

Supplementary Information

Effect of Alumina Hydroxylation on Glycerol Hydrogenolysis to 1,2-propanediol over
 $\text{Cu}/\text{Al}_2\text{O}_3$: Combined Experiment and DFT Investigation

Pussana Hirunsit*, Chuleeporn Luadthong, Kajornsak Faungnawakij

National Nanotechnology Center (NANOTEC), National Science and Technology
Development Agency (NSTDA), 111 Thailand Science Park, Thanon Phahonyothin, Tambon
Khlong Nueng, Amphoe Khlong Luang, Pathum Thani, Thailand.

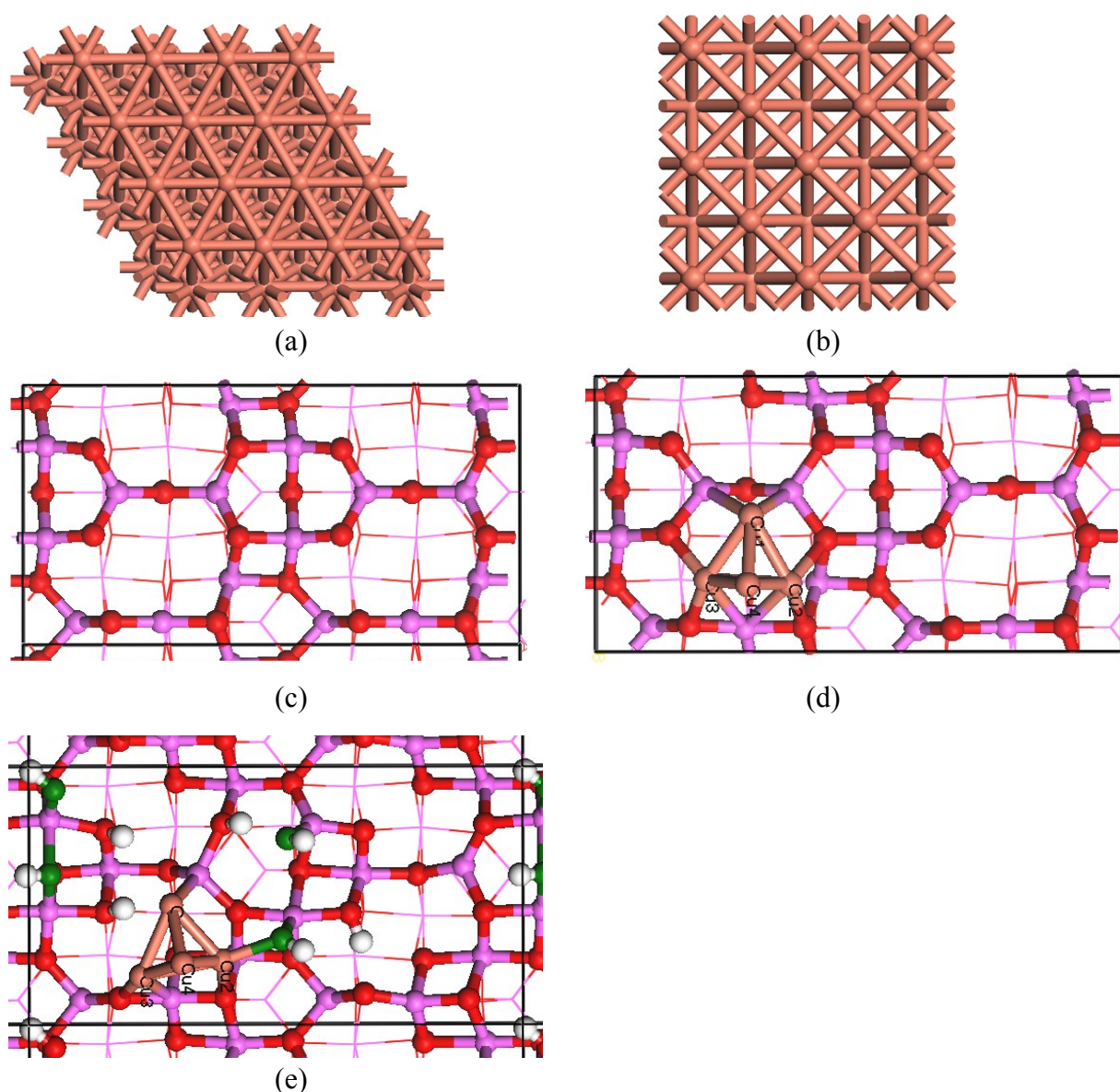


Fig. S1. The structures of (a) Cu(111), (b) Cu(100), (c) $\gamma\text{-Al}_2\text{O}_3(110)$, (d) Cu_4 /non-hydroxylated $\gamma\text{-Al}_2\text{O}_3(110)$, and (e) Cu_4 /hydroxylated $\gamma\text{-Al}_2\text{O}_3(110)$. Green atoms are O from hydroxylation.

