Supporting Information

CO_2 Photoreduction on Mixed Ti/Zr-MOF-525: Bicarbonate as the Active Intermediate and the Role of Ti Substitution

Thanyaporn Puengpoka,[a] Jirapat Santatiwongchai,[b] Warot Chotpatiwetchkul,[a*] Sareeya Bureekaew,[c] Muhammad Saleh,[d] Anchalee Junkaew[b] and Sarawoot Impeng[b*]

[a]*Applied Computational Chemistry Research Unit, Department of Chemistry, School of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand*

[b]*National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathum Thani, Thailand*

[c]*Department of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand*

[d]*Lehrstuhls für Theoretische Physik elektrifizierter Flüssig-Festkörper-Grenzflächen Ruhr-Universität Bochum Universitätsstraße 150 44801 Bochum, Germany*

*Corresponding author

E-mail address: sarawoot.imp@nanotec.or.th (S. Impeng), warot.ch@kmitl.ac.th (W. Chotpatiwetchkul)

Table S1. Optimized adsorption geometries and corresponding relative Gibbs free energies (ΔG, eV) of intermediates in the OH-passive pathway on Zr_6-MOF-525, Ti_1Zr_5-MOF-525, and Ti_1Zr_5-MOF-525 clusters.

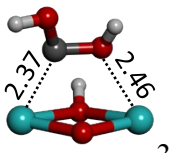
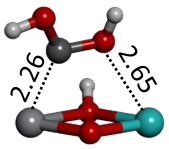
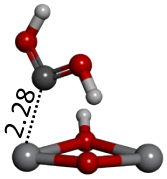
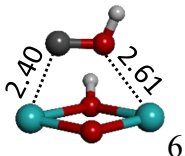
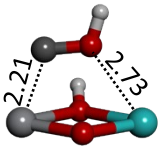
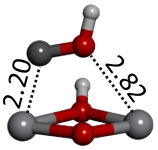
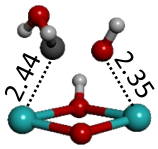
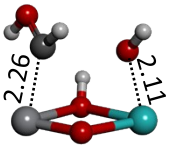
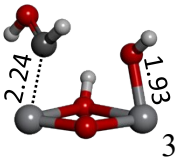
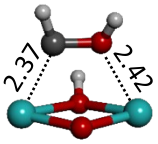
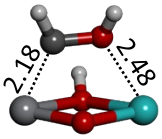
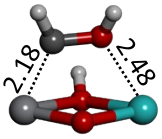
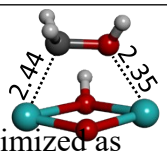
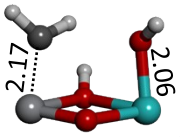
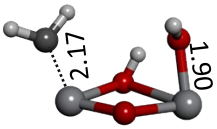
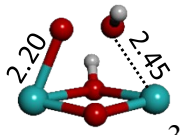
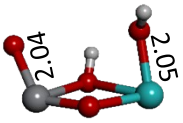
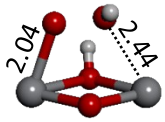
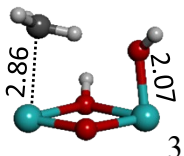
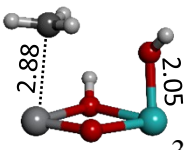
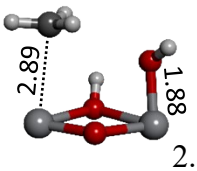
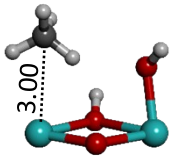
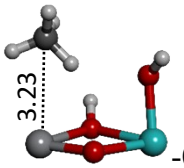
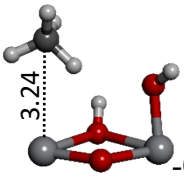
Intermediates	Zr_6-MOF-525	Ti_1Zr_5-MOF-525	Ti_1Zr_5-MOF-525
	ΔG	ΔG	ΔG
*COH (optimized as *COHOH)	 3.79	 4.51	 3.87
*C (optimized as *COH)	 6.36	 5.73	 5.57
*CHOH	 4.08	 4.02	 3.99
*CH (optimized as *CHOH)	 4.97	 4.85	 4.58
*CH_2	 (optimized as CH_2OH) 3.47	 4.00	 3.81
*O (optimized as *OOH)	 3.79	 4.37	 3.62
*CH_3	 3.31	 3.10	 2.92
*CH_4	 -0.01	 -0.17	 -0.31

