Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Rational Design of Metal Node-modified Ti-Based MOFs for Selective Photoreduction of Carbon Dioxide to Ethanol by Computational Screening

Shuang Wang, [a#] Xiaowa Nie, [a#*] Chunshan Song, [b*] and Xinwen Guo [a*]

[a] State Key Laboratory of Fine Chemicals, Frontier Science Center for Smart Materials, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024.

[b] Department of Chemistry, Faculty of Science, The Chinese University of Hong Kong, Shatin, NT, Hong Kong 999077.

*Corresponding Authors: Xiaowa Nie: niexiaowa@dlut.edu.cn; Chunshan Song: chunshansong@cuhk.edu.hk; Xinwen Guo: guoxw@dlut.edu.cn.

#These authors contributed equally to this work.

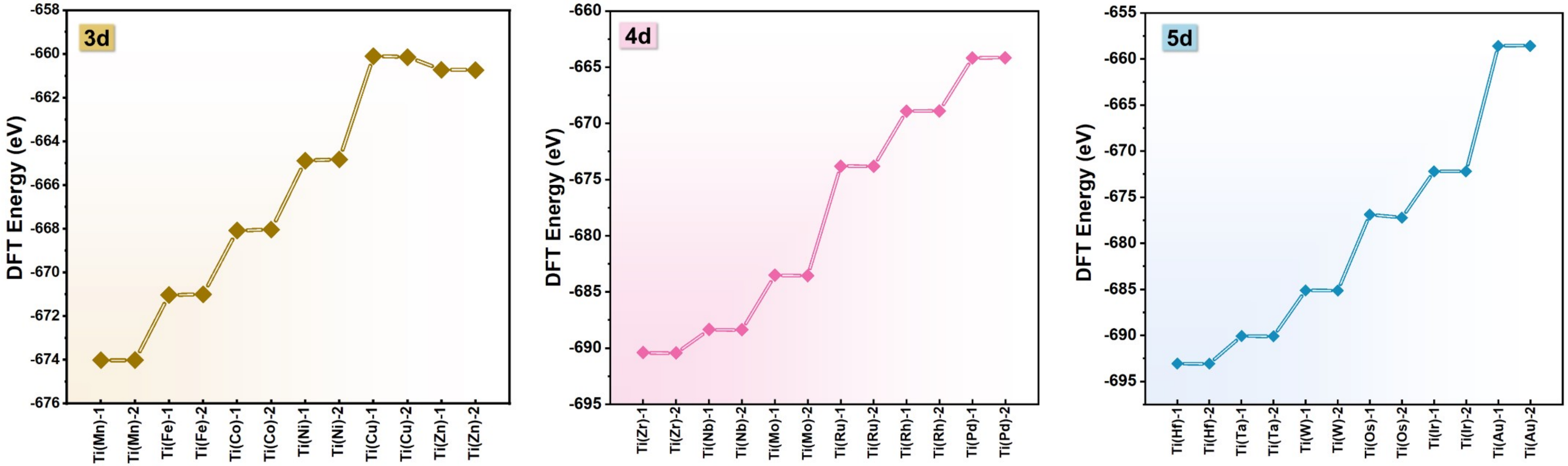


Fig. S1. The calculated DFT energies of two different configurations of metal-modified nodes (as shown in **Fig. 1(d)**) of the Ti(M)-ATA catalysts (M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au).

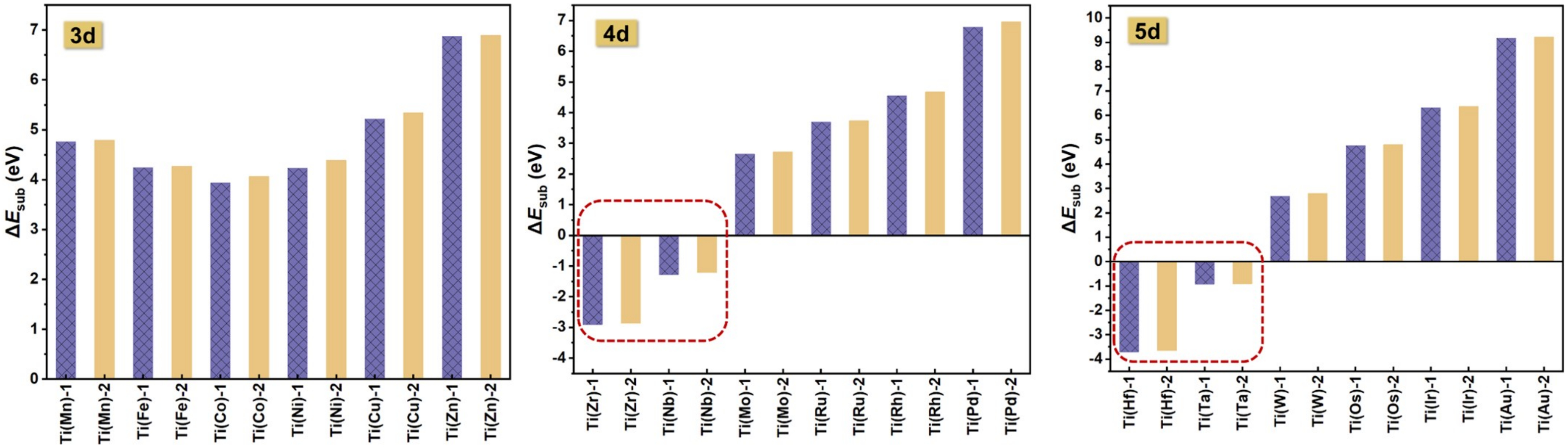


Fig. S2. The calculated substitution energies of two different configurations of metal-modified nodes of the Ti(M)-ATA catalysts (M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au).

Note: The formula for substitution energy calculation is: Ti-ATA + 2M → Ti(M)-ATA + 2Ti (M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au). The substitution energy (ΔE_{sub}) of Ti(M)-ATA is determined by the equation of $\Delta E_{\mathrm{sub}} = E_{\mathrm{Ti(M)\text{-}ATA}} + 2E_{\mathrm{Ti}} - E_{\mathrm{Ti\text{-}ATA}} - 2E_{\mathrm{M}}$ where $E_{\mathrm{Ti(M)\text{-}ATA}}$, $E_{\mathrm{Ti\text{-}ATA}}$, E_{M}, and E_{Ti} represent the DFT energy of Ti(M)-ATA, the DFT energy of Ti-ATA, and the energies of single atom M and Ti, respectively.

