Electronic Supplementary Information

How is CO_2 hydrogenated to ethanol on metal–organic framework HKUST-1? Microscopic insights from density-functional theory calculations

Bikun Zhang and Jianwen Jiang*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 117576, Singapore

**Email: chejj@nus.edu.sg*

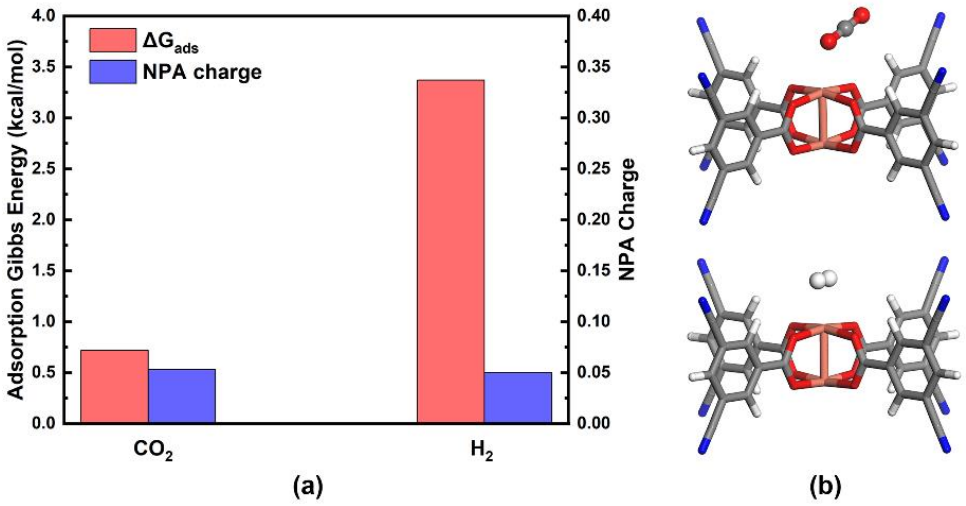

Fig. S1 (a) Adsorption Gibbs energies, NPA charges and (b) structures of CO_2 and H_2 on o_PW.

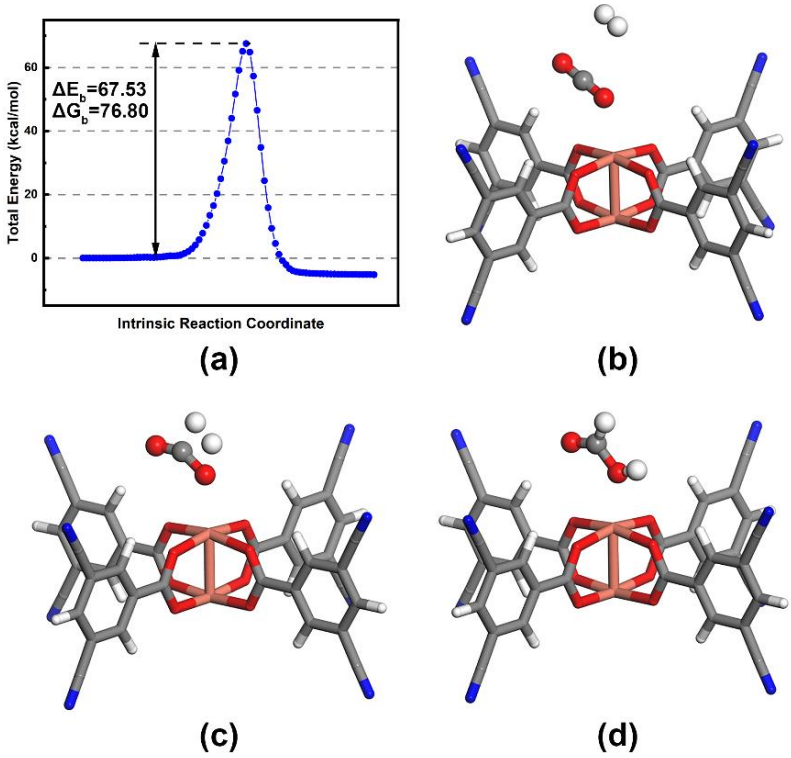

Fig. S2 (a) Total energy versus intrinsic reaction coordinate; structures of (b) initial state, (c) transition state and (d) final state of $CO_2 + H_2 \rightarrow HCOOH$ on o_PW.

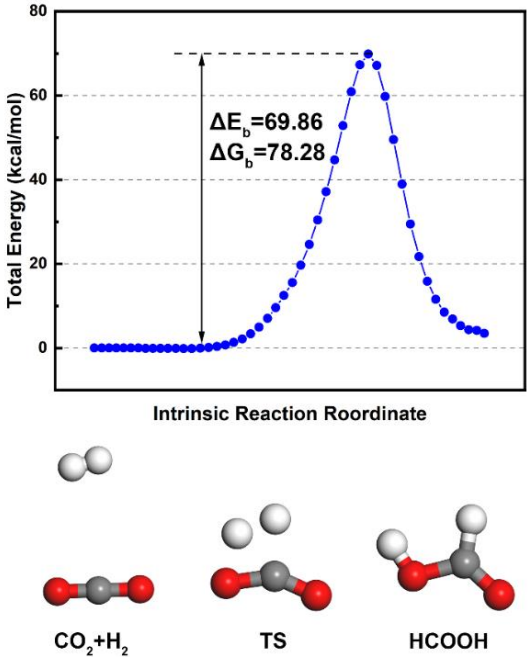

Fig. S3 (a) Total energy versus intrinsic reaction coordinate of $CO_2 + H_2 \rightarrow HCOOH$ in the gas phase and (b) structures of $CO_2 + H_2$, transition state (TS) and HCOOH.