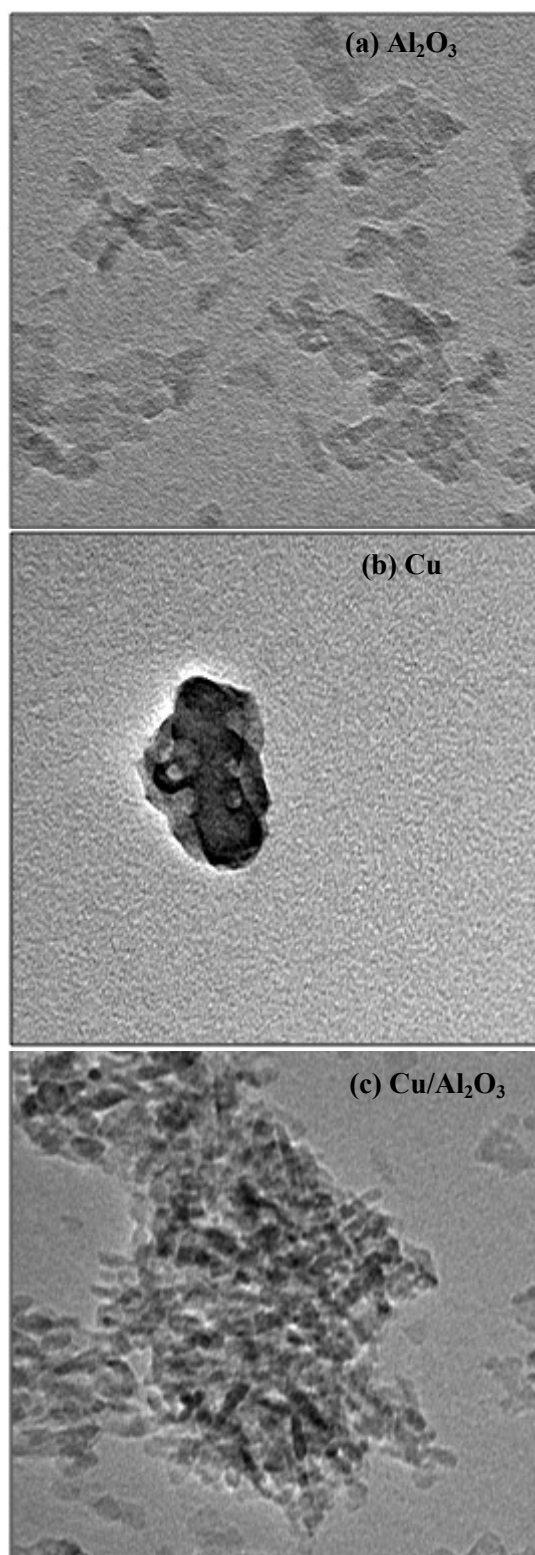


Fig. S2. Typical TEM images of (a) Al_2O_3 , (b) Cu, and (c) Cu/ Al_2O_3 samples. Alumina is in the form of thin sheet and less crystallinity with particle size range of 10 to 30 nm. Bare Cu is a dense particle with sphere-like shape, and its size is in the range of 20-40 nm. The fringe in the inset confirmed the crystal structure of metallic copper. For Cu/ Al_2O_3 , the particle of copper is in the range of 2-10 nm which is smaller than that found in the unsupported one. The images were obtained by a transmission electron microscopy (TEM; JEM-2100 JEOL, Japan) with an accelerating voltage of 200 kV.

