The role of oxygen vacancies in biomass deoxygenation by reducible zinc/zinc oxide catalysts

Xiao Xiao,^{*a*,^b} Helen Bergstrom,^{*a*} Ryan Saenger,^{*a*} Benjamin Johnson,^{*a*} Runcang Sun,^{*b*} Andrew Peterson^{*a*,*}

^aSchool of Engineering Brown University, Providence, Rhode Island, 02912, United States. ^bBeijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing, 100083, China.

Details of deoxygenatiaon calculations The detail electronic energies of the intermediate state are summarized in Tables S1 and S2. The optimized geometries are shown for all adsorbates. The reference energy of the adsorbate is determined from the electronic energy of a stable gas phase molecule. [1,2]

$$E_{ads}[\mathbf{H}] = E[\mathbf{H}_2]/2 \tag{1}$$

$$E_{ads}[O] = E[H_2O] - 2E[H]$$
⁽²⁾

$$E_{ads}[CH_3COO] = E[CH_3COOH] - E[H]$$
(3)

$$E_{ads}[CH_3CO] = E[CH_3CHO] - E[H]$$
(4)

The contribution to the free energies of individual adsorbate and gas phase molecules were calculated, which are shown in Table S3 and Table S4.

Table S1: Energies of the deoxygenation intermediate states of vacancy-driven pathway. ΔE is the electronic energy of the state minus the electronic energy of the clean slab associated with the state. All values are shown in eV.

| Step | Geometry | Slab | ΔE |
|--------------------------|----------|--|------------|
| * | | $4 \times 4 \times 3$ (Single vacancy) | 0.00 |
| $CH_3COO\Box + H^*$ | | $4 \times 4 \times 3$ (Single vacancy) | -0.39 |
| $CH_3CO^* + O\Box + H^*$ | | $4 \times 4 \times 3$ (Single vacancy) | 0.84 |
| $CH_3CHO^* + O\Box$ | | $4 \times 4 \times 3$ (Single vacancy) | -0.62 |
| ОП | | $4 \times 4 \times 3$ (Single vacancy) | -0.27 |

Table S2: Energies of the deoxygenation intermediate states of surface-driven pathway. ΔE is the electronic energy of the state minus the electronic energy of the clean slab associated with the state. All values are shown in eV.

| Step | Geometry | Slab | ΔE |
|--|----------------|------------------------------------|------------|
| * | °°°°° © 9 (| $4 \times 4 \times 3$ (No vacancy) | 0.00 |
| $CH_3COO^* + H^*$ | | $4 \times 4 \times 3$ (No vacancy) | 0.80 |
| $\mathrm{CH}_3\mathrm{CO}^* + \mathrm{O}^* + \mathrm{H}^*$ | | $4 \times 4 \times 3$ (No vacancy) | 5.25 |
| $CH_3CHO^* + O^*$ | 2 | $4 \times 4 \times 3$ (No vacancy) | 3.84 |
| O* | | $4 \times 4 \times 3$ (No vacancy) | 4.19 |

Table S3: Free energy corrections of adsorbate, including zero-point energy, entropy and heating capacity.

 All values are reported in eV.

| Adsorbate | ZPE | $\int C_p dT$ | -TS | <i>G</i> - <i>E</i> |
|----------------------|-------|---------------|--------|---------------------|
| CH ₃ COO* | 1.377 | 0.469 | -1.054 | 0.792 |
| CH ₃ CO* | 1.297 | 0.505 | -1.137 | 0.665 |
| CH ₃ CHO* | 1.607 | 0.542 | -1.273 | 0.876 |
| O* | 0.075 | 0.099 | -0.197 | -0.023 |
| H* | 0.312 | 0.046 | -0.249 | 0.282 |
| $CH_3COO\square$ | 1.374 | 0.468 | -1.007 | 0.835 |

Table S4: Free energy corrections of gas phase molecule, including zero-point energy, entropy and heating
capacity. CH_3COOH and CH_3CHO were calculated at the operating pressure of the experiments.
H2 (ref) was calculated at atmosphere pressure for evaluating the chemical potentials by compu-
tational hydrogen electrode model.

