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

First-principles study of the atomic layer deposition of ZnO on carboxyl functionalized carbon nanotubes (CNTs): the role of water molecules

(Supplementary section)

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Hydrogen saturation in carbon dangling bonds

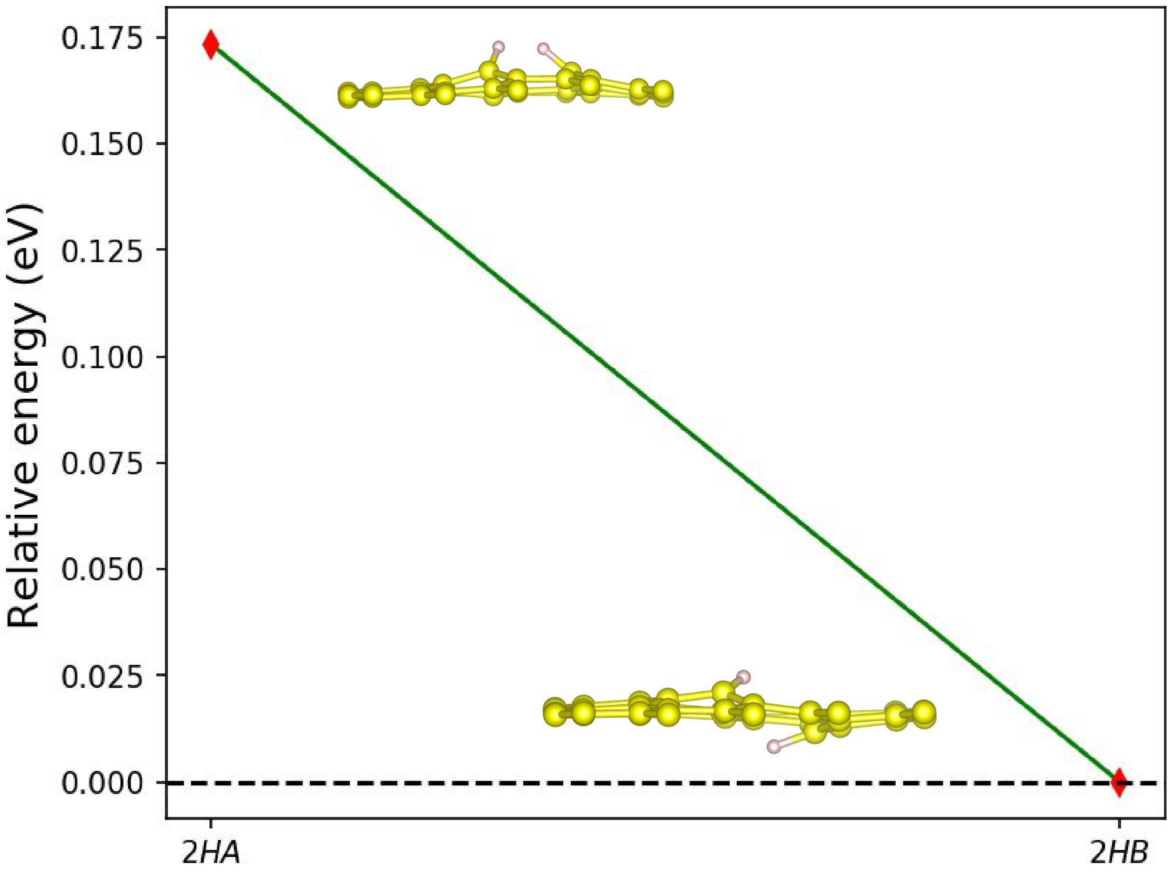

Figure S1. Comparison between hydrogen adsorption on the same side of the surface in configuration A **(2HA)**, and adsorption of each H atom on each side in configuration B **(2HB)**.

To saturate two of the three-carbon dangling bonds the adsorption of hydrogen adatoms has been tested. The minimum energy configuration corresponds to (2HB) where each hydrogen atom is located at each side of the surface. This configuration is 0.17 eV more favorable than (2HA).

The first partial reaction for DEZ with COOH considering two final states (FS1) and (FS2).