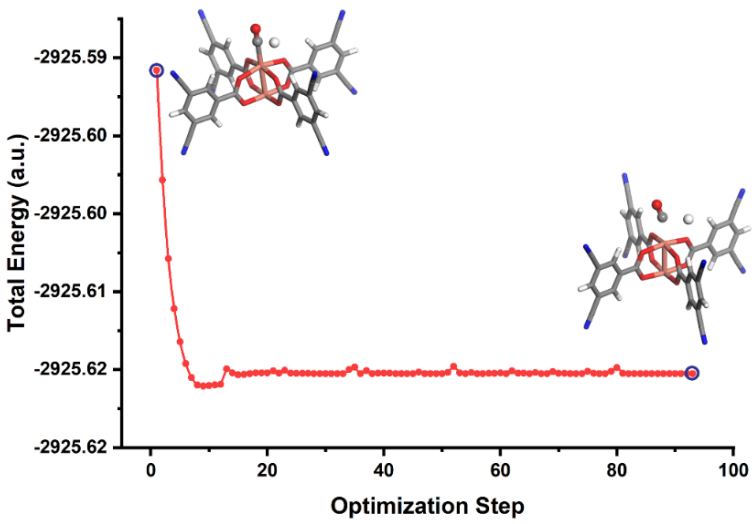

Fig. S4 Total energy evolution during transition state search for *CO hydrogenation on o_PW, with the structures of the first and last step shown.

One isolated H atom was put near *CO during transition state search between *CO + H and *CHO/*COH. However, the calculation ended with H atom moving away from *CO, indicating that CO strongly repels H atom.

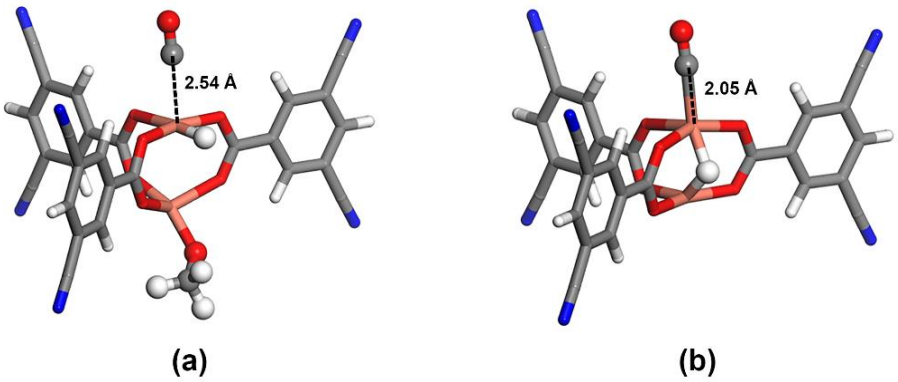

Fig. S5 *H + *CO co-adsorption structures on (a) CH_3O_PW and (b) d_PW.

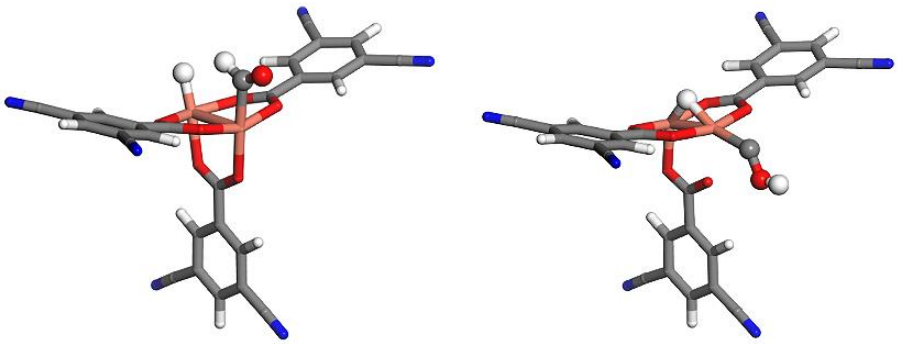

Fig. S6 Structures and total energies of (a) *CHO + *H and (b) *COH + *H on d_PW.