| Adsorbate | Fugacity (Pa) | E(eV) | ZPE (eV) | $\int C_p dT (\text{eV})$ | -TS | <i>G</i> - <i>E</i> (eV) |
|----------------------|---------------|----------|----------|---------------------------|--------|--------------------------|
| CH ₃ COOH | 110000 | -1250.27 | 1.649 | 0.462 | -2.042 | 0.069 |
| CH ₃ CHO | 110000 | -812.41 | 1.476 | 0.384 | -1.733 | 0.127 |
| H_2 (ref) | 101325 | -32.03 | 0.275 | 0.189 | -0.981 | -0.518 |

Deoxygenation reaction rate estimates. A coverage-dependent microkinetic model would provide the best estimate of reaction rates, but to provide a rough comparison of rates we calculated the rate based on the highest barrier along the reaction pathway referenced to the initial state of the catalytic cycle. This estimate was made with the Eyring equation:

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$
(5)

where k refers to the reaction rate constant, k_B is the Boltzmann constant, h is Planck's constant, T is the absolute temperature, R is the ideal gas constant, and ΔG^{\ddagger} is the relative free energy of the transition state. ΔG^{\ddagger} in the present study are 2.23 eV and 2.11 eV for the sequential mechanism and the concerted mechanism, respectively, resulting in reaction rate constants of 9.8×10^{-6} M s⁻¹ and 1.1×10^{-4} M s⁻¹, respectively. From the experimental data of HDO, the rate constant k in the experiment is 4.38×10^{-4} M s⁻¹

Oxygen vacancy density calculation. The surface oxygen vacancy creation reaction is described below [3]:

$$H_{2(g)} + ZnO \longrightarrow H_2O_{(g)} + Zn$$
 (6)

The equilibrium constant is given by:

$$K = e^{\frac{-\Delta G}{RT}} \tag{7}$$

where ΔG is the free energy change of an oxygen vacancy creation (0.62 eV in the present study), *R* is the gas constant, *T* is the absolute temperature, and *K* is the equilibrium constant. In the present study, K is $9.64 \times 10^{-6} \text{ s}^{-1}$.

$$K = \frac{[\mathrm{H}_2][\mathrm{ZnO}]}{[\mathrm{H}_2\mathrm{O}][\mathrm{Zn}]}$$
(8)

which can be written as:

$$\theta_V = \frac{P_{H_2}[\text{Zn}]}{K P_{H_2O}} \tag{9}$$

Turnover frequency of the zinc catalyst. We note that, by design, the looped-oxide experiments with the zinc catalysts are not capable of running at steady state, thus turnover frequencies should be interpreted appropriately. The turnover frequency of the zinc catalyst was calculated by:

$$TOF = \frac{M_{\text{products}}}{M_{\text{sites}} \times \text{time}}$$
(10)

From the data of the amount and particle size of zinc, the amount of the surface vacant sites can be estimated, which is about 3.53×10^{-3} mol. This leads to an estimate of the turnover frequency of zinc to be 3×10^{-4} s⁻¹.



Figure S1: Surface vacant site formation. Left: Typical mechanism of the vacant site formation in HDO, in which oxygen on catalyst surface is removed as water. Right: Vacant site formation mechanism of LOC, in which the vacancies migrate from the lower-valence metal to the higher-valence catalyst surface.



Figure S2: Schematic of the experimental setup for the HDO and LOC reactions.

Experimental schematic. A schematic of the experimental setup is shown in Figure S2.

References

- [1] Peterson, A.A.; Abild-Pedersen, F.; Studt, F.; Rossmeisl, J.; Nørskov, J.K. How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. *Energy & Environmental Science* **2010**; 3, 1311–1315.
- [2] Nørskov, J.K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J.R.; Bligaard, T.; Jonsson, H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *The Journal of Physical Chemistry B* 2004; 108, 17886–17892.
- [3] Moberg, D.R.; Thibodeau, T.J.; Amar, F.G.; Frederick, B.G. Mechanism of hydrodeoxygenation of acrolein on a cluster model of MoO3. *The Journal of Physical Chemistry C* **2010**; 114, 13782–13795.