Supplementary Information (SI) for Dalton Transactions.

Supplementary Information

The Role of Defect-Modulated HKUST-1 MOF Nodes in Non-Oxidative Ethanol Dehydrogenation : An Observed Phenomenon of Catalyst Transfiguration

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S1 Details on the Structure of HKUST-1(OH)

In order to confirm the placement of -OH group in defective HKUST-1(OH), we tried to optimize a structure of defective HKUST-1(OH) where the -OH group is attached to one Cu centre (instead of the bridging mode). However, the optimization process ended with the -OH group placed symmetrically between two Cu-centres in a bridging fashion.

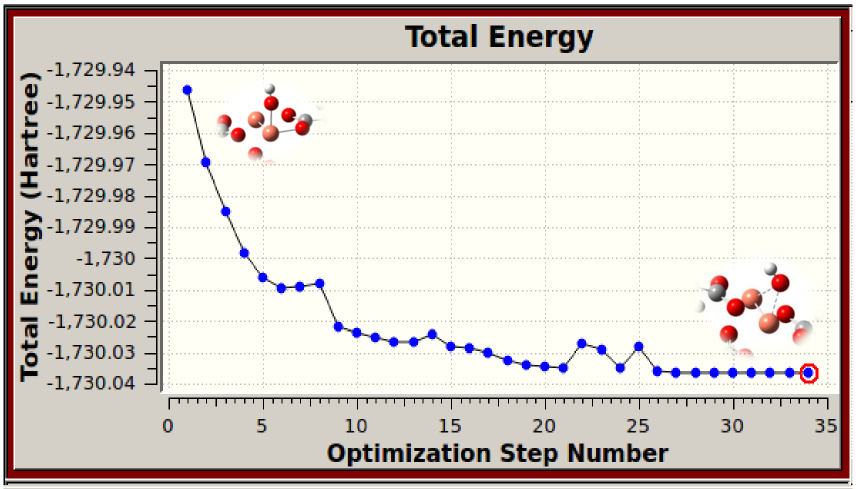


Figure S1: Optimized structures involved in acetaldehyde synthesis via. path-a over HKUST-1(H) MOF node. [Colour code- Cu: orange; O: red; C: grey; H: white]

S2 Microkinetic Modelling Analysis

The microkinetic model used here is an accordance with what has been used by Xue et al. in their computational study on CO oxidation reaction.[1]

S2.1 Calculation of Sabatier Rate for Acetaldehyde Formation via. Path-a over HKUST-1(H)

The microkinetic model is represented as follows:

$$\begin{array}{rl} \mathrm{CH_3CH_2OH\ (g) + {}^{*} \rightarrow {}^{*}CH_3CH_2OH} & \mathrm{R1} \\ \mathrm{{}^{*}CH_3CH_2OH + H \rightarrow {}^{*}CH_3CH_2O + H_2(g)} & \mathrm{R2} \\ \mathrm{{}^{*}CH_3CH_2O \rightarrow CH_3CHO(g) + H + {}^{*}} & \mathrm{R3} \end{array}$$

rate(R1) $= \mathrm{k_{for,1}\ p_{ethanol}}\ \theta_* - \mathrm{k_{rev,1}}\ \theta_{\mathrm{CH_3CH_2OH}}$

rate(R2) $= \mathrm{k_{for,2}}\ \theta_{\mathrm{CH_3CH_2OH}} - \mathrm{k_{rev,2}}\ \theta_{\mathrm{CH_3CH_2O}}\ \mathrm{p_{H_2}}$

rate(R3) $= \mathrm{k_{for,3}}\ \theta_{\mathrm{CH_3CH_2O}} - \mathrm{k_{rev,3}}\ \theta_*\ \mathrm{p_{acetaldehyde}}$