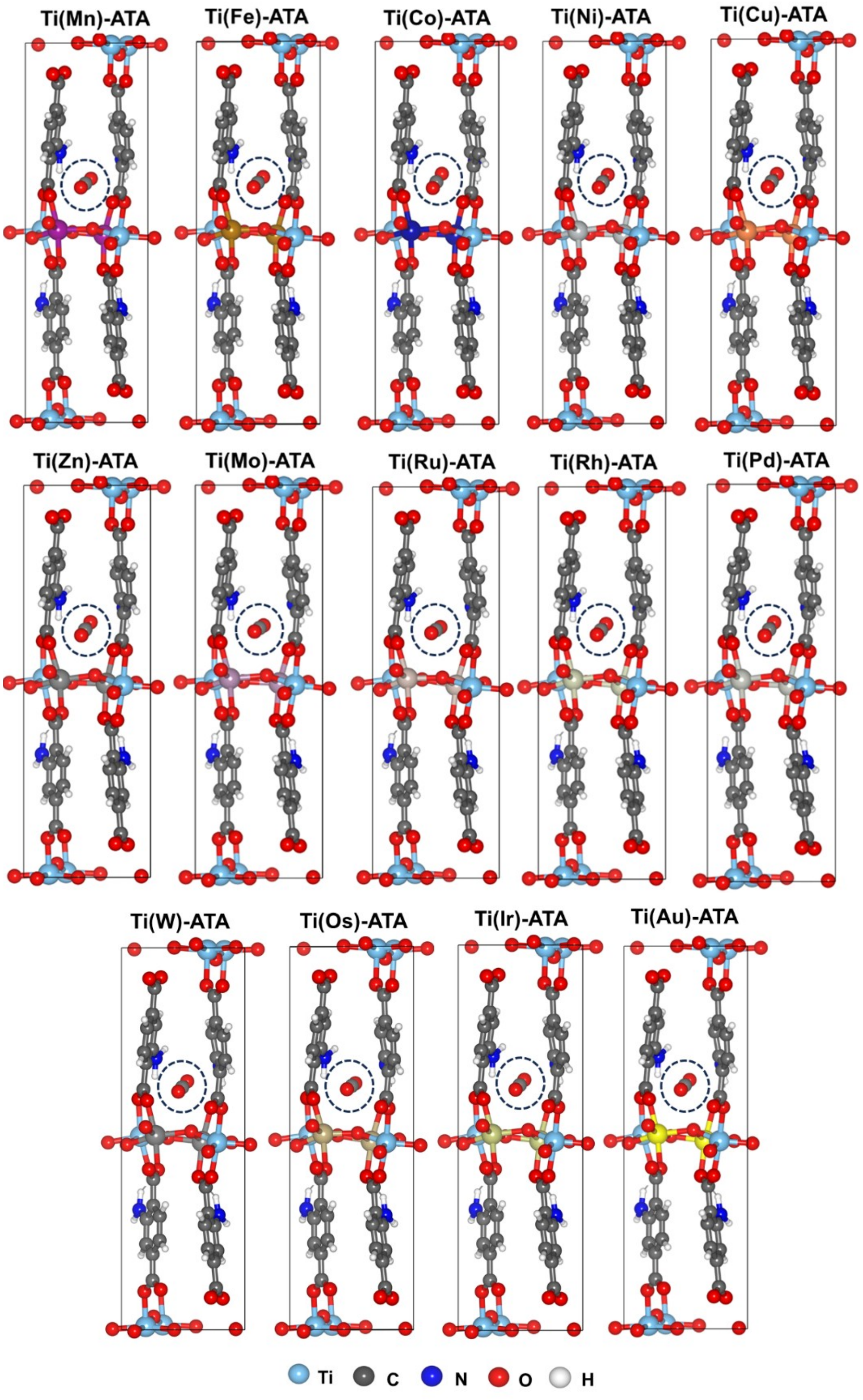


Fig. S3. The optimized adsorption configurations of CO_2 molecule on metal-modified **structure 1** (as shown in **Fig. 1(d)**) of Ti(M)-ATA (M = Mn, Fe, Co, Ni, Cu, Zn, Mo, Ru, Rh, Pd, W, Os, Ir, Au).

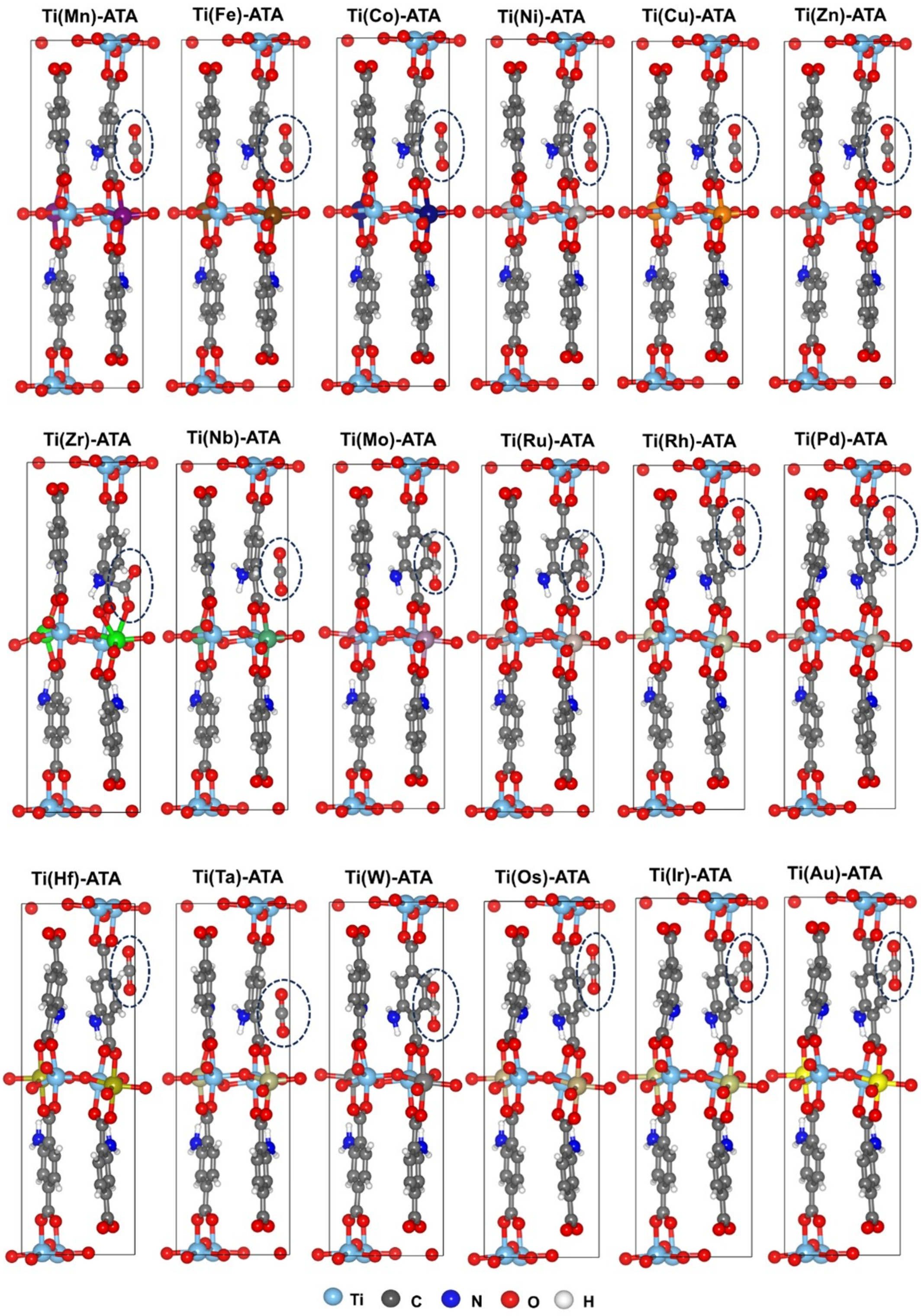


Fig. S4. The optimized adsorption configurations of CO_2 molecule on metal-modified **structure 2** (as shown in **Fig. 1(d)**) of Ti(M)-ATA (M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au).