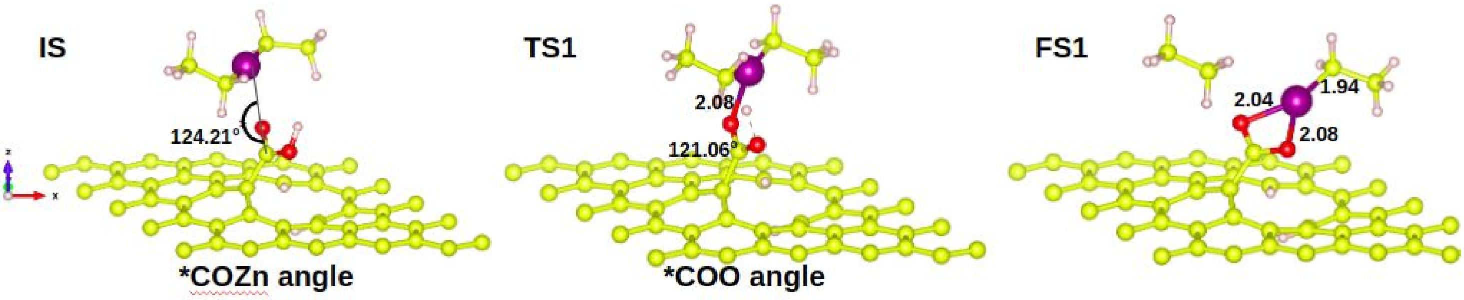

Figure S2a. Ligand exchange mechanism taking into account the contribution of CO and HO group from carboxyl. In the initial state **(IS)**, DEZ adsorbs on top of the CO group and reach a transition state **(TS1)** to perform an exchange ligand mechanism with the H proton, where Zn is captivated by from the O acceptor at 2.08 Å. In the final state **(FS1)** Zn is three-fold coordinated with two oxygens at 2.04 and 2.08 Å, and the remaining ethyl group at 1.94 Å.

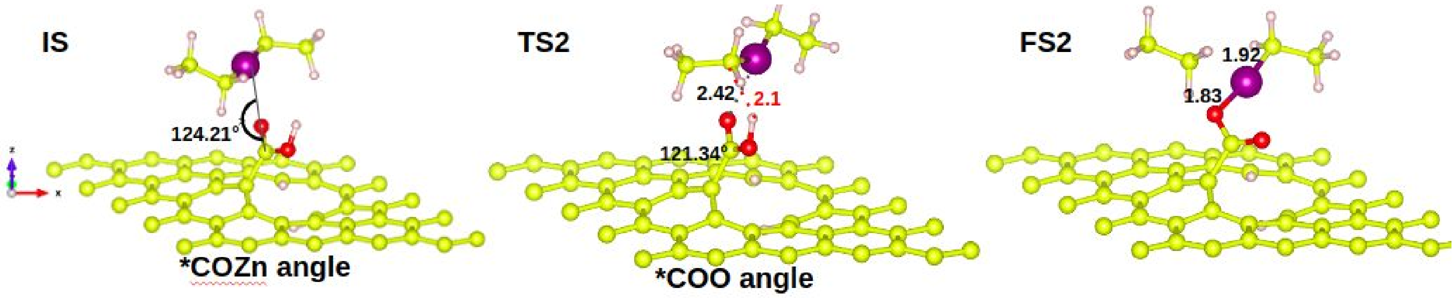

Figure S2b. Ligand exchange mechanism isolating the contribution of the CO group from carboxyl. In the initial state **(IS)**, DEZ adsorbs on top of the CO group at 2.47 Å. In the transition state **(TS2)** the distance has been shortened to 2.42 Å, and the H proton is directly above the carbon acceptor at 2.1 Å. In this final state **(FS2),** Zn is two-fold coordinated with the oxygen from the CO group at 1.83 Å, and the ethyl group at 1.92 Å.

