

Supporting Information

Revealing the nature of the active site on the carbon catalyst for the C–H bond activation

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Computational Setup

The calculations reported here are performed by using periodic, spin-polarized DFT as implemented in Vienna *ab initio* program package (VASP).^{1,2} The electron-ion interactions are described by the projector augmented wave (PAW) method proposed by Blöchl³ and implemented by Kresse.⁴ PBE functional⁵ is used as exchange-correlation functional approximation and a plane wave basis set with an energy cutoff of 400 eV is used. The (5,5) and (8,0) single-walled carbon nanotube (SWCNT) are used to model the armchair and zigzag terminated edges respectively. The (5, 5) SWCNT is in a $16.78 \times 16.78 \times 23.07$ Å cubic cell and the (8, 0) SWCNT is in a $16.26 \times 16.26 \times 24.36$ Å cubic cell for x, y, z dimension respectively. The space between neighboring image is 10 Å which is enough to exclude the interactions between images. The total number of carbon atoms in the cell is 100 and 96 for (5, 5) and (8, 0) SWCNT respectively and the edges are saturated by the hydrogen atoms. Only gamma point is used in the calculations for SWCNT. During structure optimization all atoms in the unit cells are allowed to relax and no symmetry is imposed. The optimization is stopped when the maximum force on the atoms is smaller than 0.02 eV/Å. The barrier of the propane dissociation is estimated by using the climbing image nudged elastic band (CI-NEB) method.⁶

The E_{ro} is defined as the following,

$$E_{\text{ro}} = E_{\text{SWCNT}} + 1/2 E_{\text{O}_2} - E_{\text{O-SWCNT}}$$

where E_{SWCNT} is the total energy of SWCNT without the oxygen functional group, E_{O_2} is the total energy of the oxygen molecule in gas phase, and $E_{\text{O-SWCNT}}$ is the total energy of SWCNT with the oxygen functional group respectively.

References

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- (3) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.

- (4) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.
- (5) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (6) Henkelman, G.; Uberuaga, B. P.; Jonsson, H. *J. Chem. Phys.* **2000**, *113*, 9901–9904.

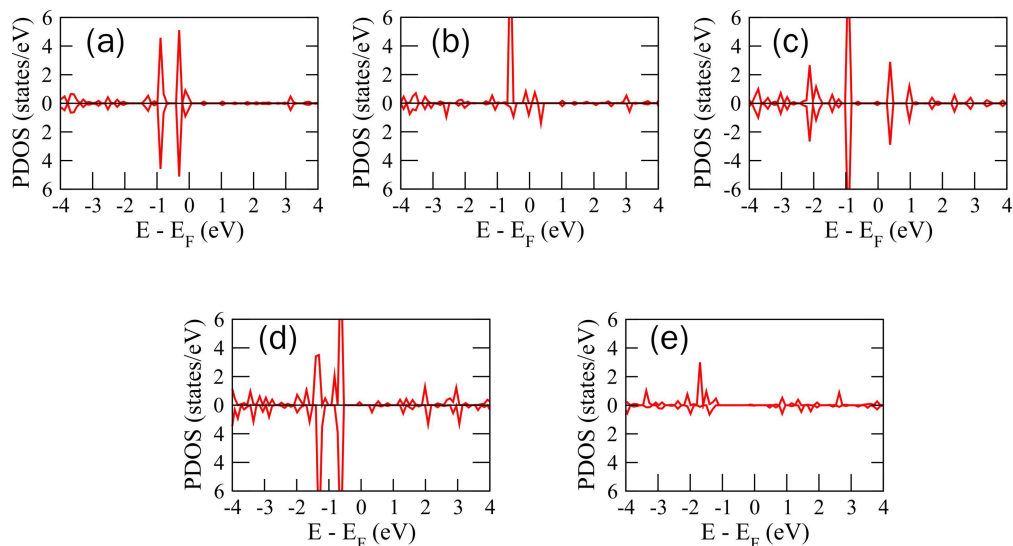


Figure S1: The partial density of states (PDOS) of the oxygen in the various functional groups. (a) diketone (A) (b) ketone (A) (c) quinone (A) (d) diketone (Z) (e) ketone (Z).