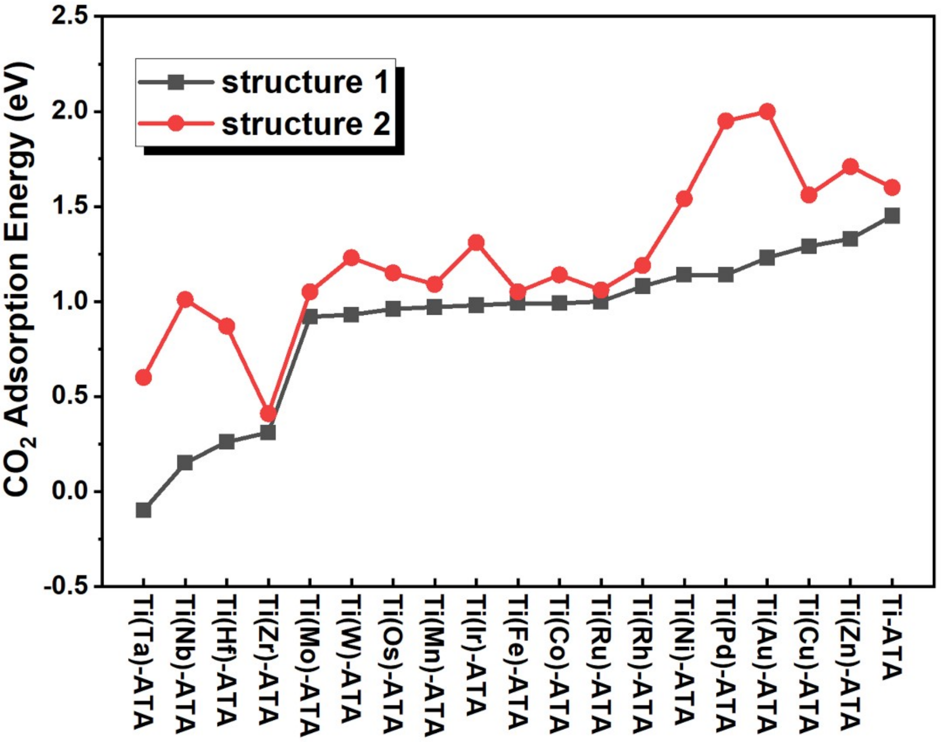
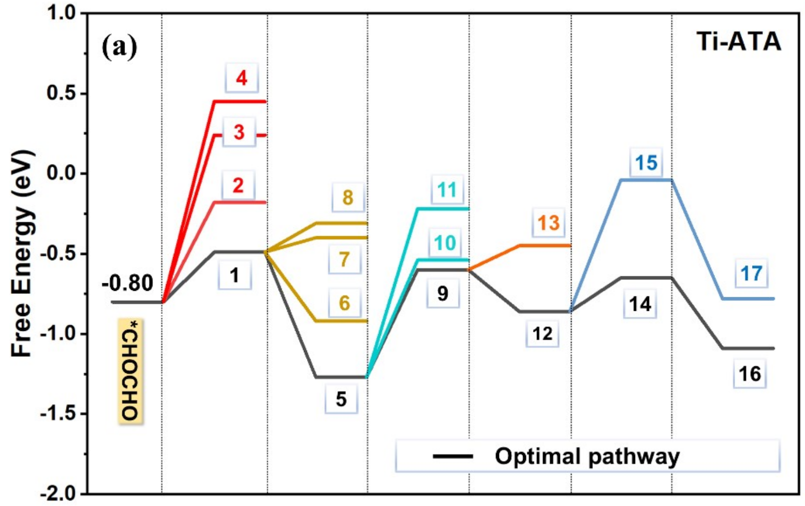


Fig. S5. The calculated adsorption energy of CO_2 on metal-modified model **structure1** and **structure 2** of Ti(M)-ATA (M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au) and pristine Ti-ATA catalysts.