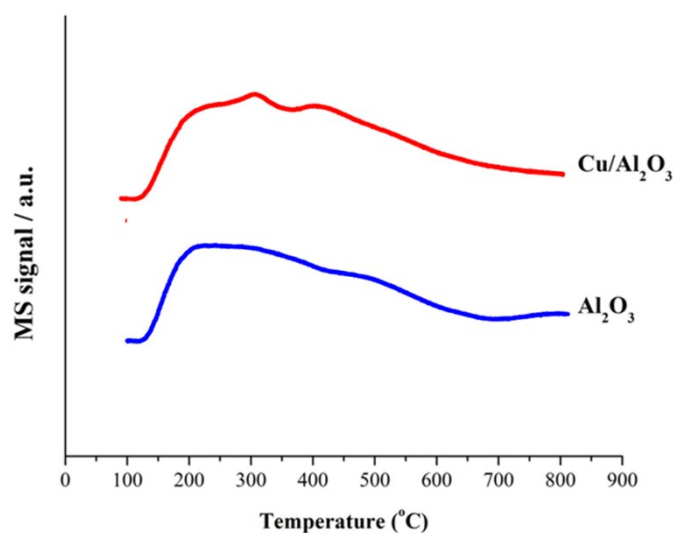
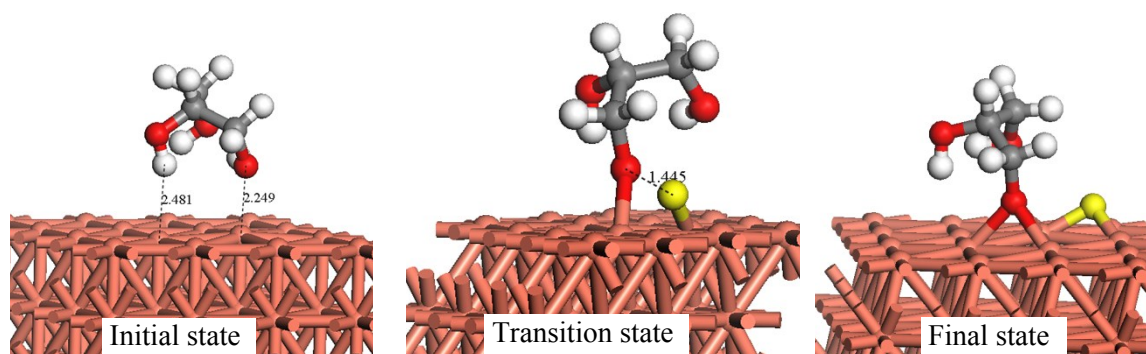
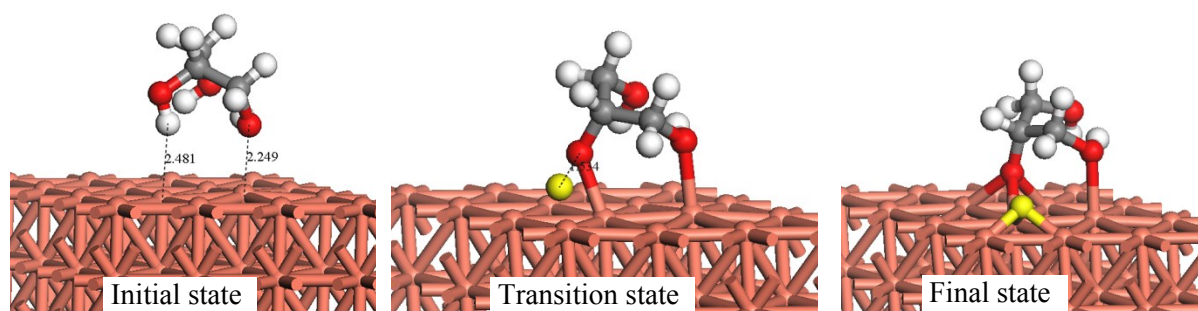


Fig. S3. Ammonia temperature-programmed desorption (NH₃-TPD) profiles of Al₂O₃ and Cu/Al₂O₃. NH₃-TPD was carried on a Multitrack TPD equipment (BELCAT B, Japan). Before the measurement, the samples were treated in a He flow at 350 °C for 2 h, and then in a H₂ flow at 300 °C for 3 h. NH₃ was adsorbed at 80 °C till saturation and then the sample was purged with a He flow at 100 °C for 2 h. NH₃-desorption profiles were recorded in the range of 100-800 °C at a rate of 10 °C/min.

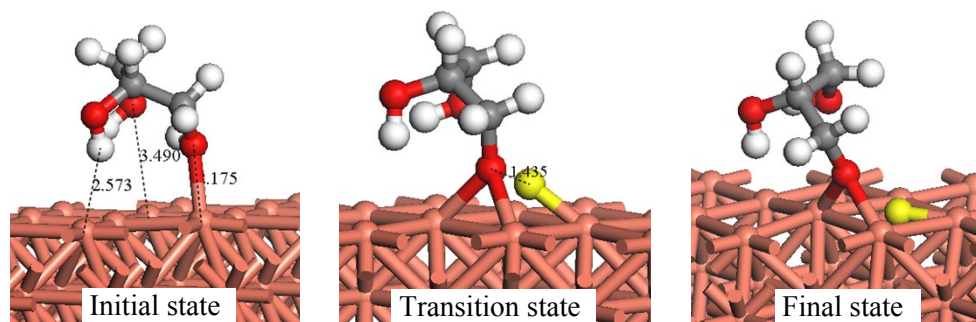
(a) terminated O-H cleavage on Cu(111)