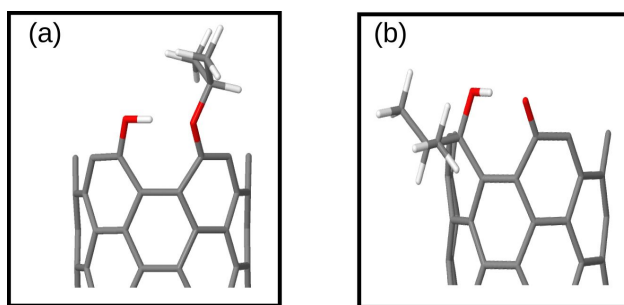


Figure S2: The optimized structures of the dissociated adsorbed propane on (5,5) SWCNT at (a) O-O site (b) O-C site. The color code is same with the Figure 1.

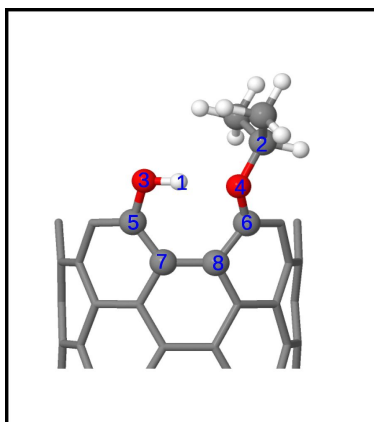


Figure S3: The structure of the dissociated propane via the primary C–H breaking at the diketone on (5,5)SWCNT. Color code: carbon is gray, oxygen is red, hydrogen is white.

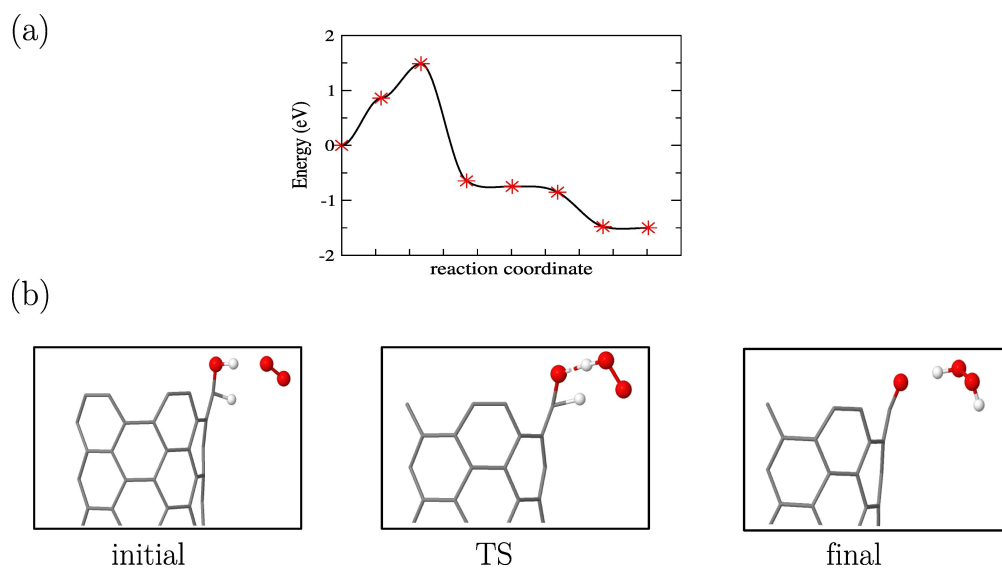


Figure S4: The reoxidation of the catalysts by the oxygen molecule takes place at the ketone-A group. (a) The reaction path. (b) The important structures on the reaction path: the initial structure (initial), the transition state (TS), and the final state (final) Color code: carbon is gray, oxygen is red, hydrogen is white.

Table S1: The charges for the various oxygen functional groups shown in Figure 1. The atoms of O, C1-3 are indicated in Figure 1. The charges of C1 and C3 in quinone group are transferred to O_a and O_b respectively.

groups	O	C1	C2	C3
ketone (A)	-1.09	0.88	-0.01	-0.03
diketone (A)	-1.06	0.94	-0.07	-0.02
quinone(A)	-1.04	0.92	0.08	0.92
ketone (Z)	-1.07	0.96	-0.04	-0.04
diketone (Z)	-1.07	0.95	-0.08	0.04