On the basis of calculated Gibbs free energy profile R3 step is assumed to be the rate determining step while all other steps (R1 and R2) are treated as quasi-equilibrium. The rate R1 and R2 can be written as follows:

$$\begin{aligned} rate(R1) &= \mathrm{k_{for,1}\ p_{ethanol}}\ \theta_* - \mathrm{k_{rev,1}}\ \theta_{\mathrm{CH_3CH_2OH}} = 0 \\ &\implies \theta_{\mathrm{CH_3CH_2OH}} = \mathrm{K_{eq,1}\ p_{ethanol}}\ \theta_* \end{aligned}$$

$$\begin{aligned} rate(R2) &= \mathrm{k_{for,2}}\ \theta_{\mathrm{CH_3CH_2OH}} - \mathrm{k_{rev,2}}\ \theta_{\mathrm{CH_3CH_2O}}\ \mathrm{p_{H_2}} = 0 \\ &\implies \theta_{\mathrm{CH_3CH_2O}} = \mathrm{K_{eq,2}}\ \frac{\theta_{\mathrm{CH_3CH_2OH}}}{\mathrm{p_{H_2}}} = \mathrm{K_{eq,2}}\ \frac{\theta_*}{\mathrm{p_{H_2}}}\ \mathrm{K_{eq,1}\ p_{ethanol}} \end{aligned}$$

where $\mathrm{K_{eq,i}}$ is the equilibrium constant for $\mathrm{R_i}$ and $\mathrm{p_{ethanol}}$. $\mathrm{p_{acetaldehyde}}$ and $\mathrm{H_2}$ are the partial pressures of ethanol, acetaldehyde and $\mathrm{H_2}$ molecule respectively. $\mathrm{k_{for,i}}$ and $\mathrm{k_{rev,i}}$ are the forward and reverse reaction rate constants for R_i.

The sum of coverage of all the species must be equal to 1. Therefore,

$$\theta_* + \theta_{CH_3CH_2OH} + \theta_{CH_3CH_2O} = 1$$

$$\implies \theta_*[1 + K_{eq,1}\, p_{ethanol} + K_{eq,1}\, K_{eq,2}\, \frac{p_{ethanol}}{p_{H_2}}] = 1$$

$$\implies \theta_* = \frac{1}{1+ K_{eq,1}\, p_{ethanol} + K_{eq,1}\, K_{eq,2}\, \frac{p_{ethanol}}{p_{H_2}}}$$

The reaction rate R3 can de defined as follows: rate(R3) = $k_{for,3}\, \theta_{CH_3CH_2O} - k_{rev,3}\, \theta_*\, p_{acetaldehyde}$ Since acetaldehyde pressure is low and readsorption of acetaldehyde is negligible (as is evident from the reaction profile diagrams), R3 an be rewritten as

$$\begin{aligned} \text{rate(R3)} &= k_{for,3}\, \theta_{CH_3CH_2O} \\ &= \frac{k_{for,3}\, K_{eq,1}\, K_{eq,2} \frac{p_{ethanol}}{p_{H_2}}}{1 + K_{eq,1}\, p_{ethanol} + K_{eq,1}\, K_{eq,2}\, \frac{p_{ethanol}}{p_{H_2}}} \end{aligned}$$

The Sabatier rate of acetaldehyde formation is determined by the Sabatier rates of reaction R3. Hence,

Rate[HKUST-1(H)-path-a] = rate(R3) = $\frac{k_{for,3}\, K_{eq,1}\, K_{eq,2} \frac{p_{ethanol}}{p_{H_2}}}{1+ K_{eq,1}\, p_{ethanol} + K_{eq,1}\, K_{eq,2}\, \frac{p_{ethanol}}{p_{H_2}}}$

Acetaldehyde formation rate has been calculated at the experimental conditions of T=453.15 K with the partial pressures for ethanol, hydrogen and acetaldehyde being 0.05 kPa, 10^{-6} kPa and 10^{-6} kPa respectively.

Following a similar procedure, microkinetic modelling analysis was carried out for both path-b and path-c.