Optimal pathway

1 *CHOCHOH：-0.49

5 *CHOCH：-1.27

9 $*CHOCH_2$：-0.60

12 $*CHOHCH_2$：-0.86

14 $*CHCH_2$：-0.65

16 $*CH_2CH_2$：-1.09

Other possible pathways

2 $*CHOCH_2O$：-0.18

3 *CHOHCHO：0.24

4 $*CH_2OCHO$：0.45

6 *CHOHCHOH：-0.92

7 $*CH_2OCHOH$：-0.40

8 $*CHOCH_2OH$：-0.31

10 $*CH_2OCH$：-0.54

11 *CHOHCH：-0.22

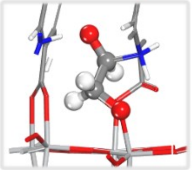
13 $*CH_2OCH_2$：-0.45

15 $*CH_2OHCH_2$：-0.04

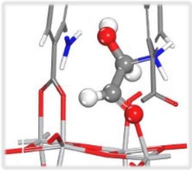
17 $*CH_2OHCH_3$：-0.78

Ti-ATA

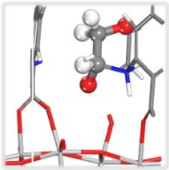
2:$*CHOCH_2O$



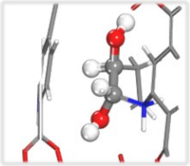
3:*CHOHCHO



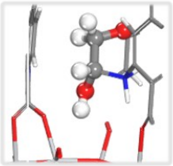
4:$*CH_2OCHO$



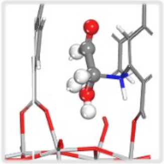
6:*CHOHCHOH



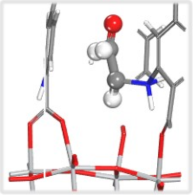
7:$*CH_2OCHOH$



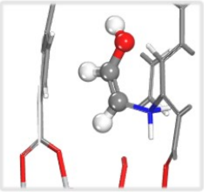
8:$*CHOCH_2OH$



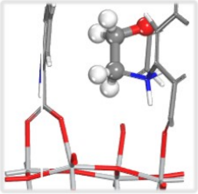
10:$*CH_2OCH$



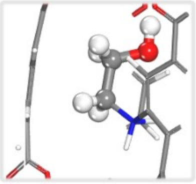
11:*CHOHCH



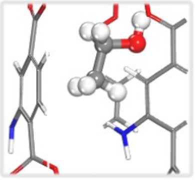
13:$*CH_2OCH_2$

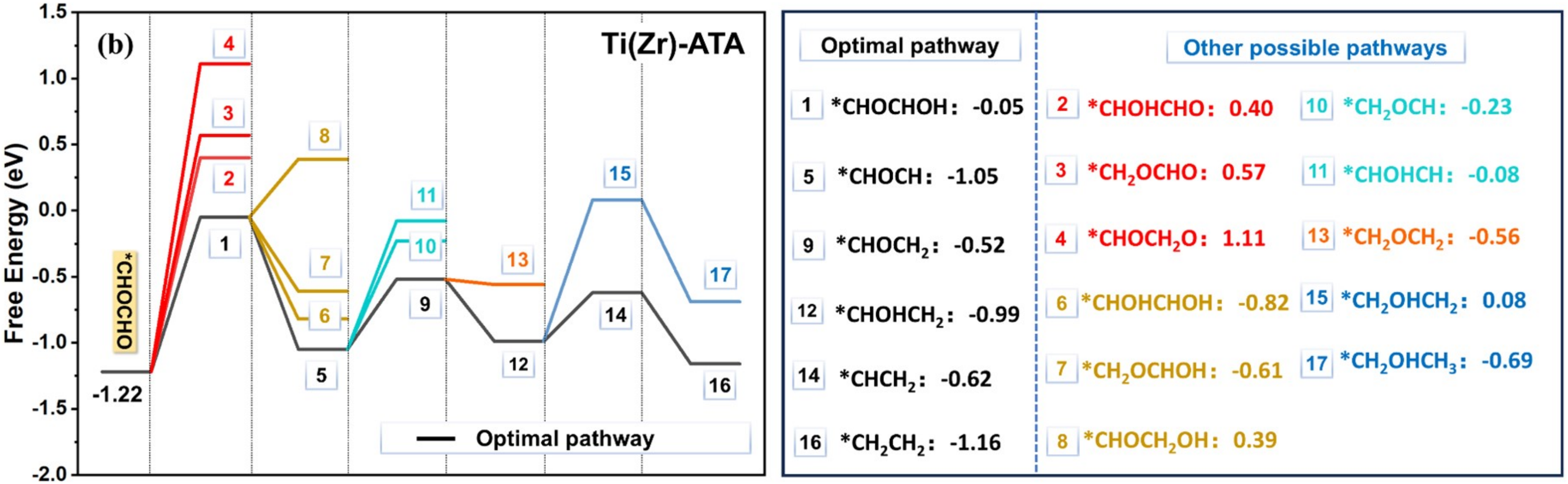


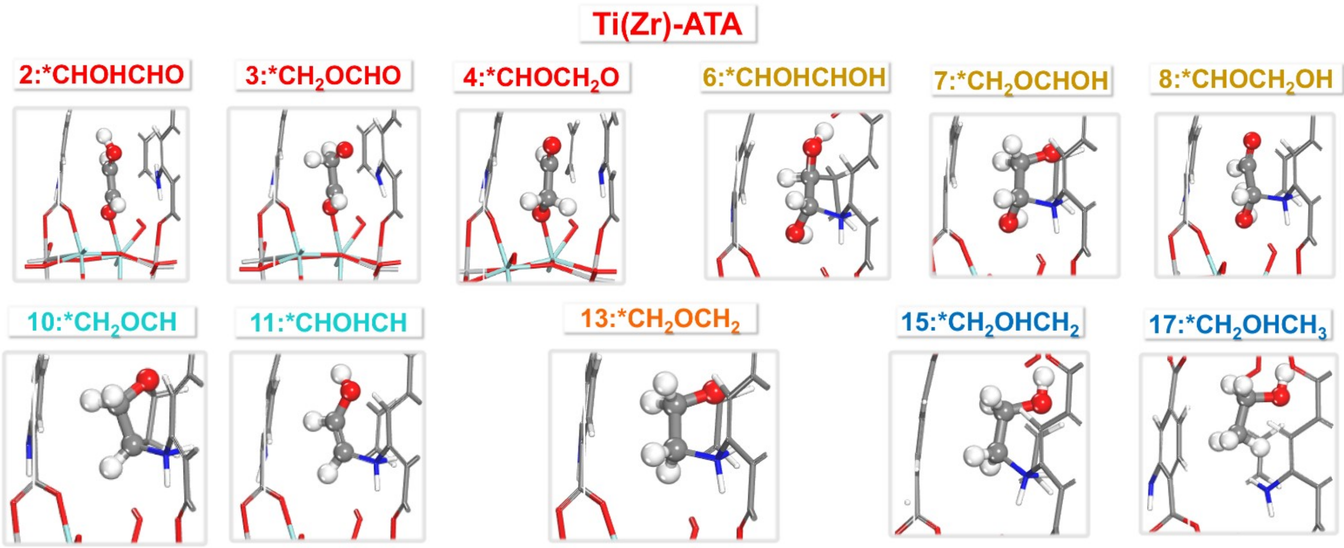
15:$*CH_2OHCH_2$

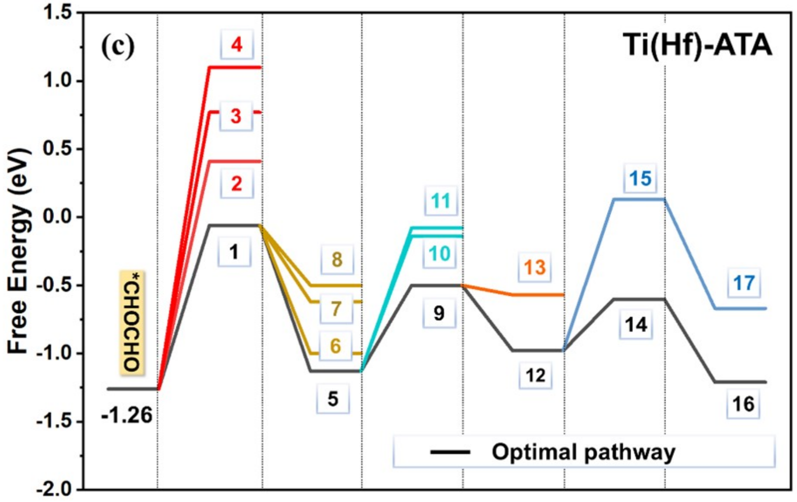


17:$*CH_2OHCH_3$




(b)
Ti(Zr)-ATA
Free Energy (eV)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
*CHOCHO
-1.22
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Optimal pathway
Optimal pathway
1 *CHOCHOH：-0.05
5 *CHOCH：-1.05
9 $*CHOCH_2$：-0.52
12 $*CHOHCH_2$：-0.99
14 $*CHCH_2$：-0.62
16 $*CH_2CH_2$：-1.16
Other possible pathways
2 *CHOHCHO：0.40
3 $*CH_2OCHO$：0.57
4 $*CHOCH_2O$：1.11
6 *CHOHCHOH：-0.82
7 $*CH_2OCHOH$：-0.61
8 $*CHOCH_2OH$：0.39
10 $*CH_2OCH$：-0.23
11 *CHOHCH：-0.08
13 $*CH_2OCH_2$：-0.56
15 $*CH_2OHCH_2$：0.08
17 $*CH_2OHCH_3$：-0.69


Ti(Zr)-ATA
2:*CHOHCHO
3:$*CH_2OCHO$
4:$*CHOCH_2O$
6:*CHOHCHOH
7:$*CH_2OCHOH$
8:$*CHOCH_2OH$
10:$*CH_2OCH$
11:*CHOHCH
13:$*CH_2OCH_2$
15:$*CH_2OHCH_2$
17:$*CH_2OHCH_3$



