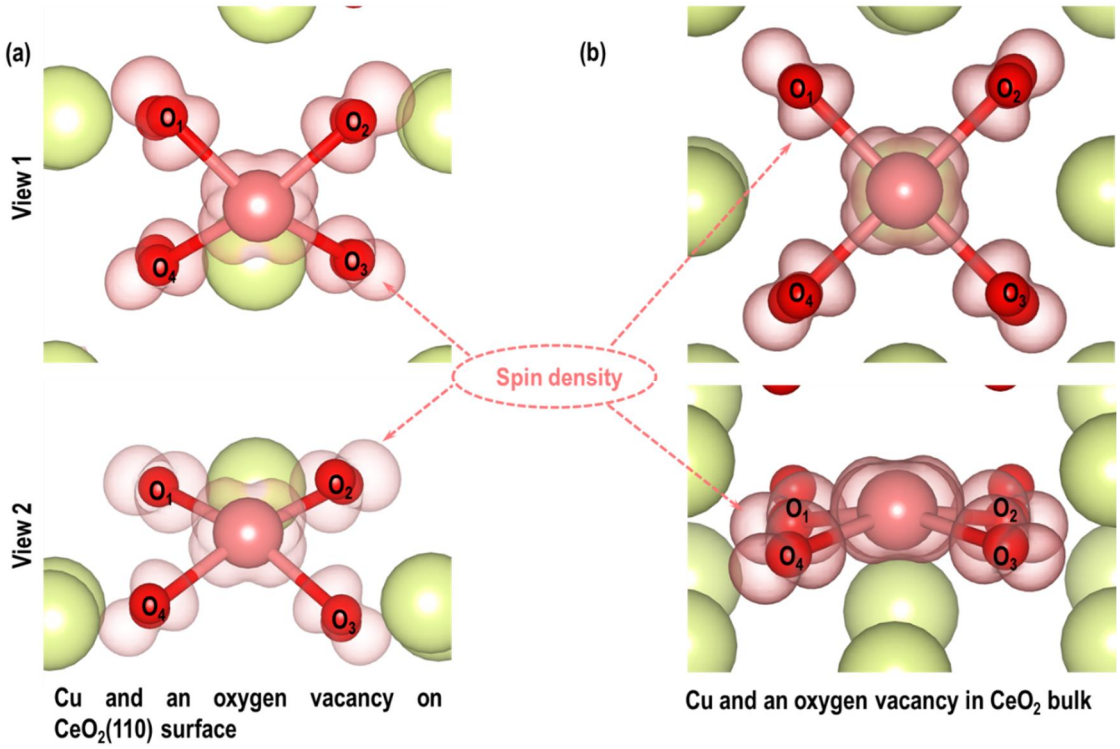

Figure S1. Spin-density localised around Cu–O moiety (a) on the surface of CeO_2(110). The $O_{n(=1-4)}$ represents the O-atoms in close proximity of Cu-atoms. (b) Spin-density localised around Cu–O moiety in the bulk of CeO_2.