S2.2 Calculation of Sabatier Rate for Acetaldehyde Formation via. Path-b over HKUST-1(H)

The microkinetic model is represented as follows:

$$\begin{array}{cr} CH_3CH_2OH\ (g) +\ ^* \rightarrow\ ^*CH_3CH_2OH & R1 \\ ^*CH_3CH_2OH +\ H \rightarrow\ ^*CH_3CH_2O +\ H_2(g) & R2 \\ ^*CH_3CH_2O \rightarrow\ CH_3CHOH & R3 \\ ^*CH_3CHOH \rightarrow\ CH_3CHO(g) +\ H +\ ^* & R4 \end{array}$$

On the basis of calculated Gibbs free energy profile R3 step is assumed to be the rate determining step while all other steps (R1, R2 and R4) are treated as quasi-equilibrium. Considering the surface coverage of all species, we finally obtain,

$$\text{Rate[HKUST-1(H)-path-b]} = \text{rate(R3)} = \frac{k_{for,3}\ K_{eq,1}\ K_{eq,2}\frac{p_{ethanol}}{p_{H_2}}}{1+\ K_{eq,1}\ p_{ethanol}+\ K_{eq,1}\ K_{eq,2}\ \frac{p_{ethanol}}{p_{H_2}}+\ \frac{p_{acetaldehyde}}{K_{eq,4}}}$$

S2.3 Calculation of Sabatier Rate for Acetaldehyde Formation via. Path-c over HKUST-1(H)

The microkinetic model is represented as follows:

$$\begin{array}{cr} CH_3CH_2OH\ (g) +\ ^* \rightarrow\ ^*CH_3CH_2OH & R1 \\ ^*CH_3CH_2OH +\ H \rightarrow\ ^*CH_3CHOH +\ H_2(g) & R2 \\ ^*CH_3CHOH \rightarrow\ CH_3CHO(g) +\ H +\ ^* & R3 \end{array}$$

On the basis of calculated Gibbs free energy profile R2 step is assumed to be the rate determining step while all other steps (R1 and R3) are treated as quasi-equilibrium. Considering the surface coverage of all species, we finally obtain,

$$\text{Rate[HKUST-1(H)-path-c]} = \text{rate(R2)} = \frac{k_{for,2}\ K_{eq,1}\ p_{ethanol}}{1+\ K_{eq,1}\ p_{ethanol}+\ \frac{p_{acetaldehyde}}{K_{eq,3}}}$$

S3 Optimized Structures

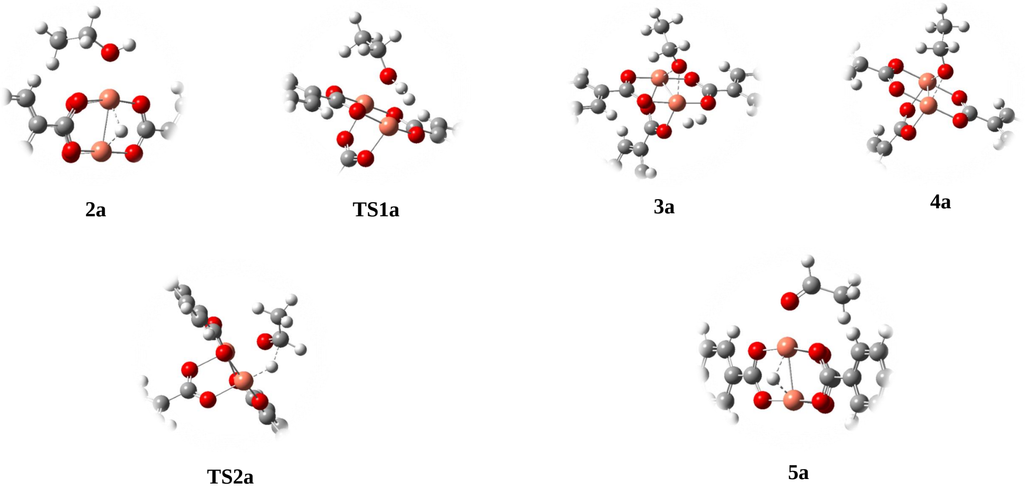
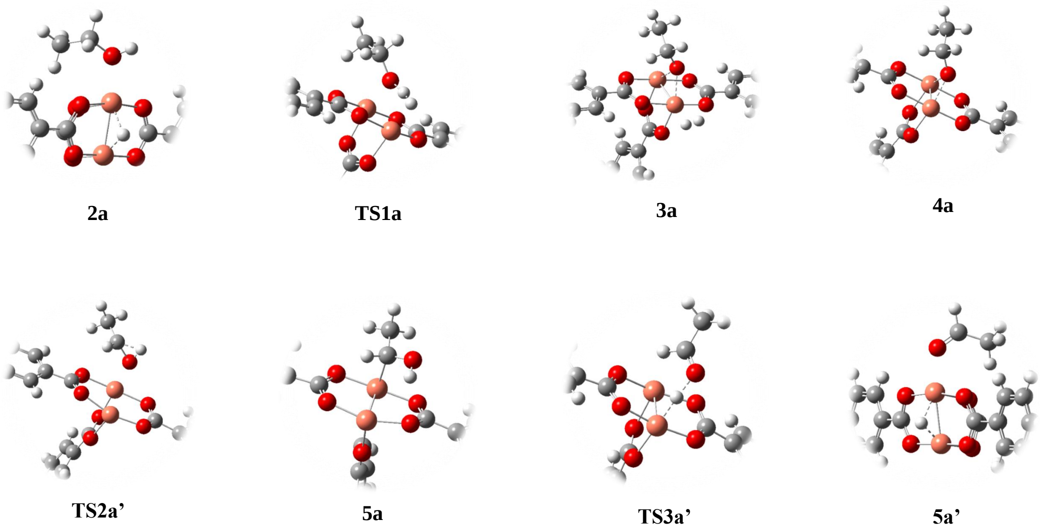