Optimal pathway

1 $*CHOCHOH$: -0.06

5 $*CHOCH$: -1.13

9 $*CHOCH_2$: -0.50

12 $*CHOHCH_2$: -0.98

14 $*CHCH_2$: -0.60

16 $*CH_2CH_2$: -1.21

Other possible pathways

2 $*CHOHCHO$: 0.41

3 $*CH_2OCHO$: 0.77

4 $*CHOCH_2O$: 1.10

6 $*CHOHCHOH$: -1.00

7 $*CH_2OCHOH$: -0.62

8 $*CHOCH_2OH$: -0.50

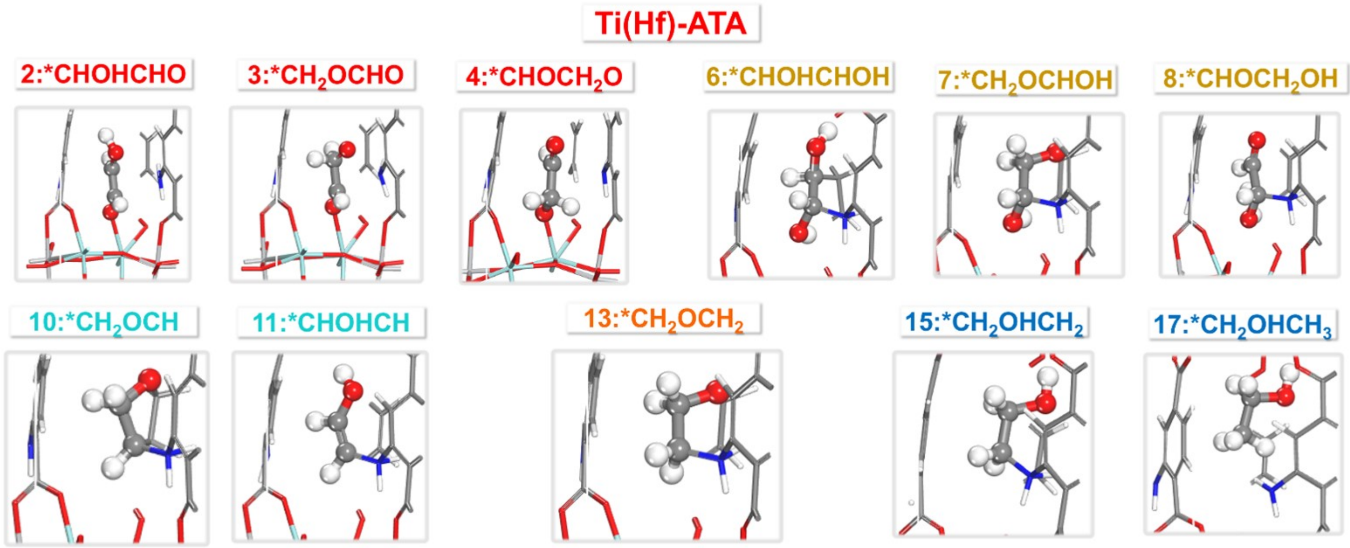
10 $*CH_2OCH$: -0.14

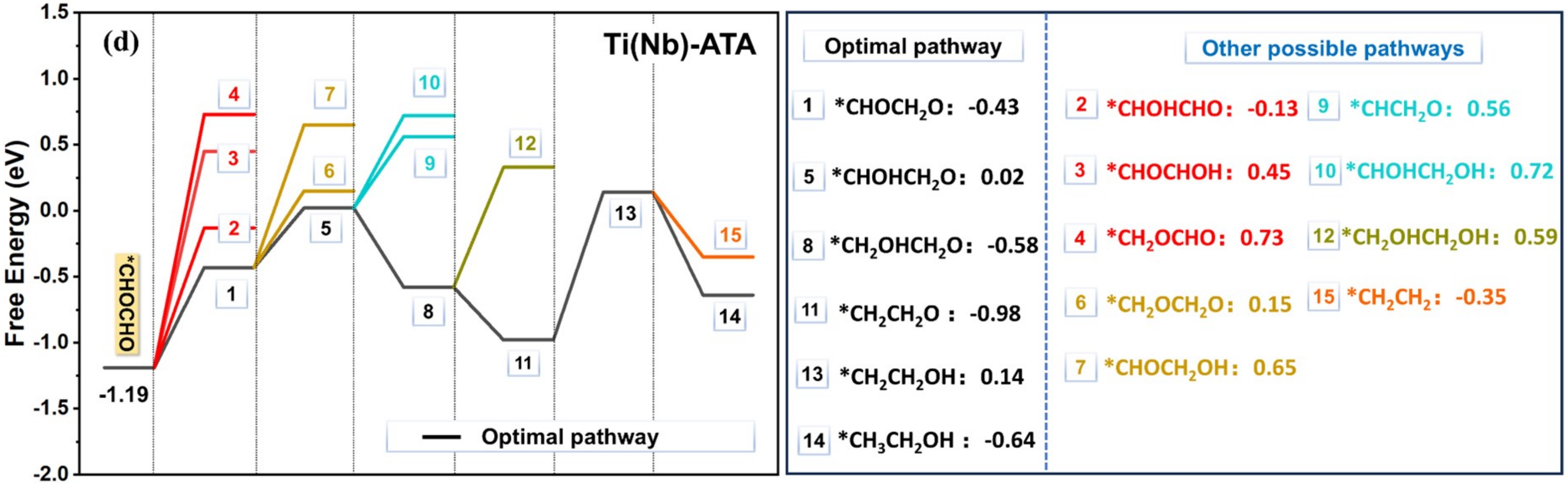
11 $*CHOHCH$: -0.08

13 $*CH_2OCH_2$: -0.57

15 $*CH_2OHCH_2$: 0.13

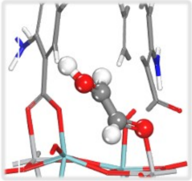
17 $*CH_2OHCH_3$: -0.67



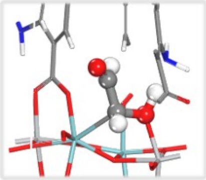


Ti(Nb)-ATA

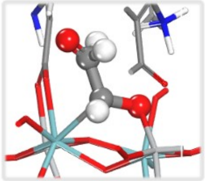
2:*CHOHCHO



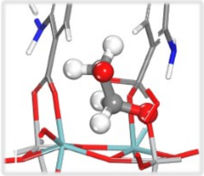
3:*CHOCHOH



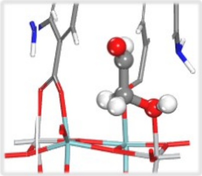
4:*CH$_2$OCHO



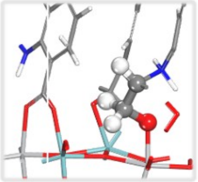
6:*CH$_2$OCH$_2$O



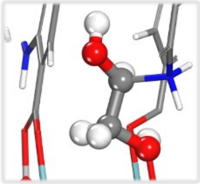
7:*CHOCH$_2$OH



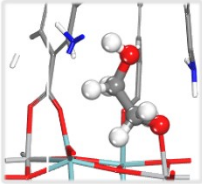
9:*CHCH$_2$O



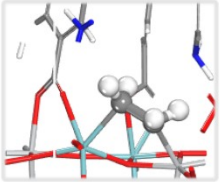
10:*CHOHCH$_2$OH

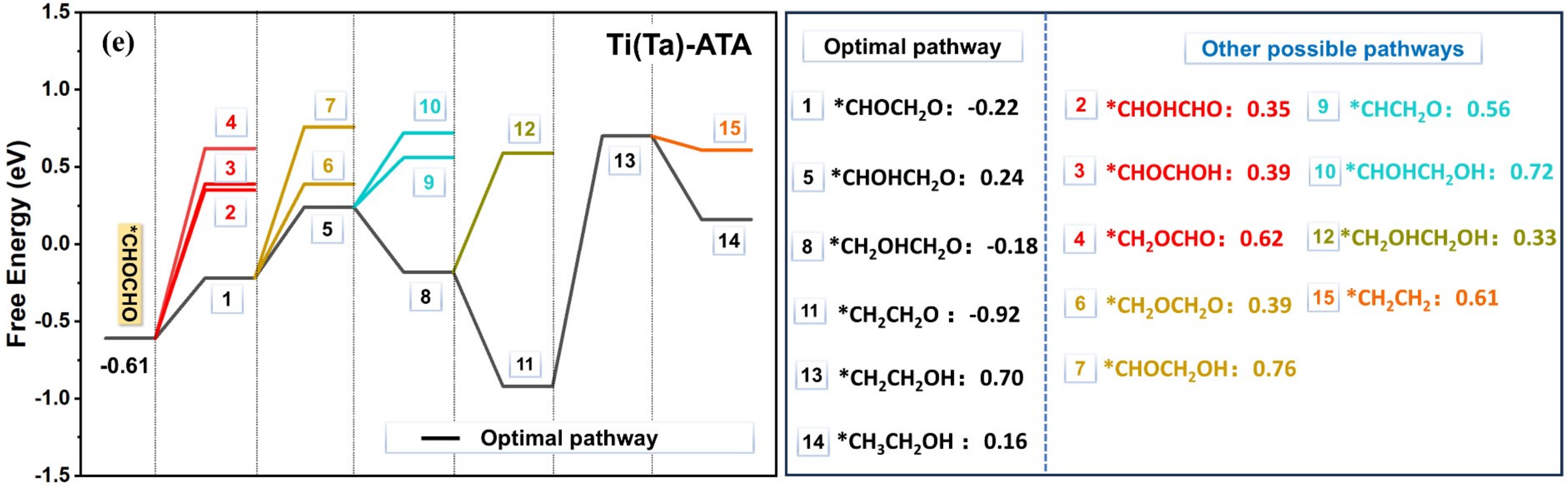


12:*CH$_2$OHOCH$_2$OH



15:*CH$_2$CH$_2$




(e)
Ti(Ta)-ATA
Free Energy (eV)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
*CHOCHO
-0.61
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Optimal pathway
Optimal pathway
1 *CHOCH$_2$O: -0.22
5 *CHOHCH$_2$O: 0.24
8 *CH$_2$OHCH$_2$O: -0.18
11 *CH$_2$CH$_2$O : -0.92
13 *CH$_2$CH$_2$OH: 0.70
14 *CH$_3$CH$_2$OH : 0.16
Other possible pathways
2 *CHOHCHO: 0.35
3 *CHOCHOH: 0.39
4 *CH$_2$OCHO: 0.62
6 *CH$_2$OCH$_2$O: 0.39
7 *CHOCH$_2$OH: 0.76
9 *CHCH$_2$O: 0.56
10 *CHOHCH$_2$OH: 0.72
12 *CH$_2$OHCH$_2$OH: 0.33
15 *CH$_2$CH$_2$: 0.61

