

(Supporting Information)

Modeling C–H Bond Activation and Oxidations of Alkanes over Cu-MOR Using First-Principles Methods

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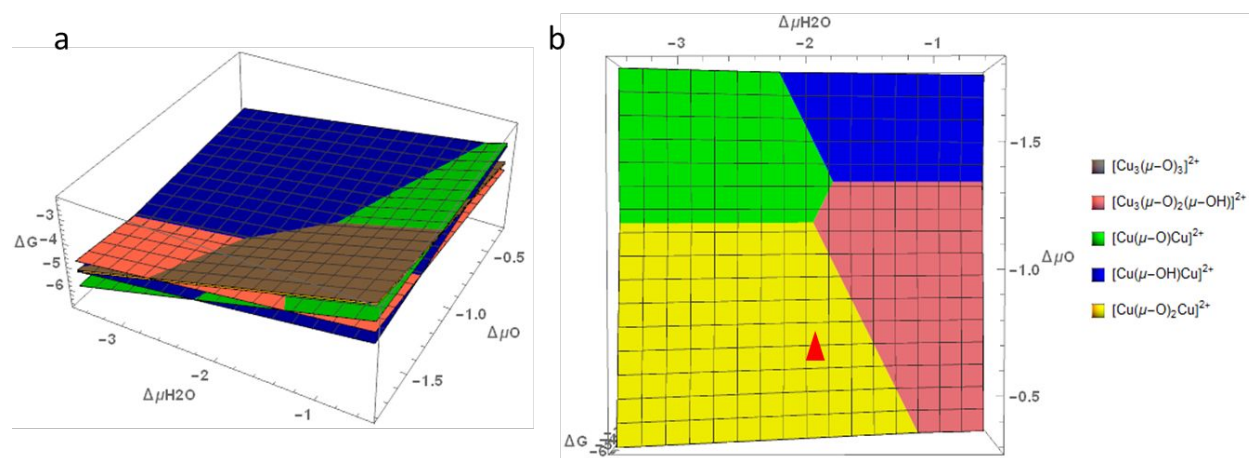
**Figure S1.** Phase diagram (a) of Cu-oxo active centers as a function of  $\mu_{H_2O}$  and  $\mu_O$ , and (b) the most stable active center configuration (indicated by the red triangle) from the bottom view.

**Figure S2.** Energetics of methane partial oxidation over (a) Cu-trioxo, (b) mono ( $\mu$ -oxo) dicopper, and (c) bis ( $\mu$ -oxo) dicopper with different spin multiplicities. Computational errors are based on the Bayesian error estimation.

**Figure S3.** Potential energy surfaces of respective ethane and propane conversions into ethanol (a), 1-propanol (b), and isopropanol (c) over site II of Cu-trioxo active site at doublet (yellow), quartet (blue), and sextet (red) spin multiplicities. Computational errors are based on the Bayesian error estimation.

**Figure S4.** Potential energy surfaces of respective ethane and propane conversions into ethanol (a), 1-propanol (b), and isopropanol (c) over site I of Cu-trioxo active site at doublet (yellow), quartet (blue), and sextet (red) spin multiplicities. Computational errors are based on the Bayesian error estimation.

**Figure S5.** Methane C-H bond activation considering doublet (yellow), quartet (blue), and sextet (red) spin multiplicities. The energy barriers (in eV) are also labeled numerically.



