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CO_2 Conversion to Methanol on Cu(I) Oxide Nanolayers and Clusters: Electronic Structure Insight into the Reaction Mechanism

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Computational Details

Periodic calculations:

The periodic calculations of crystalline solid Cu_2O and Cu_2O nanolayers were performed with the HSE06 density functional. The unit cell volume was allowed to change, while the cell shape was kept fixed. Diffuse exponents were excluded in the basis sets for solid state calculations, as suggested in ref.1; thus a modified version of the 6-311G(d) basis was used, where exponents smaller than 0.12 were replaced to reach smooth representation.

Hybrid density functionals, which include Hartree-Fock exchange, were used in our study. The choice of a density functional is not straightforward. The GGA (Generalized Gradient Approximation) functionals severely underestimate the Cu_2O band gap of 2.17 eV, yielding much lower values, 0.5-0.7 eV, see ref.2,3, while range-separated hybrid density functional calculations are in far better agreement with experiment, at reduced computational cost, compared to B3LYP.

The shorter bond lengths obtained in our study are due to the cell volume relaxation applied to the thin layer, while previous studies with plane-wave basis set rely on the cell volume optimized for the bulk crystalline solid and use a vacuum layer to divide the surface from bulk. [3-5]

Cluster models

The B3LYP and HSE06 density functionals were used in cluster calculations. The 6-311G(d) basis set which consists of the Wachters-Hay all electron basis set for the first transition row, using the scaling factors of Raghavachari and Trucks was applied for copper atoms, [6] and the 6-31G(d,p) basis set was applied for oxygen, carbon and hydrogen atoms. We have tested the performance of the two different density functionals on Cu_2O clusters, for which electron photodetachment energies were determined. Adding diffusion functions proved essential for studying anionic species and for accurate calculations of adiabatic electron affinities. HSE06 and B3LYP results are in very good agreement, with Cu-O bond lengths of 1.770-1.771 Å; the HSE predicted Cu-Cu internuclear distances are slightly shorter than the B3LYP calculated ones, 2.615 Å for the neutral Cu_2O and 2.511 Å for its monoanion vs 2.692 Å for Cu_2O and 2.589 Å for its monoanion according to B3LYP. The Cu-Cu internuclear distance is shortened by nearly the same value according to either B3LYP or HSE; the Cu-O bonds are lengthened in the monoanion, reaching 1.817 Å according to B3LYP and 1.898 Å according to HSE. Both functionals predict correctly the adiabatic electron affinity: 1.22 eV according to B3LYP and 1.12 eV according to HSE, vs 1.10 eV from experiment. [7]

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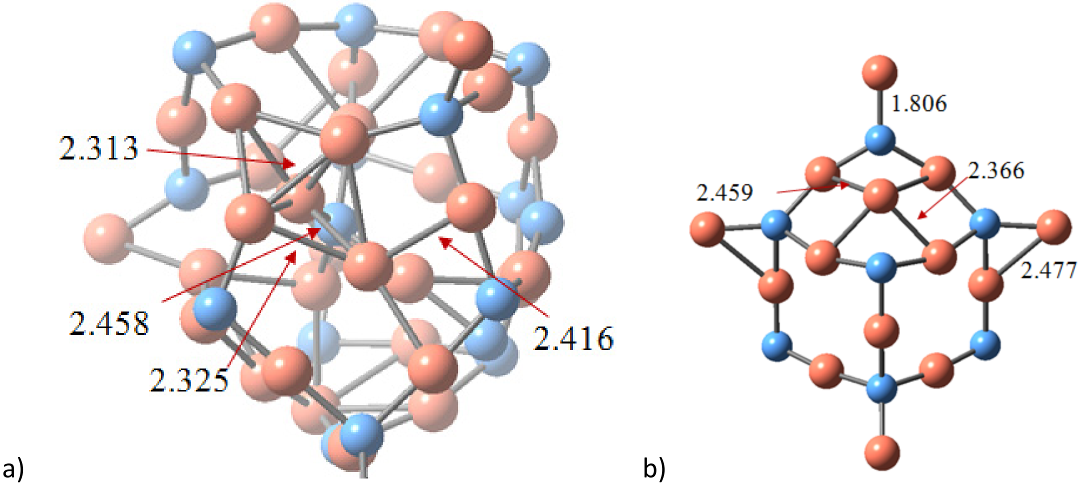

Figure 2S. The nanoclusters a)$Cu_{32}O_{16}$ and b) $Cu_{14}O_7$ with Cu-Cu internuclear distances denoted.