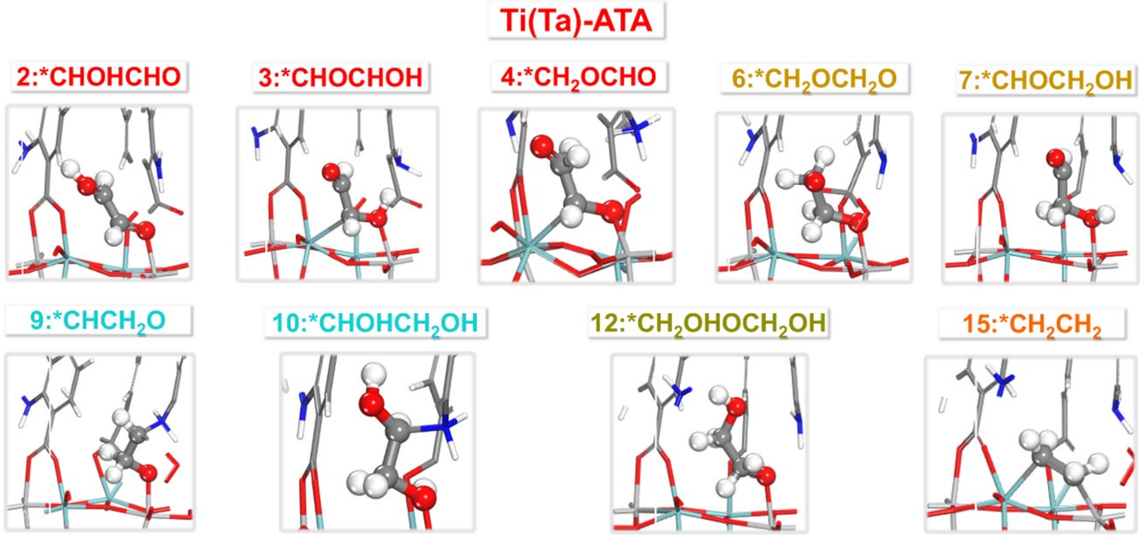

Ti(Ta)-ATA
2:*CHOHCHO
3:*CHOCHOH
4:*CH$_2$OCHO
6:*CH$_2$OCH$_2$O
7:*CHOCH$_2$OH
9:*CHCH$_2$O
10:*CHOHCH$_2$OH
12:*CH$_2$OHOCH$_2$OH
15:*CH$_2$CH$_2$

Fig. S6. The calculated Gibbs free energy diagrams of the optimal reaction pathway and other possible pathways for the reduction of CO_2 to C_2 (C_2H_4 and C_2H_5OH) products on (a) pristine Ti-ATA, (b) Ti(Zr)-ATA, (c) Ti(Hf)-ATA, (d) Ti(Nb)-ATA, and (e) Ti(Ta)-ATA, as well as the optimized structures of intermediate species. The MOF framework structure is omitted for clarity.

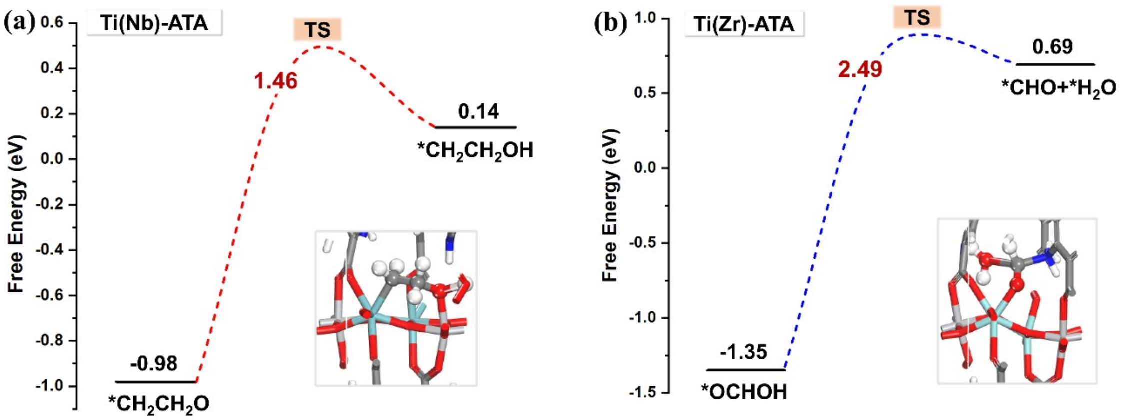


Fig. S7. Free energy diagrams involving kinetic barriers for the rate-determining step for C_2 product generation over (a) Ti(Nb)-ATA and (b) Ti(Zr)-ATA.

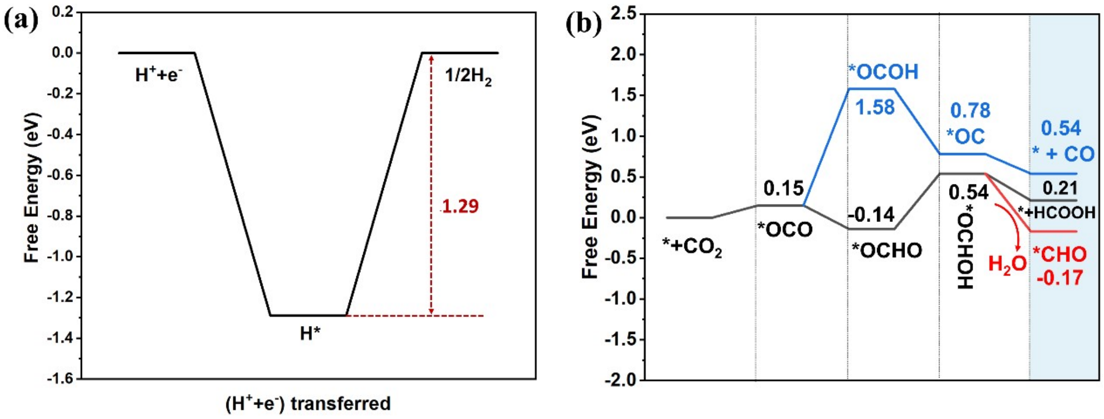


Fig. S8. (a) The calculated Gibbs free energy diagrams for (a) HER, and (b) CO and HCOOH production from CO_2 on Ti(Nb)-ATA.

