Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

CO_2 Activation on Cu-based Zr-Decorated Nanoparticles

Natalie Austin, Jingyun Ye and Giannis Mpourmpakis*

Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States

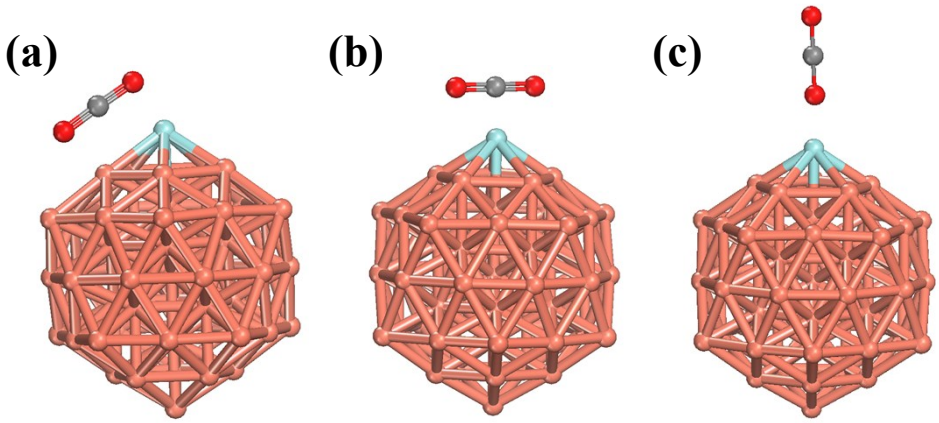

Figure S1. Three initial adsorption configurations of CO_2 on the $Cu_{54}Zr$ NP were considered: (a) CO_2 molecule parallel to the Cu-Zr bond, (b) CO_2 adsorption to the NP with C of CO_2 interacting with Zr on the NP, and (c) perpendicular CO_2 adsorption with the O atom pointing to Zr.

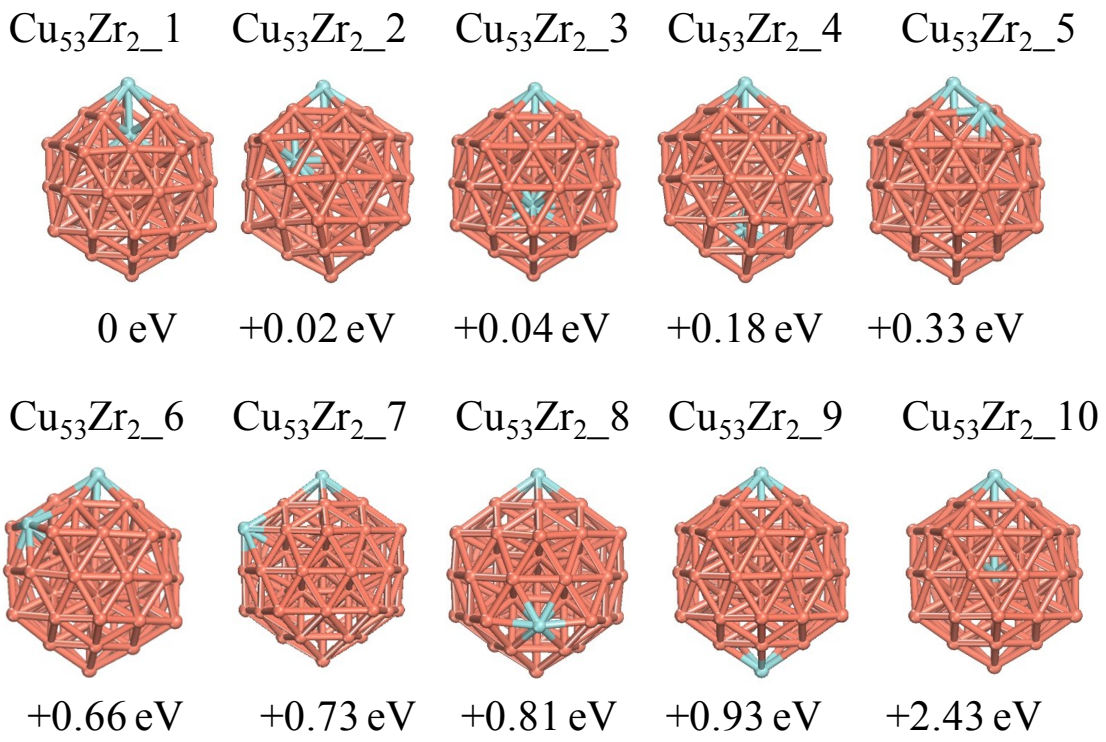

Figure S2a. Different dopant sites of two Zr atoms in the 55-atom $Cu_{53}Zr_2$ NP. The value below each NP is the stability of the NPs relative to the most stable structure found ($Cu_{53}Zr_2$_1).