Table S2. Optimized adsorption geometries and corresponding relative Gibbs free energies (ΔG, eV) of intermediates in the OH-assisted pathway on Zr_6-MOF-525, Ti_1Zr_5-MOF-525, and Ti_1Zr_5-MOF-525 clusters.

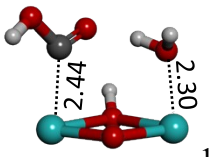
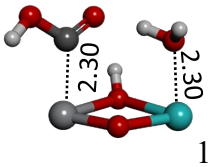
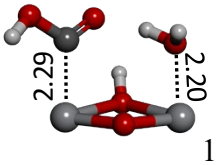
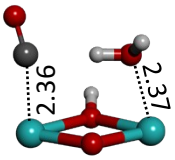
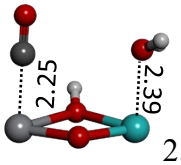
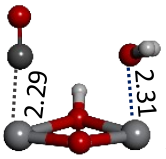
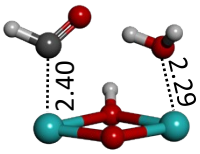
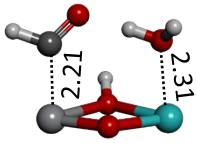
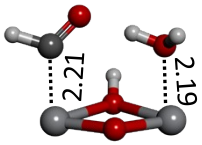
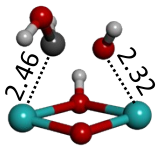
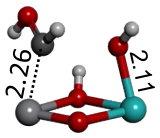
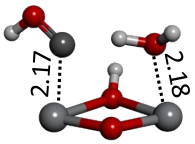
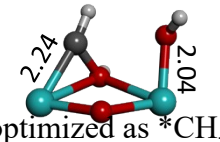
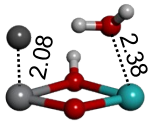
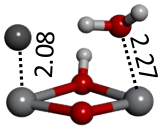
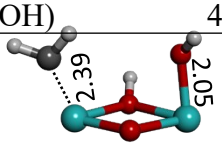
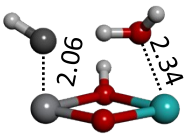
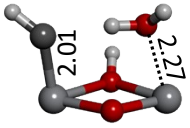
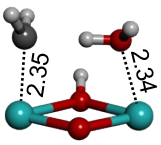
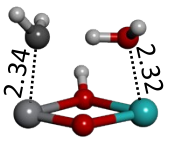
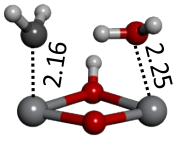
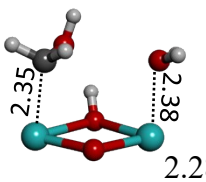
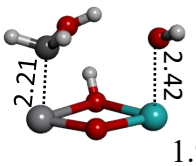
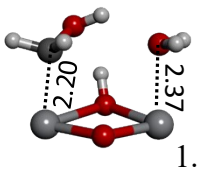
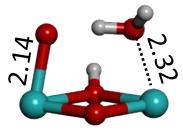
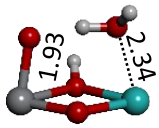
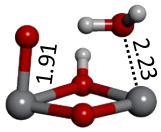
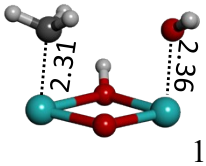
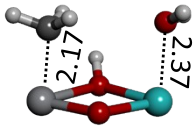
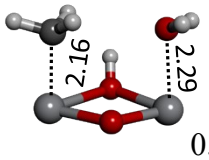
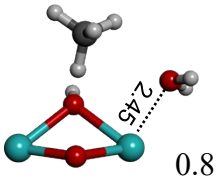
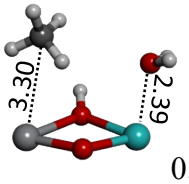
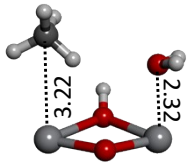
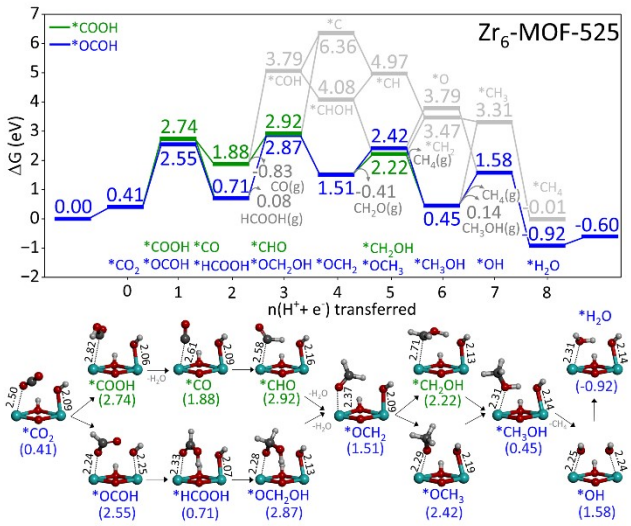
Intermediates	Zr_6-MOF-525	Ti_1Zr_5-MOF-525	Ti_2Zr_4-MOF-525
	ΔG	ΔG	ΔG
*COOH-H_2O	 1.67	 1.39	 1.31
*CO-H_2O	 2.74	 2.16	 1.92
*CHO-H_2O	 2.30	 1.87	 1.92
*COH-H_2O (optimized as *CHOH)	 2.88	 2.85	 3.96
*C-H_2O	 (optimized as *CH_2-OH) 4.46	 6.15	 5.87
*CH-H_2O	 (optimized as *CH_2-OH) 3.33	 4.54	 4.43
*CH_2-H_2O	 3.07	 3.13	 2.68
*CH_2OH-H_2O	 2.28	 1.92	 1.79