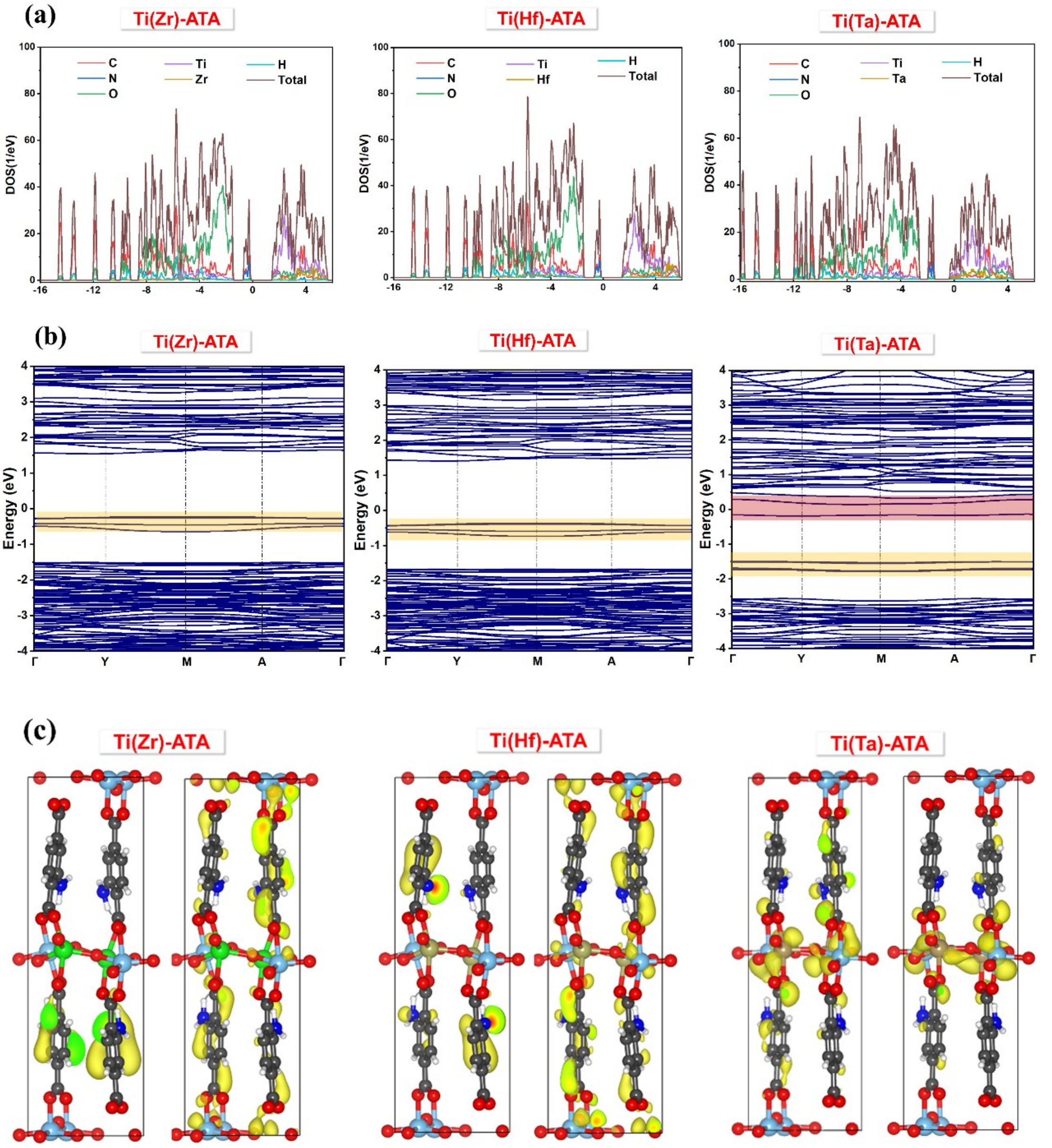


Fig. S9. The calculated (a) total and projected density of states (TDOS and PDOS), Fermi energy level set to zero. (b) energy band structures of Ti(M)-ATA (M = Zr, Hf, Ta). (c) The calculated valence-band maximum (VBM) (left side) and conduction-band minimum (CBM) (right side) of Ti(M)-ATA (M = Zr, Hf, Ta).

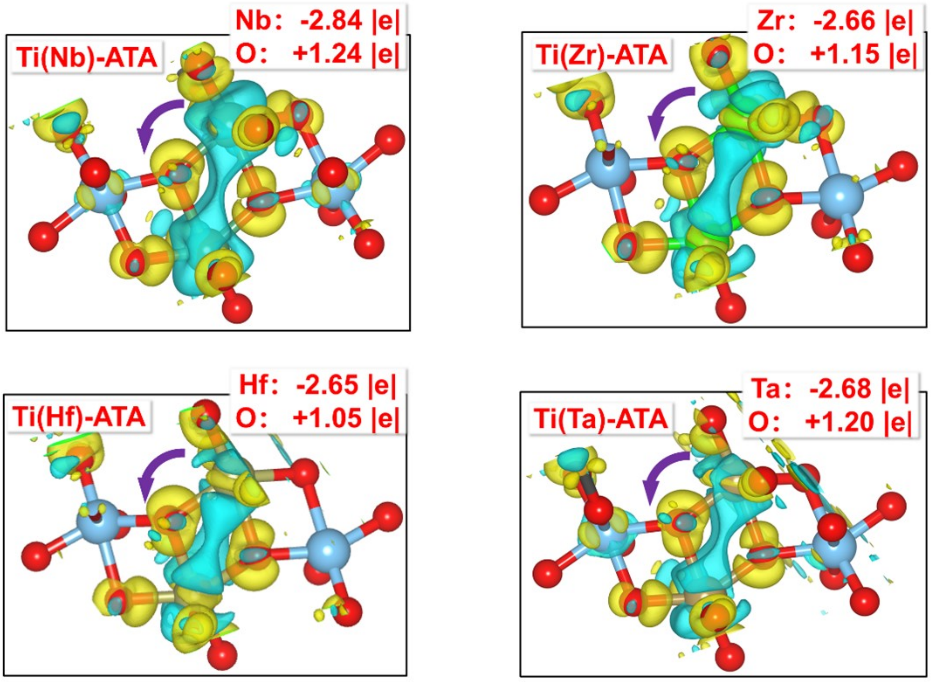


Fig. S10. The calculated differential charge density maps of the Ti(M)-ATA (M = Nb, Zr, Hf, Ta) catalysts. The Fermi level was set to zero; the isosurface value was set to 0.005 e Å^{-3}; cyan and yellow regions in the differential charge density map represent positive and negative charges, respectively.

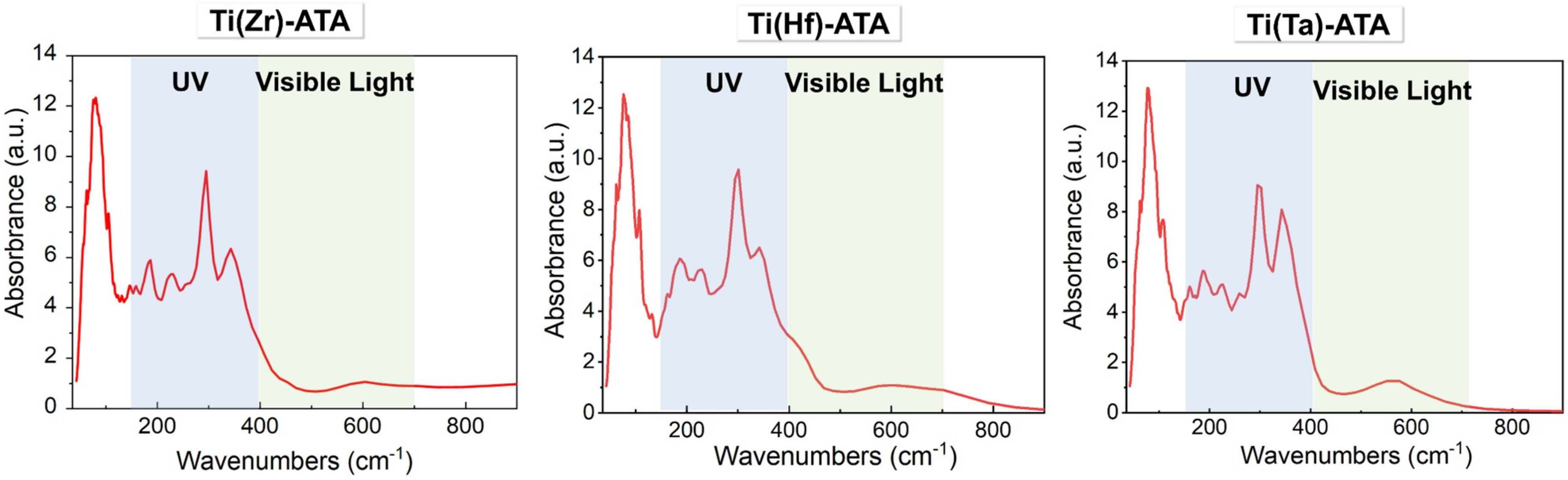


Fig. S11. The optical absorption spectra for other Ti(M)-ATA (M=Zr, Hf, Ta).