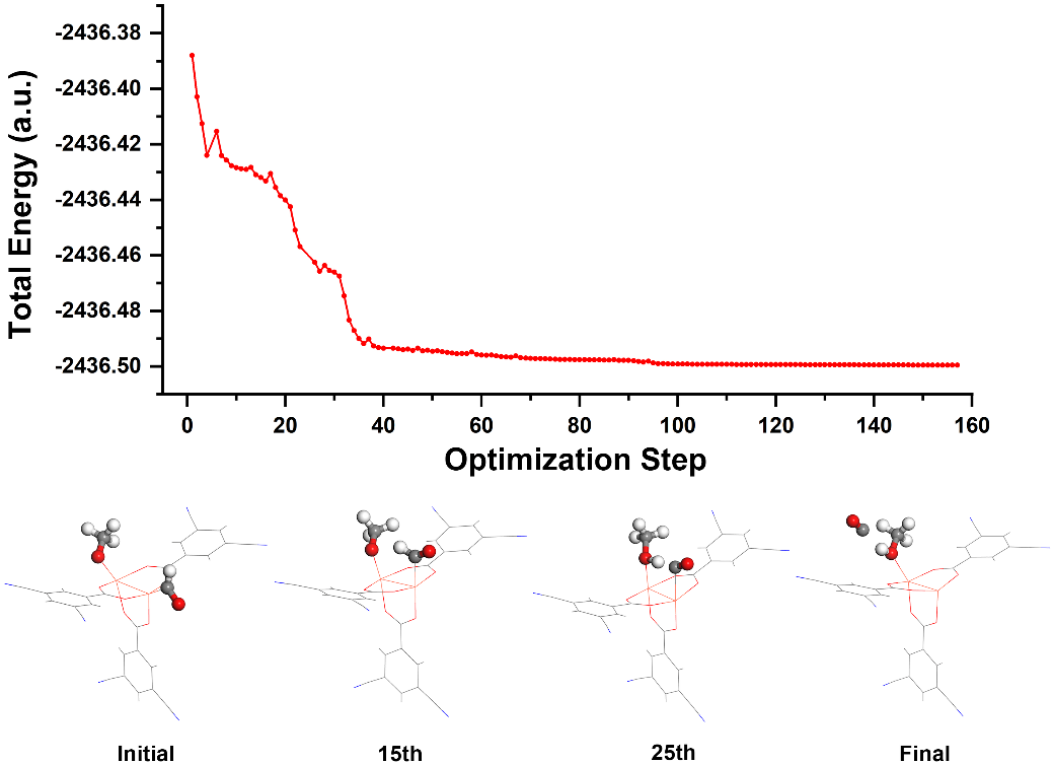

Fig. S7 (top) Total energy evolution of *CHO on CH_3O_PW during geometry optimization. (bottom) Structures at the initial, 15th, 25th and final step of optimization.

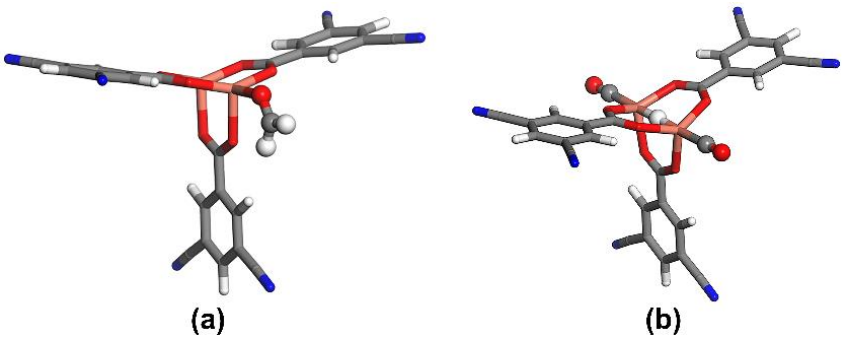

Fig. S8 Structures of (a) *OCH_2 and (b) *CO + *CO + *H on d_PW.

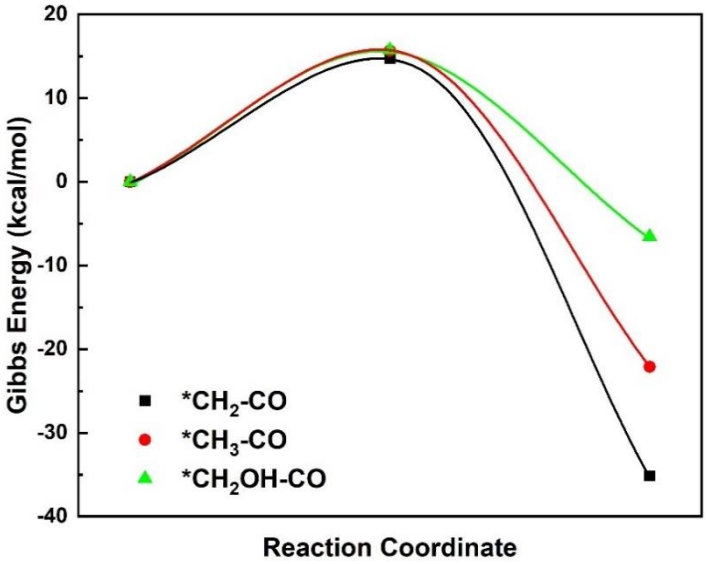

Fig. S9 Gibbs energy profiles for *CH_2-CO, *CH_3-CO and *CH_2OH-CO coupling on d_PW.