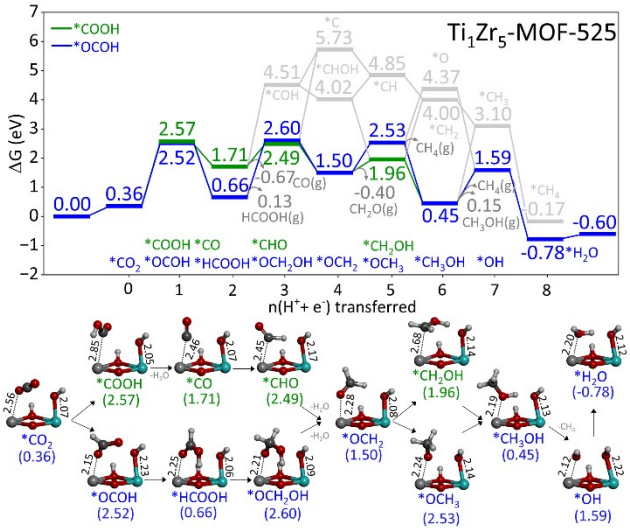
Table S2. (continued.)

Intermediates	Zr_6-MOF-525	Ti_1Zr_5-MOF-525	Ti_2Zr_4-MOF-525
	ΔG	ΔG	ΔG
*O-H_2O	 1.22	 1.33	 0.97
*CH_3-H_2O	 1.33	 1.24	 0.94
*CH_4-H_2O	 0.81	 0.40	 -0.05

Note on intermediate labeling:

Throughout this work, species labels (e.g., *CH, *C) denote the initially proposed intermediates along the reaction pathway and are retained for consistency and clarity in describing the reaction mechanism. Upon full geometry optimization, some intermediates undergo structural relaxation, including interaction or bond formation with neighboring hydroxyl groups. For example, an initially defined *CH species may relax into a CHOH-like configuration by forming a bond with an adjacent OH group. Unless otherwise stated, all reported geometries and free energies correspond to the fully optimized minimum-energy structures.