**Figure S1**

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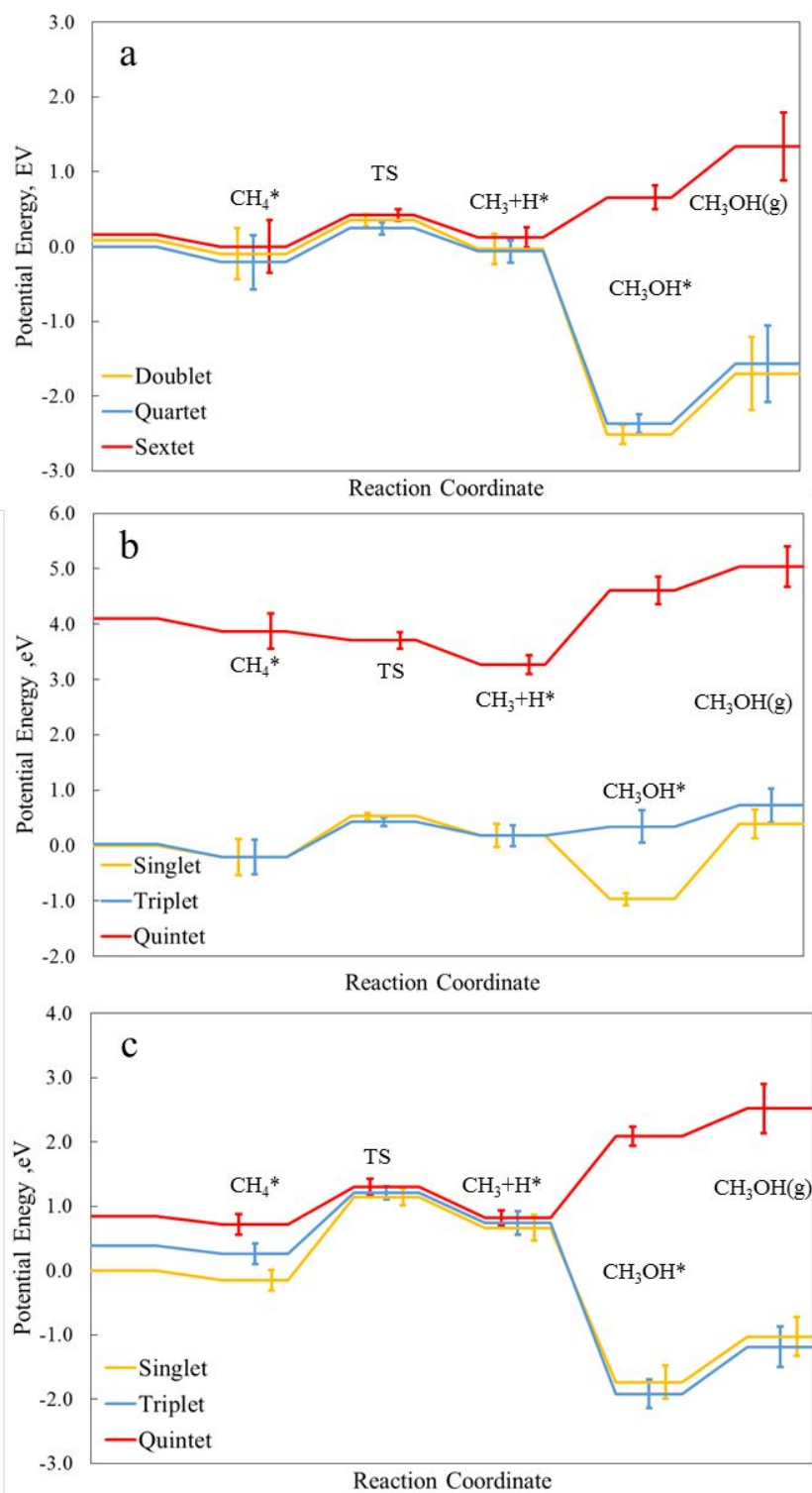


Figure S2.