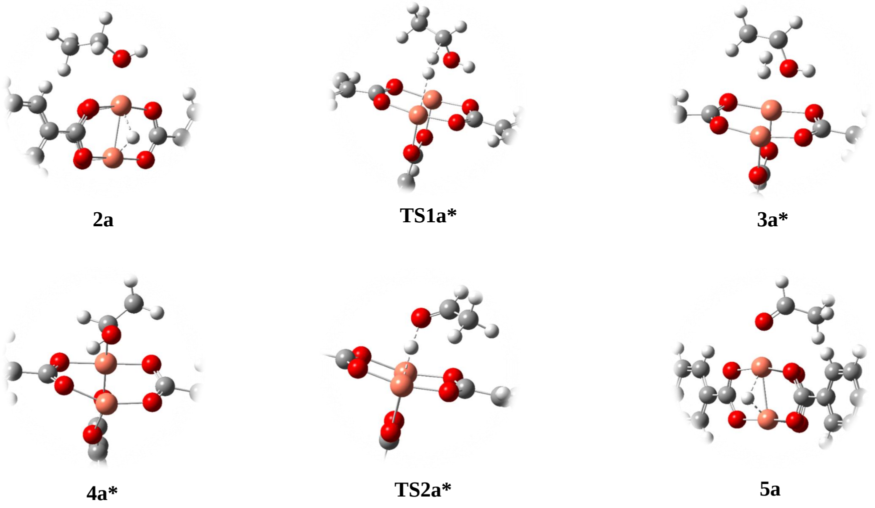
Figure S2: Optimized structures involved in acetaldehyde synthesis via. path-a over HKUST-1(H) MOF node. [Colour code- Cu: orange; O: red; C: grey; H: white]



2a **TS1a** **3a** **4a**

TS2a’ **5a** **TS3a’** **5a’**

Figure S3: Optimized structures involved in acetaldehyde synthesis via. path-b over HKUST-1(H) MOF node. [Colour code - Cu: orange; O: red; C: grey; H: white]