Zr6-MOF-525
*COOH
*OCOH
ΔG (eV)
n(H+ + e-) transferred
0.00
0.41
2.74
2.55
1.88
0.71
2.92
2.87
0.83 CO(g)
0.08 HCOOH(g)
1.51
2.42
2.22
-0.41 CH2O(g)
0.45
3.79 *COH
6.36 *C
4.08 *CHOH
4.97 *CH
3.79 *O
3.47 *CH2
CH4(g)
3.31 *CH3
1.58
CH4(g)
0.14 CH3OH(g)
*CH4
0.01
0.92
-0.60
*COOH *CO *CHO *CH2OH
*CO2 *OCOH *HCOOH *OCH2OH *OCH2 *OCH3 *CH3OH *OH *H2O
*CO2 (0.41)
*COOH (2.74)
*CO (1.88)
*CHO (2.92)
*OCH2 (1.51)
*CH2OH (2.22)
*CH3OH (0.45)
*H2O (-0.92)
*OCOH (2.55)
*HCOOH (0.71)
*OCH2OH (2.87)
*OCH3 (2.42)
*OH (1.58)


Ti1Zr5-MOF-525
*COOH
*OCOH
ΔG (eV)
n(H+ + e-) transferred
0.00
0.36
2.57
2.52
1.71
0.66
2.60
2.49
0.67 CO(g)
0.13 HCOOH(g)
1.50
2.53
1.96
0.40 CH2O(g)
0.45
5.73 *C
4.51 *COH
4.02 *CHOH
4.85 *CH
4.37 *O
4.00 *CH2
CH4(g)
3.10 *CH3
1.59
CH4(g)
0.15 CH3OH(g)
*CH4
0.17
-0.60
-0.78
*COOH *CO *CHO *CH2OH
*CO2 *OCOH *HCOOH *OCH2OH *OCH2 *OCH3 *CH3OH *OH *H2O
*CO2 (0.36)
*COOH (2.57)
*CO (1.71)
*CHO (2.49)
*OCH2 (1.50)
*CH2OH (1.96)
*CH3OH (0.45)
*H2O (-0.78)
*OCOH (2.52)
*HCOOH (0.66)
*OCH2OH (2.60)
*OCH3 (2.53)
*OH (1.59)

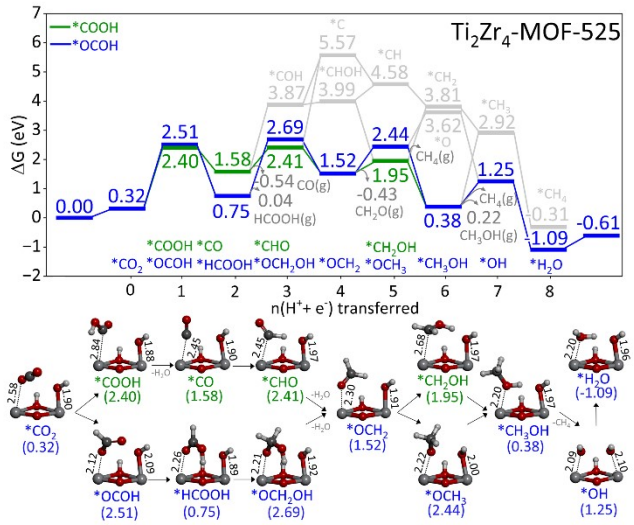
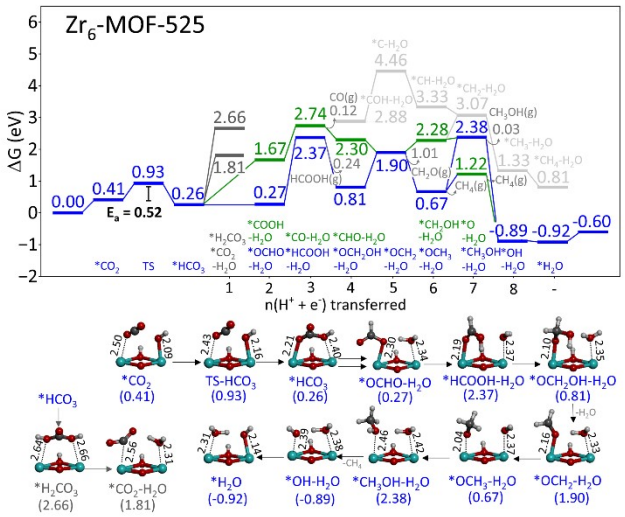
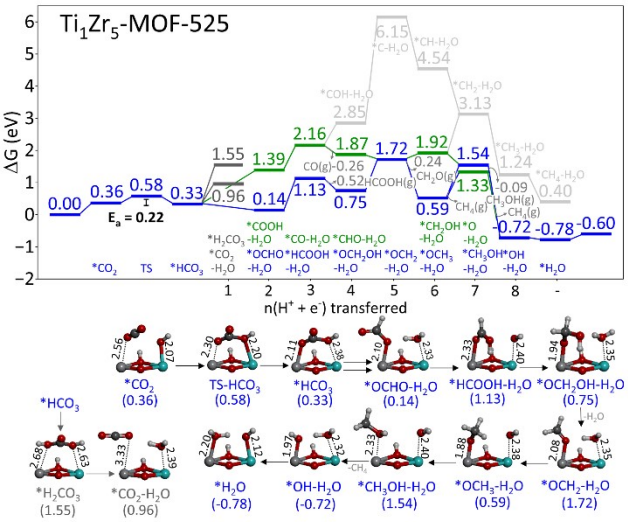