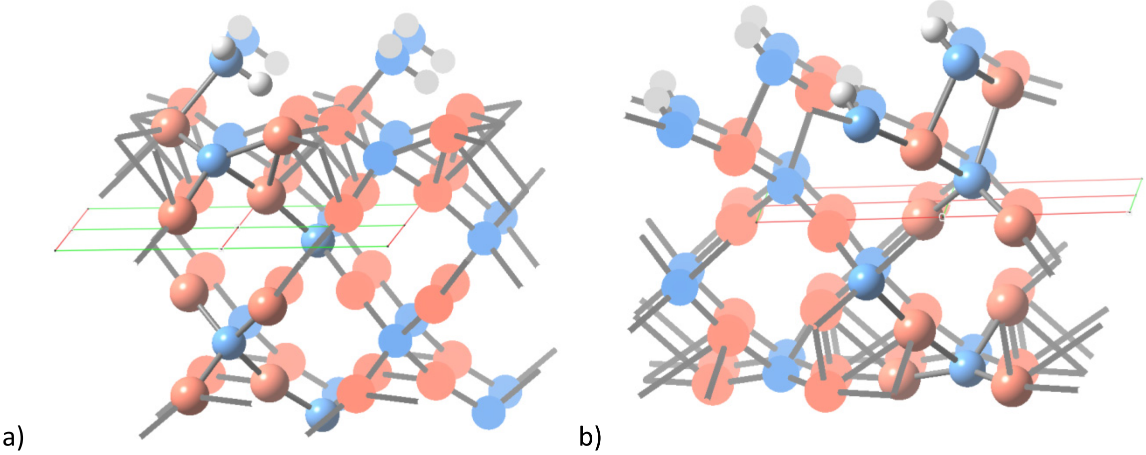

Figure 3S. Water adsorption at Cu_2O nanolayer: a) molecular adsorption on the Cu_2O (001) copper-terminated surface; b) dissociation on the Cu_2O (001) oxygen-terminated surface with bridging hydroxyl groups formed, –Cu(OH)Cu–.

Table 4S. Reaction Activation Barriers (E_a), Binding Energies (BE) and IR frequencies ν of Reaction Intermediates (in bold) for the Elementary Steps of CO_2 Hydrogenation Using Water as a Source of Hydrogen, Calculated by B3LYP on a $Cu_{14}O_7$ cluster.

Reaction	BE, kJ mol^{-1}	E_a, kJ mol^{-1}	ν, cm^{-1}
$CO_2 + O^{\bullet\bullet}_{surf} \Rightarrow CO_3^{\bullet\bullet}{}_{surf}$	123		1887 1260 815 776
$CO_2 + Cu_2^{\bullet\bullet}{}_{surf} + O^{\bullet\bullet}_{surf} \Rightarrow \mathbf{CO_2}^{\delta-}{}_{surf} + Cu_2O^{\delta+}$	240		1552 1198 925 759
$CO_2 + H^{\bullet} \Rightarrow {}^{\bullet}CO(OH)$	395	13.8	3625 3024 1624 1302 1167 1104 1051
${}^{\bullet}CO(OH) + H^{\bullet} \Rightarrow HCO(OH)_{surf}$	152	121	3703 2767 1688 1453 1350 1209 1122
$HCO(OH)_{ads.} + H^{\bullet} \Rightarrow \mathbf{H_2CO}_{surf} + OH^{\bullet}_{surf}$ via $H_2C(OH)_2{}^{\bullet}$ as TS	85	27.3	3096 2985 2284 1613 1537 1415 1334 1272 1206 1123 1080 792
$H_2CO_{ads.} + H^{\bullet} \Rightarrow H_3CO^{\bullet}_{surf}$	211	61	3054 2929 1986 1517 1350 1283 1252 1198 1081 737 706
$H_3CO^{\bullet} + H^{\bullet} \Rightarrow H_3C(OH)_{surf}$	127	24	3062, 2868, 2818, 2254, 1750 1571 1478 1445 1244 1177 1136 916