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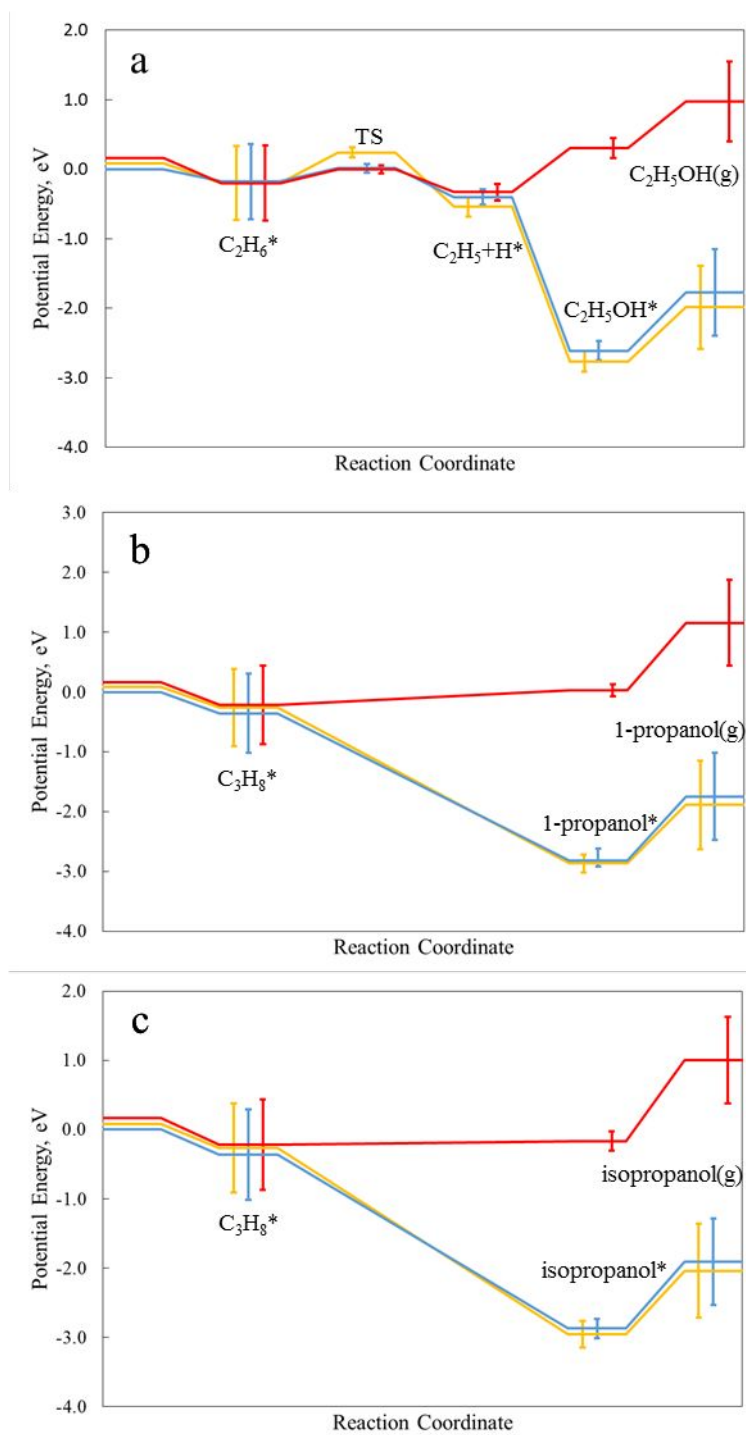


Figure S3.