Ti2Zr4-MOF-525
*COOH
*OCOH
ΔG (eV)
n(H+ + e-) transferred
0.00
0.32
2.51
2.40
1.58
0.75
2.69
2.41
0.54 CO(g)
0.04 HCOOH(g)
1.52
2.44
1.95
0.43 CH2O(g)
0.38
3.87 *COH
5.57 *C
3.99 *CHOH
4.58 *CH
3.81 *CH2
3.62 *O
CH4(g)
2.92 *CH3
1.25
CH4(g)
0.22 CH3OH(g)
*CH4
0.31
-0.61
1.09
*COOH *CO *CHO *CH2OH
*CO2 *OCOH *HCOOH *OCH2OH *OCH2 *OCH3 *CH3OH *OH *H2O
*CO2 (0.32)
*COOH (2.40)
*CO (1.58)
*CHO (2.41)
*OCH2 (1.52)
*CH2OH (1.95)
*CH3OH (0.38)
*H2O (-1.09)
*OCOH (2.51)
*HCOOH (0.75)
*OCH2OH (2.69)
*OCH3 (2.44)
*OH (1.25)

Figure S1. Free-energy profile (ΔG, eV) of the OH-passive pathway on Zr_6-, Ti_1Zr_5- and Ti_2Zr_4-MOF-525, together with the corresponding optimized structures of the adsorbed intermediates.


Zr6-MOF-525
ΔG (eV)
n(H+ + e-) transferred
Ea = 0.52
*CO2
TS
*HCO3
*H2CO3
*CO2-H2O
*HCO3 (0.41)
TS-HCO3 (0.93)
*HCO3 (0.26)
*OCHO-H2O (0.27)
*HCOOH-H2O (2.37)
*OCH2OH-H2O (0.81)
*H2CO3 (2.66)
*CO2-H2O (1.81)
*H2O (-0.92)
*OH-H2O (-0.89)
*CH3OH-H2O (2.38)
*OCH3-H2O (0.67)
*OCH2-H2O (1.90)


Ti1Zr5-MOF-525
ΔG (eV)
n(H+ + e-) transferred
Ea = 0.22
*CO2
TS
*HCO3
*CO2 (0.36)
TS-HCO3 (0.58)
*HCO3 (0.33)
*OCHO-H2O (0.14)
*HCOOH-H2O (1.13)
*OCH2OH-H2O (0.75)
*H2CO3 (1.55)
*CO2-H2O (0.96)
*H2O (-0.78)
*OH-H2O (-0.72)
*CH3OH-H2O (1.54)
*OCH3-H2O (0.59)
*OCH2-H2O (1.72)