Three-fold coordination for MEZ on COOH

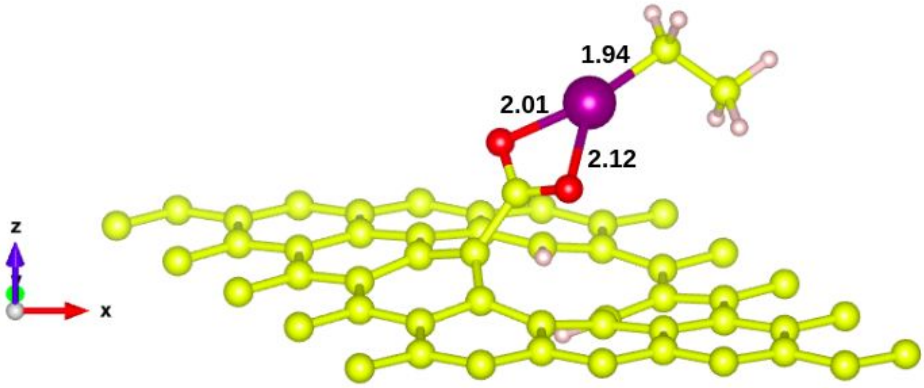

Figure S3. Once ethane has been purged from the system, the atomic configuration tends to adopt three-fold coordination as a consequence of the loss of the interaction between ethane and Zn bound to the remaining ethyl.

The initial state for the adsorption of one water molecule on MEZ to form a three-fold coordinate system.

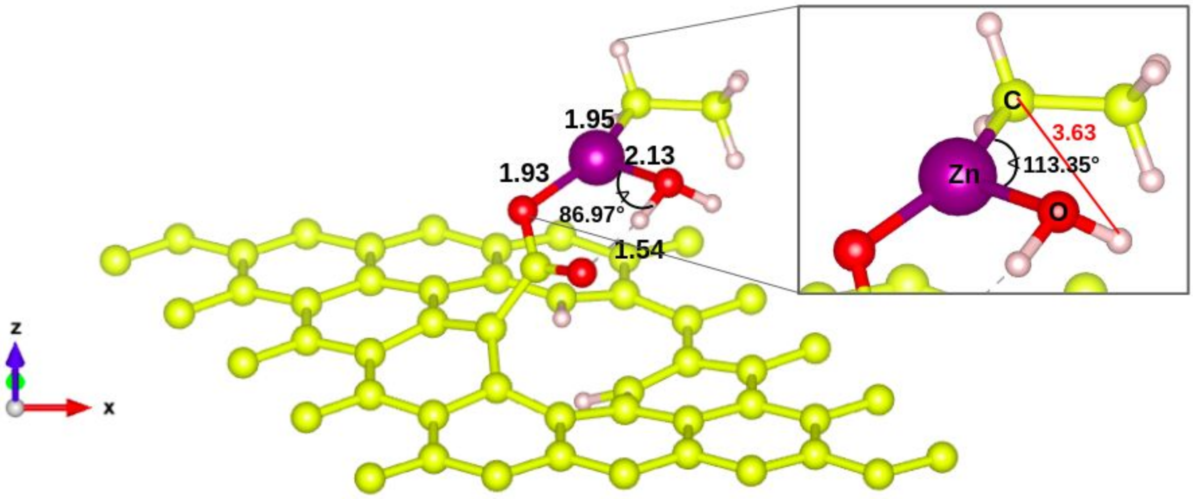

Figure S4. The adsorption of the first water molecule stabilizes the system by forming a hydrogen bridge with the remaining O atom. In this configuration, the distance between the H proton and the carbon acceptor is 3.63 Å. The angle C-Zn-O depicted by a continuous black line is 113.35°.

Initial, transition, and final states for the removal of the second ligand of MEZ with one water molecule.