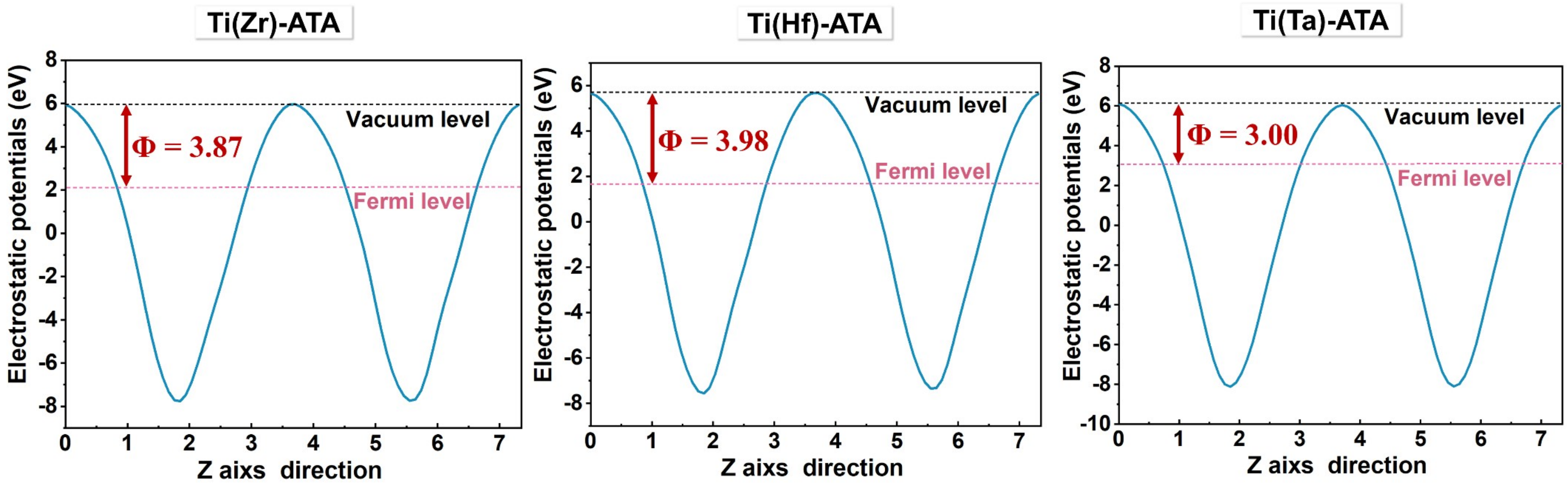


Fig. S12. The electrostatic potential profiles of other Ti(M)-ATA (M=Zr, Hf, Ta).

Table S1. The values of U_{eff} parameters for DFT calculations in this work.

3*d*	**Ti**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
U_{eff}/eV	3.0	3.0	3.0	3.4	3.4	3.8	4.1

4*d*	**Zr**	**Nb**	**Mo**	**Ru**	**Rh**	**Pd**
U_{eff}/eV	2.0	2.0	2.2	2.4	2.8	3.3

5*d*	**Hf**	**Ta**	**W**	**Os**	**Ir**	**Au**
U_{eff}/eV	2.7	3.1	2.2	2.2	2.3	/

Table S2. The zero-point energy (ZPE) values for all adsorbed species involved in CO_2 reduction to C_2 products over the pristine Ti-ATA and metal-modified Ti(M)-ATA (M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au) catalysts.

Adsorbate	**ZPE**	**Adsorbate**	**ZPE**
$^*CO_2$	0.33	$^*CH_2OHCH_2$	1.90
$^*OCOH$	0.62	$^*CHCH_2$	1.18
$^*OCHO$	0.63	$^*CH_3CH_2OH$	2.18
$^*OCHOH$	0.87	$^*CH_2CH_2$	1.47
$^*CHO$	0.53	$^*CH_2OCH_2O$	1.75
$^*CHO$-$^*CHO$	1.04	$^*CHOHCH_2O$	1.74
$^*CHOCHOH$	1.36	$^*CHCH_2O$	1.33
$^*CHOHCHO$	1.36	$^*CH_2OHCH_2O$	2.02
$^*CHOCH_2O$	1.33	$^*CHOHCH_2OH$	2.00
$^*CH_2OCHO$	1.33	$^*CH_2OHCH_2OH$	2.34
$^*CHOHCHOH$	1.75	$^*CH_2CH_2O$	1.61
$^*CH_2OCHOH$	1.74	$^*CH_2CH_2OH$	1.87
$^*CHOHCH$	1.29	$^*CHOCH_2OH$	1.68
$^*CH_2OCH$	1.33	$^*CHOCH$	0.91
$^*CHOCH_2$	1.27	H_2O	0.58
$^*CH_2OCH_2$	1.61	H_2	0.27
$^*CHOHCH_2$	1.60	CO_2	0.31

Table S3. The calculated substitution energies (ΔE_{sub}) of two different node configurations via metal atom modification of the Ti(M)-ATA (M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au) catalysts.

Ti(M)-ATA	**1 (ΔE_{sub})(eV)**	**2 (ΔE_{sub})(eV)**
Ti(Mn)	4.76	4.79
Ti(Fe)	4.24	4.27
Ti(Co)	3.93	4.06
Ti(Ni)	4.23	4.39
Ti(Cu)	5.21	5.34
Ti(Zn)	6.87	6.89
Ti(Zr)	-2.90	-2.86
Ti(Nb)	-1.28	-1.21
Ti(Mo)	2.64	2.71
Ti(Ru)	3.69	3.73
Ti(Rh)	4.54	4.67
Ti(Pd)	6.78	6.95
Ti(Hf)	-3.70	-3.65
Ti(Ta)	-0.93	-0.91
Ti(W)	2.67	2.79
Ti(Os)	4.76	4.79
Ti(Ir)	6.31	6.37
Ti(Au)	9.16	9.21

Table S4. Adsorption energies (E_{ads}) of CO_2 molecule on different metal-modified model structures (1 and 2) of Ti(M)-ATA (M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au) and pristine Ti-ATA catalysts.

Ti(M)-ATA	**structure1(E_{ads})**	**structure2 (E_{ads})**
Ti-ATA	1.45	1.60
Ti(Mn)	0.97	1.09
Ti(Fe)	0.99	1.05
Ti(Co)	0.99	1.14
Ti(Ni)	1.14	1.54
Ti(Cu)	1.29	1.56
Ti (Zn)	1.33	1.71
Ti(Zr)	0.31	0.41
Ti(Nb)	0.15	1.01
Ti(Mo)	0.92	1.05
Ti(Ru)	1.00	1.06
Ti(Rh)	1.08	1.19
Ti(Pd)	1.14	1.95
Ti(Hf)	0.26	0.87
Ti(Ta)	-0.10	0.60
Ti(W)	0.93	1.23
Ti(Os)	0.96	1.15
Ti(Ir)	0.98	1.31
Ti(Au)	1.23	2.00

Table S5. The calculated activation barrier based on Gibbs free energy (ΔG_{act}/eV) and reaction rate constant (k_{cat}) of the rate-determining step for CO_2 to C_2 product over Ti(Nb)-ATA and Ti(Zr)-ATA.

	ΔG_{act}	k_{cat}
Ti(Nb)-ATA	1.46	2.51×10^{-14}
Ti(Zr)-ATA	2.49	2.83×10^{-33}

Note: The reaction rate constant k_{cat} is calculated based on Arrhenius equation:

$$k_{cat} = \frac{k_B T}{h} e^{-\frac{\Delta Gact}{RT}}$$

in which T is temperature, R is gas constant, k_B is Boltzmann constant, h is Planck nstant, and ΔG_{act} is Gibbs free energy barrier.

Table S6. The values of work function, vacuum energy level and Fermi energy level for Ti-ATA and Ti(M)-ATA.

	Work function (eV)	**Vacuum level (eV)**	**Fermi level (eV)**
Ti(Nb)-ATA	2.91	5.92	3.00
Ti(Ta)-ATA	3.00	6.09	3.09
Ti(Zr)-ATA	3.87	5.96	2.09
Ti(Hf)-ATA	3.98	5.67	1.69
Ti-ATA	4.23	5.95	1.73