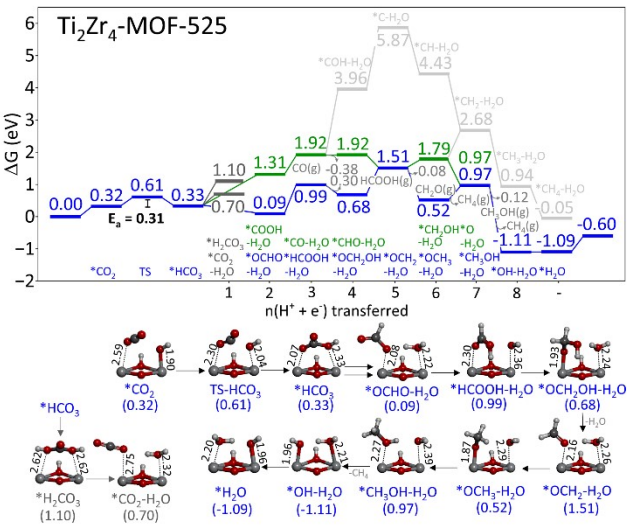

Ti2Zr4-MOF-525
ΔG (eV)
n(H+ + e-) transferred
Ea = 0.31
*CO2
TS
*HCO3
*H2CO3
*CO2-H2O
*CO2 (0.32)
TS-HCO3 (0.61)
*HCO3 (0.33)
*OCHO-H2O (0.09)
*HCOOH-H2O (0.99)
*OCH2OH-H2O (0.68)
*H2CO3 (1.10)
*CO2-H2O (0.70)
*H2O (-1.09)
*OH-H2O (-1.11)
*CH3OH-H2O (0.97)
*OCH3-H2O (0.52)
*OCH2-H2O (1.51)

Figure S2. Free-energy profile (ΔG, eV) of the OH-assisted pathway on Zr_6-, Ti_1Zr_5- and Ti_2Zr_4-MOF-525, together with the corresponding optimized structures of the adsorbed intermediates.

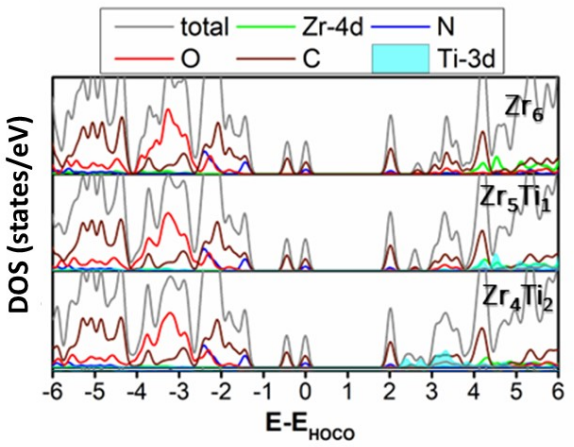


Figure S3. Density of states (DOS) of Zr_6-, Ti_1Zr_5-, and Ti_2Zr_4-MOF-525 calculated at the HSE06//PBE-D3(BJ) level of theory, with energies referenced to the highest occupied crystal orbital (HOCO = 0 eV).

Periodic electronic structure calculations

Band gap and density of states (DOS) calculations were performed using periodic density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP).(1) The atomic structures were first optimized using the PBE functional (2) with Grimme's D3 dispersion correction and Becke–Johnson damping (PBE-D3(BJ)).(3) Single-point electronic structure calculations were then carried out using the HSE06 hybrid functional (4) on the optimized PBE-D3(BJ) geometries (HSE06//PBE-D3(BJ)). Projector-augmented wave (PAW) potentials (5) were employed with a plane-wave kinetic energy cutoff of 520 eV and Γ-point sampling was used due to the large unit cell of MOF-525. These periodic calculations were performed to characterize the photophysical properties of the frameworks, while reaction energetics and mechanistic pathways were evaluated using finite cluster models.

References

(1) G. Kresse, J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.

(2) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1999, **77,** 3865–3868.

(3) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

(4) J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207–8215.

(5) G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.