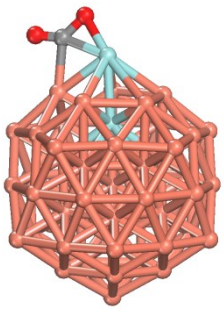

Figure S2b. Chemisorbed CO_2 on $Cu_{53}Zr_2$_1 (most stable $Cu_{53}Zr_2$ nanoparticle). The binding energy of CO_2 has been calculated to be -1.18 eV, which is strong and comparable to the segregated case of Zr.

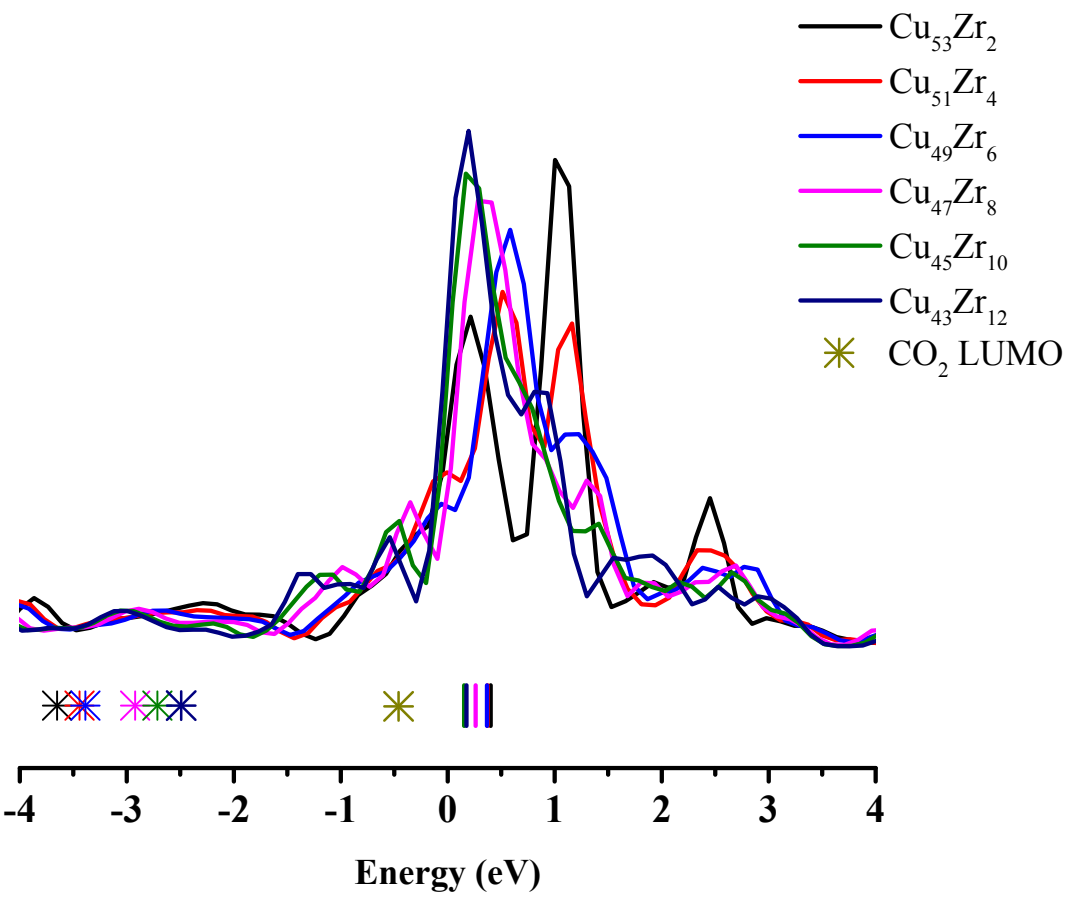

Figure S3. Local partial density of states (PDOS) of the d electrons for the $Cu_{55-x}Zr_x$ NPs. The asterisks and the solid lines below the PDOS represent the HOMO orbital energies and d_C of the $Cu_{55-x}Zr_x$ NPs. (x = 2 -12), respectively. The green asterisk corresponds to the LUMO orbital of the CO_2 molecule. It should be noticed that the increasing Zr content brings the NP HOMO orbitals closer to the CO_2 LUMO, resulting to stronger CO_2 adsorption. The IP correlations presented in Figure 5(b) of the manuscript are relevant to the energy of the HOMO orbitals (HOMO energy can approximate the IP).