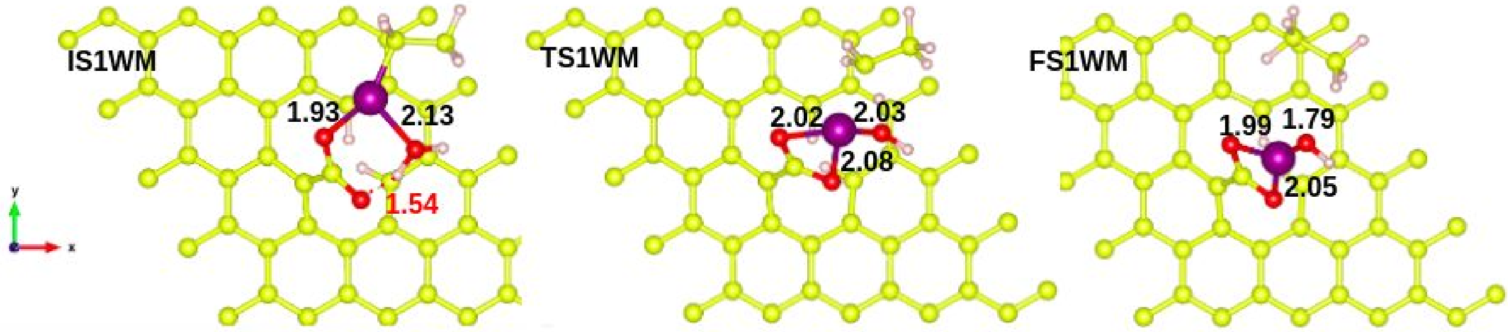

Figure S5. Initial state **(IS1WM)** with Zn three-fold coordinated, transition state **(TS1WM)** where the hydrogen bond has disappeared to translate the water molecule, and finally in the final state **(FS1WM)** ethyl has been saturated to form ethane.

Initial, transition, and final states for the removal of the second ligand of MEZ with two water molecules.

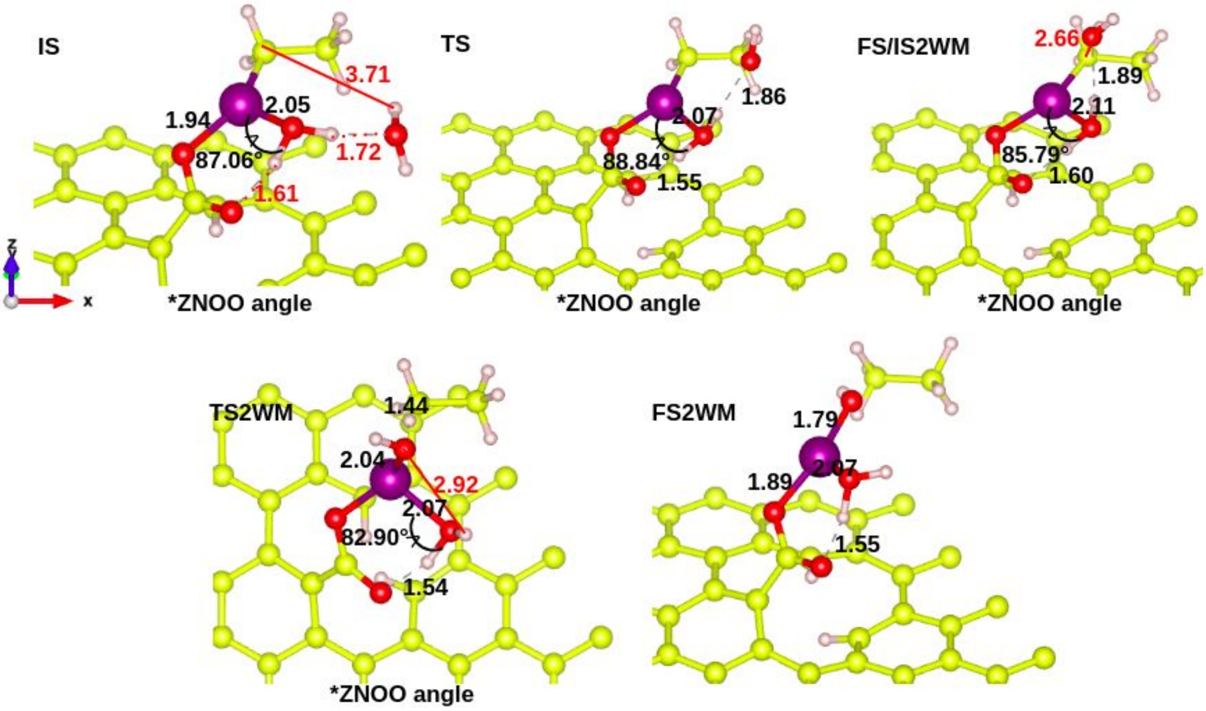

Figure S6. Initial state (IS), Transition state (TS) and Final state(FS/IS2WM) involve the translation of the first water molecule, once fixed, the H proton transfer is achieved in (TS2WM) and ethane is formed in the final state (FS2WM).