2a

TS1a*

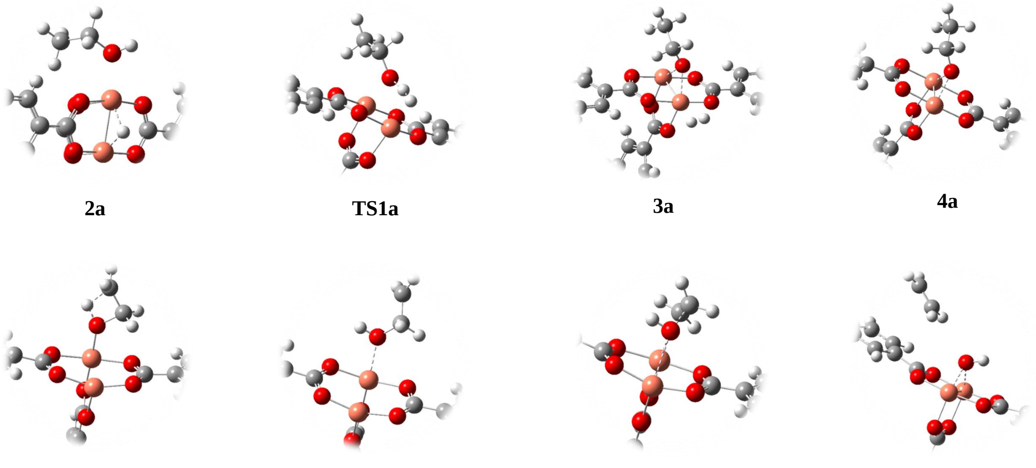
3a*

4a*

TS2a*

5a

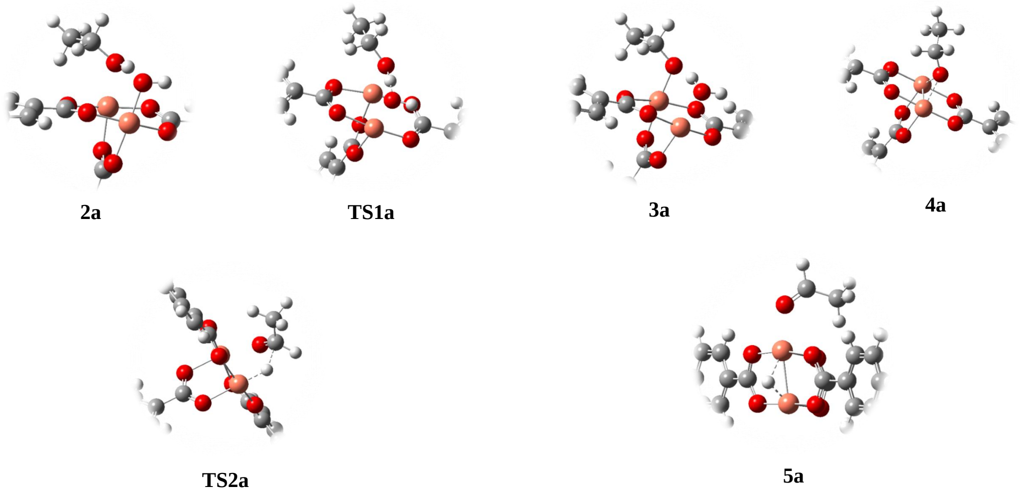
Figure S4: Optimized structures involved in acetaldehyde synthesis via. path-c over HKUST-1(H) MOF node. [Colour code - Cu: orange; O: red; C: grey; H: white]



