Supporting Information

For

A comparative DFT study of HCHO decomposition on different terminations of the Co$_3$O$_4$ (110) surface

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Surface phase diagram calculation method

The surface energy is calculated by:

$$E_{surf} = \frac{1}{2A}\left(E^{slab} - N_O\mu_0 - N_H\mu_H - N_{Co}\mu_{Co}\right) \quad \text{(S1)}$$

where E^{slab} is the total energy of the slab model, N_i and μ_i (i=O, H, Co) are the number and chemical potential of the constituent i, respectively. In Eqn. (S1), the chemical potential of μ_O, μ_H and μ_{Co} have the following relationships:

$$\mu_O = \frac{1}{2}\mu_{O_2}(g) \quad \text{(S2)}$$

$$\mu_H = \frac{1}{2}\mu_{H_2}(g) = \frac{1}{2}\left[\mu_{H_2O}(g) - \mu_O\right] = \frac{1}{2}\mu_{H_2}(g) - \frac{1}{4}\mu_{O_2}(g) \quad \text{(S3)}$$

$$4\mu_O + 3\mu_{Co} = E^{bulk} \quad \text{(S4)}$$

where $\mu_i(g)$ (i=O$_2$, H$_2$, H$_2$O) is the chemical potential of corresponding gas, and E^{bulk} is the total energy of the bulk Co$_3$O$_4$. Then based on the above Eqn. (S2-S4), the Eqn. (S2) can be re-written as:

$$E_{surf} = \frac{1}{2A}\left[E^{slab} - \frac{1}{2}N_H\mu_{H_2O(g)} + \frac{1}{2}\left(\frac{1}{2}N_H + \frac{4}{3}N_{Co} - N_O\right)\mu_{O_2(g)} - \frac{1}{3}N_{Co}E^{bulk}\right] \quad \text{(S5)}$$

It is seen that, in the Eqn. (S5), the surface energy is only dependent on the $\mu_{H_2O(g)}$ and $\mu_{O_2(g)}$, which can be calculated by:

$$\mu_{H_2O(g)} = E^{DFT}_{H_2O(g)} + E^{ZPE}_{H_2O(g)} + \Delta G^0_{H_2O(g)}(T) + k_BT\ln\left(\frac{p_{H_2O}}{p^0}\right) \quad \text{(S6)}$$

$$\mu_{O_2(g)} = E^{DFT}_{O_2(g)} + E^{ZPE}_{O_2(g)} + \Delta G^0_{O_2(g)}(T) + k_BT\ln\left(\frac{p_{O_2}}{p^0}\right) \quad \text{(S7)}$$

Where $E^{DFT}_{H_2O(g)}$ and $E^{DFT}_{O_2(g)}$ are DFT calculated electronic energies of the H$_2$O and O$_2$ gases, respectively, and $E^{ZPE}_{H_2O(g)}$ and $E^{ZPE}_{O_2(g)}$ are the corresponding zero-point energy corrections. The four terms represent the Gibbs free energies at 0K. The $\Delta G^0_{H_2O(g)}(T)$

and $\Delta G_{O_2(g)}^0(T)$ are obtained from thermodynamic tables. k_B is the Boltzmann constant. p^0 is ambient pressure (1.01×10^5 Pa) and T = 298.15 K. For the simplicity purpose, we did not consider the variation of H_2O pressure and only set the H_2O pressure at the ambient pressure (p_{H_2O}=1.01$\times 10^5$ Pa) during all calculations. According to Eqn. (S7), we can obtain a corresponding $\mu_{O_2(g)}$ with the variation of O_2 gas pressure (p_{O_2}). Then, we define a chemical penitential difference $\Delta\mu_O$ which can be expressed as:

$$\Delta\mu_O = \mu_O - \frac{1}{2}\left[E_{O_2(g)}^{DFT} + E_{O_2(g)}^{ZPE}\right] \quad \text{(S8)}$$

Based on Eqn. (S2) and (S7), the Eqn. (S8) can be re-written as:

$$\Delta\mu_O = \mu_O - \frac{1}{2}\left[E_{O_2(g)}^{DFT} + E_{O_2(g)}^{ZPE}\right] = \frac{1}{2}\left[\Delta G_{O_2(g)}^0(T) + k_B T ln\left(\frac{p_{O_2}}{p^0}\right)\right] \quad \text{(S9)}$$

Then, both the O_2 gas pressure (p_{O_2}) and chemical penitential difference $\Delta\mu_O$ can appear as horizontal axis in the in the surface phase diagram. More calculation details can be found in (*J. Phys. Chem. C 2015, 119, 9973-9979*) and (*Catal. Sci. Technol. 2014, 4, 3379-3389*).