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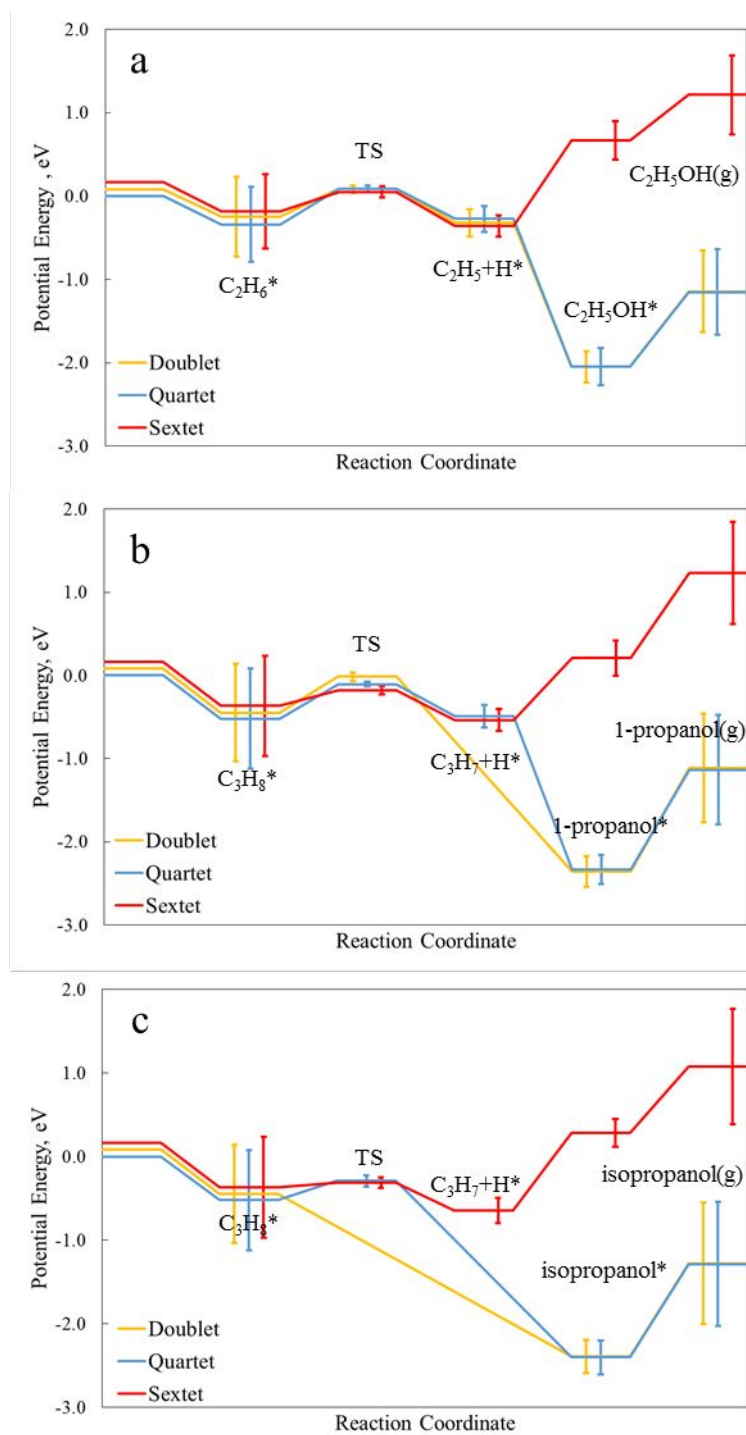


Figure S4.

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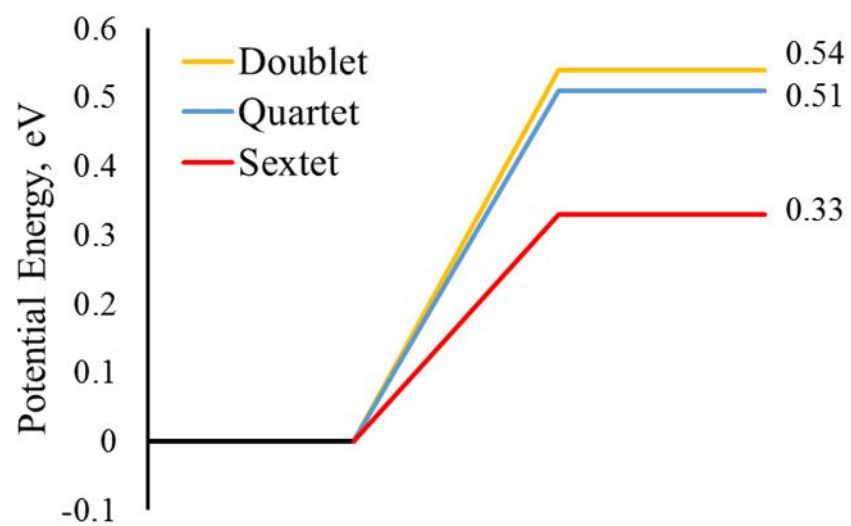


Figure S5.

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**Table S1.** Lattice parameters and magnetic moments of bulk CuO.

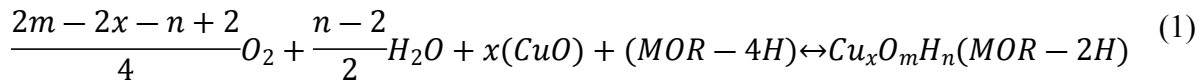
Method	a	b	c	$\gamma$	Magnetic moment
PBE	4.60	3.60	5.12	99.25	0.00
LDA+U	4.60	3.45	5.09	99.51	0.67
LDA+U <sup>a</sup>	4.59	3.35	5.04	99.39	0.66
BEEF-vdW+U	4.66	3.44	5.12	100.1	0.67
Expt. values <sup>a</sup>	4.68	3.42	5.13	99.54	0.68

<sup>a</sup>Reference <sup>2</sup>



## Computational methods for thermodynamic properties

The thermodynamic stability of different active sites was evaluated according to reaction (1), in which the bulk copper oxide (CuO), O<sub>2</sub>, H<sub>2</sub>O, and , protonated MOR framework were chosen to be the reference state as reported in Ref <sup>1</sup>. Cu<sub>x</sub>O<sub>m</sub>H<sub>n</sub>(MOR-2H) represents the active site in MOR with two protons.