(b) central O-H cleavage on Cu(111)



(c) terminated O-H cleavage on Cu(100)



(d) central O-H cleavage on Cu(100)

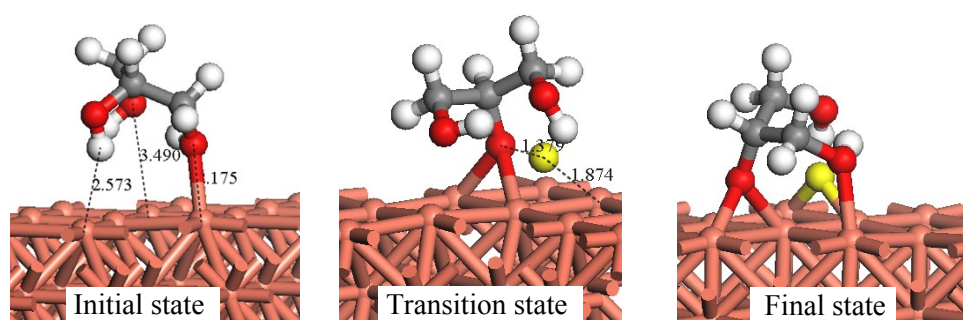
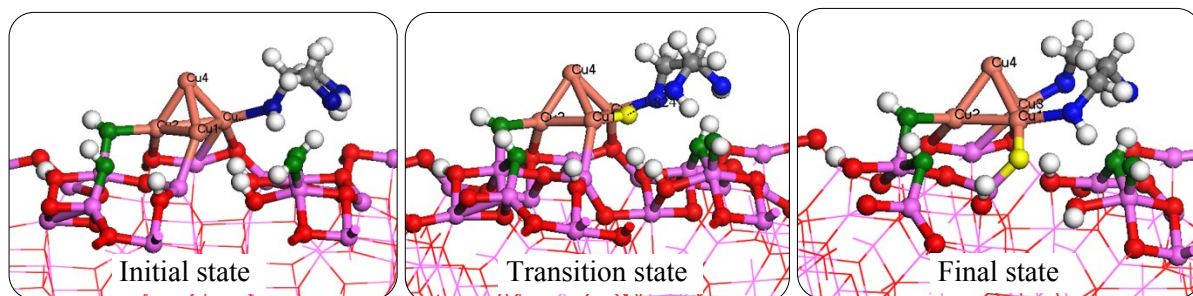


Fig. S4. Initial, transition and final structures of glycerol (a) terminated O-H cleavage on Cu(111) (barrier energy = 1.29 eV), (b) central O-H cleavage on Cu(111) (barrier energy = 1.01 eV), (c) terminated O-H cleavage on Cu(100) (barrier energy = 0.84 eV), (b) central O-H cleavage on Cu(100) (barrier energy = 0.87 eV).

(a) terminated O-H cleavage at Cu site



(b) terminated O-H cleavage at Al site

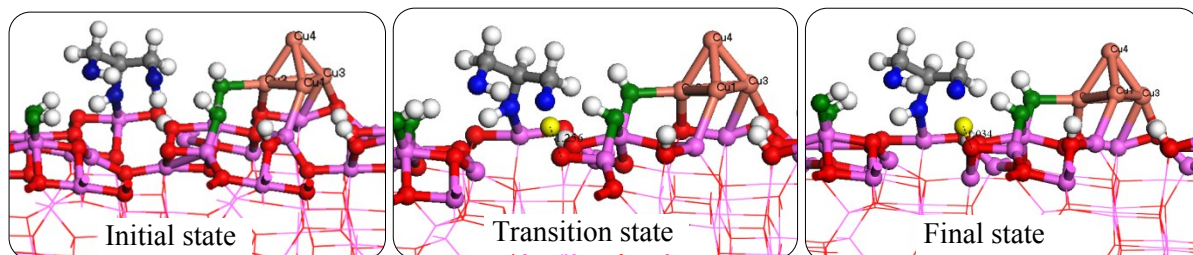


Fig. S5. Initial, transition and final structures of glycerol terminated O-H cleavage at (a) Cu site (barrier energy = 1.47 eV) and (b) Al site (barrier energy = 0.65 eV) on Cu₄/hydroxylated γ-Al₂O₃(110).