2a TS1a 3a 4a

TS2e 5e TS3e 6e

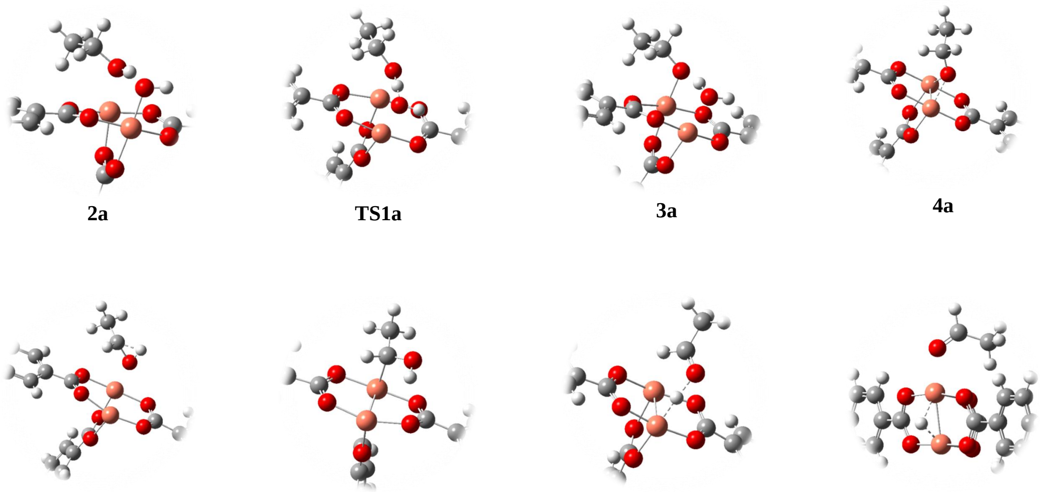
Figure S5: Optimized structures involved in ethylene synthesis over HKUST-1(H) MOF node. [Colour code - Cu: orange; O: red; C: grey; H: white]



2a TS1a 3a 4a

TS2a 5a

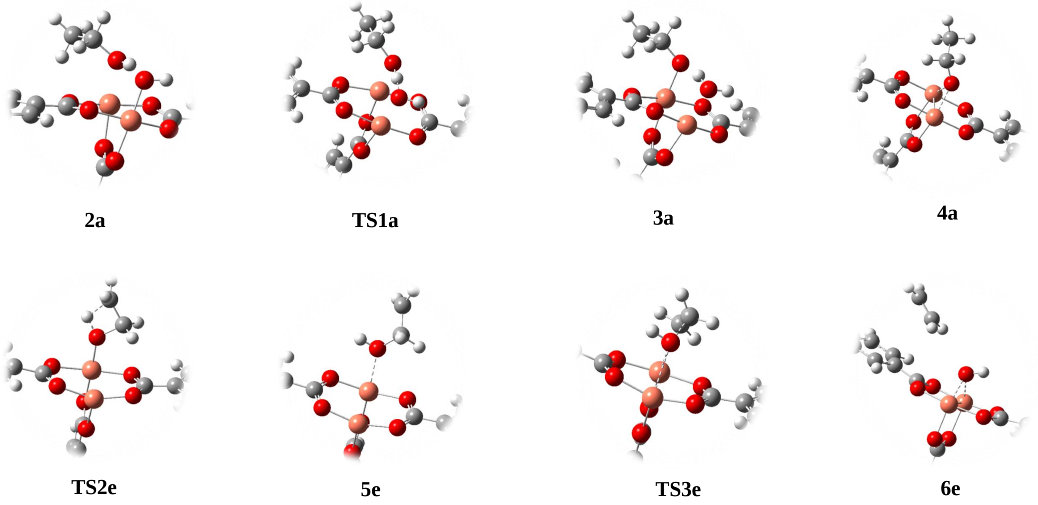
Figure S6: Optimized structures involved in acetaldehyde synthesis via. path-a over HKUST-1(OH) MOF node. [Colour code - Cu: orange; O: red; C: grey; H: white]



2a **TS1a** **3a** **4a**

TS2a' **5a** **TS3a'** **5a'**

Figure S7: Optimized structures involved in acetaldehyde synthesis via. path-b over HKUST-1(OH) MOF node. [Colour code - Cu: orange; O: red; C: grey; H: white]


2a TS1a 3a 4a

TS2e 5e TS3e 6e

Figure S8: Optimized structures involved in ethylene synthesis over HKUST-1(OH) MOF node. [Colour code - Cu: orange; O: red; C: grey; H: white]

References

(1) Xue, W.; Wang, J.; Huang, H.; Cui, Y.; Mei, D. CO Oxidation over HKUST-1 Catalysts: The Role of Defective Sites. *J Phys. Chem. C* **2022**, *126*, 9652–9664.