Hence, the reaction Gibbs free energies,  $\Delta G$ , for reaction (1) is calculated using eqn (2):

$$\Delta G(T,P) = G_{Cu_xO_mH_n(MOR-2H)} - G_{(MOR-4H)} - xG_{CuO} - \frac{2m - 2x - n + 2}{2}\mu_O - \frac{n - 2}{2}\mu_{H_2O} \quad (2)$$

where  $G_{Cu_xO_mH_n(MOR-2H)}$ ,  $G_{(MOR-4H)}$ ,  $G_{CuO}$ ,  $\mu_O$ , and  $\mu_{H_2O}$  are free energies of Cu-oxo active center located in MOR, the protonated MOR framework, bulk copper oxide, the chemical potential of O, and the chemical potential of H<sub>2</sub>O.

The entropies, mainly due to lattice vibrations, for solid-state CuO, MOR-4H, and Cu<sub>x</sub>O<sub>m</sub>H<sub>n</sub>(MOR-2H), have been neglected.<sup>1</sup> Hence, the Gibbs free energies for these three terms in eqn. (2) approximately equals to the total energies estimated by performing BEEF-vdW calculations.

The calculations of the Gibbs free energy of CuO can be sensitive to the initial guess of its magnetic moment. LDA+U was also considered for the bulk calculation. In this study, the U-J =7 eV was adopted for CuO.<sup>2,3</sup> The lattice parameters and magnetic moments of optimized CuO

are shown in Table S1. The lattice parameters and magnetic moments were in good agreements with the literature.

The chemical potentials of gas phase O and H<sub>2</sub>O at specific  $T$ , and  $P$  were calculated from eqns. (3) and (4) as

$$\mu_{gas}(T,P) = E_{gas} + \Delta\mu_{gas}(T,P) \quad (3)$$

$$\Delta\mu_{gas}(T,P) = H(T, P^0) - H(0K, P^0) - T(S(T, P^0) - S(0K, P^0)) + \frac{1}{2}RT \ln\left(\frac{P_{partial}}{P_{total}}\right) \quad (4)$$

where the total energies of gas phase species were obtained again using the BEEF-vdW functional. The molecules were placed in a box with dimensions of  $20 \times 20 \times 25$  Å. A  $\Gamma$ -k-point was employed. All the gas phase calculations were spin polarized.  $\Delta\mu_{gas}(T,P)$  was calculated from Eqn. (4), where  $H(T, P^0) - H(0K, P^0)$  represents the enthalpy change from reference state (0 K) to any temperature, which are estimated from eqns. (5) and (6).

$$\Delta H = \int_0^T C_p dT, \quad (5)$$

$$C_p = a + bT + cT^2 + dT^3, \quad (6)$$

where  $C_p$  was evaluated from eqn. (6).

Parameters  $a$ ,  $b$ ,  $c$ , and  $d$  in eqn. (6) were obtained from the NIST website.<sup>4</sup> The entropy change from the reference state (0 K) at specified temperature ( $T$ ) was calculated based on standard statistical mechanics treatment.<sup>5</sup> Hence, eqn. (2) becomes

$$\Delta G(T,P) = E_{Cu_xO_mH_n(MOR-2H)} - E_{(MOR-4H)} - xE_{CuO} - \frac{2m-2x-n+2}{2}E_O - \frac{n-2}{2}E_{H_2O} - \frac{2m-2x-n+2}{2}\Delta\mu_O - \frac{n-2}{2}\Delta\mu_{H_2O}. \quad (7)$$

With  $\Delta\mu_{H_2O}$  and,  $\Delta\mu_O$ , the equilibrium phase diagram for Cu-oxo clusters (Figure 2) at the 8MR of MOR can be generated, as shown in Figure S1.

## References

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