Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting material for

Efficient Degradation of Formaldehyde Based on DFT-Screened Metal-Doped C_3N_6 Monolayer Photocatalysts: Performance Evaluation and Mechanistic Insights

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Calculation method details

To ensure accurate screening for high-performance transition metals, we calculated the binding energy (Eb) of TM embedded in C_3N_6. This approach allowed us to gain insights into the stability and interaction between the transition metals and C_3N_6, enabling us to identify potential candidates for high-performance applications.

$$E_b = E_{M-C_3N_6} - E_M - E_{C_3N_6}$$

$$E_M = E_{M-bulk} / n$$

where E_M, $E_{C3N6,}$ and $E_{M\text{-}C3N6}$ are the energy of the bulk metal averaged over each atom, and C_3N_6 and the energy of C_3N_6 are immobilized by a single metal atom, respectively. $E_{M\text{-}bulk}$ and N are the energy of the bulk metal and the number of metal atoms in the bulk metal unit, respectively. To prevent the TM from clumping, we also considered the cohesive energy of the TM itself. We calculated the difference between the binding energy and the cohesive energy of the system (ΔEf) using the following equation：

$$\Delta E_f = E_b - E_c$$
$$E_c = E_M - E_s$$

where E_b is the binding energy of the TM embedded in C_3N_6, Ec is the cohesion energy of the TM, E_M is the energy of the bulk metal averaged over each atom, and Es is the energy of a single atom. The energy of adsorption (E_{ads}) of HCHO is calculated as follows:

$$E_{ads} = E_{HCHO\text{-}M\text{-}C_3N_6} - E_{M\text{-}C_3N_6} - E_{HCHO}$$

Where $E_{HCHO\text{-}M\text{-}C3N6}$ is the total energy of a surface interacting with adsorbate, $E_{HCHO,}$ and $E_{M\text{-}C3N6}$ are the energies of the isolated adsorbate and clean surface, respectively.

To analyze the different reaction paths, the Gibbs free energy was calculated for every gas and adsorbed material based on this expression at 298.15k, 1 atom [37].

$$G = E_{DFT} + E_{ZPE} - TS$$

Where E_{DFT} shows the free energy calculated with VASP, E_{ZPE} is the zero-point energy and TS is the entropic contribution. The E_{ZPE} and TS are calculated from temperature, pressure, and vibration energy using the standard ideal gas method.

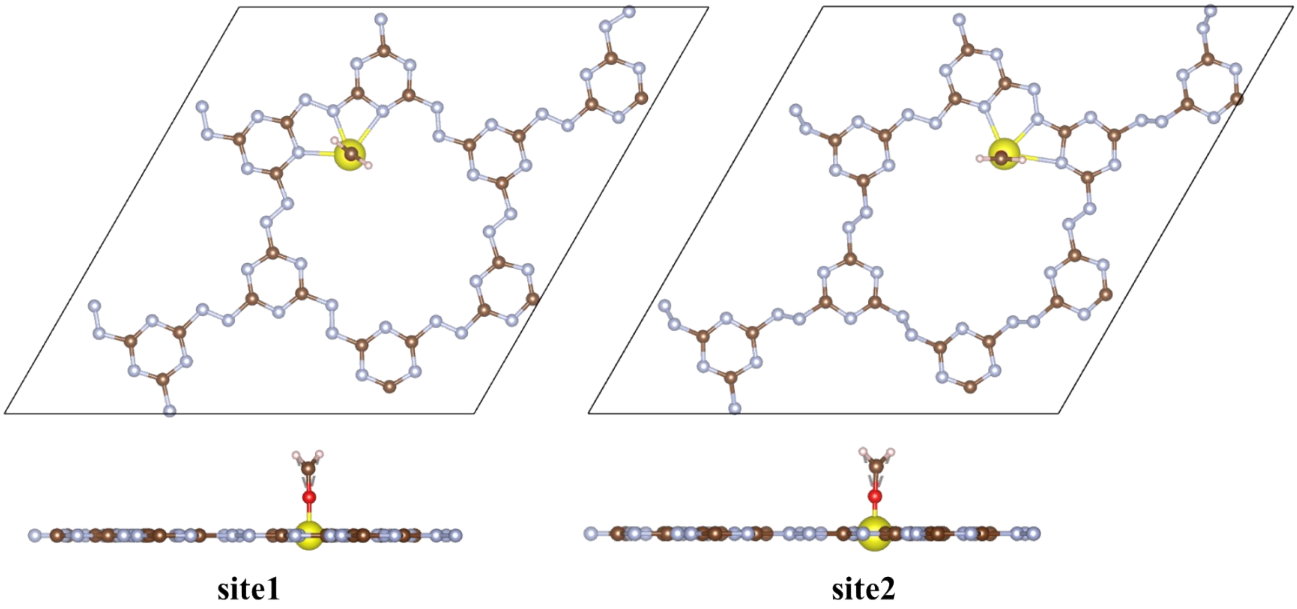
We use the Gaussian 16 package to calculate the topological analysis of the electronic delocalization

function of HCHO using the B3LYP method of density-functional theory calculations under the 6-31+G** group. The analyses were performed using Multiwfn1 and VMD software.

Table S1 Formaldehyde at TM-C_3N_6 site 1, energy at site 2, and energy at TM-C_3N_6

System	Energy-site 1-(HCHO)	Energy-site 2-(HCHO)	Energy-slab-site 1
Sc	-618.11	-617.98	-592.36
Ti	-618.15	-618.09	-592.37
V	-618.65	-618.54	-593.12
Cr	-617.99	-617.65	-593.18
Mn	-616.52	-616.43	-592.29
Fe	-616.16	-616.15	-590.54
Co	-615.19	-615.23	-589.69
Ni	-613.95	-613.93	-588.73
Cu	-612.36	-612.36	-587.07
Zn	-610.61	-610.60	-585.09
Y	-618.54	-618.53	-593.26
Zr	-619.15	-619.15	-593.29
Nb	-618.66	-618.66	-593.32
Mo	-617.95	-617.92	-592.22
Tc	-617.24	-616.98	-591.60
Ru	-616.34	-616.32	-591.01
Rh	-615.09	-615.22	-589.97
Pd	-613.31	-613.28	-588.00
Ag	-610.96	-610.93	-586.12
Cd	-608.62	-608.71	-584.56
Hf	-620.41	-620.23	-594.55
Ta	-619.92	-619.29	-593.94
W	-619.28	-619.29	-593.28
Re	-618.05	-617.97	-592.65
Os	-617.42	-617.12	-591.70
Ir	-615.92	-616.14	-590.39
Pt	-613.92	-613.84	-588.29

Au	-608.89	-608.91	-585.66



FigureS1. Adsorption model of site1 and site2 for Metel doping in C_3N_6

Table S1. Adsorption energies of O_2, H2O, HCHO@O_2, CO_2, HCHO@H_2O, HCHO in C_3N_6, Zr-C_3N_6 and Hf-C_3N_6.

Adsorption structure	Total	slab	gas	HCHO	E*ads*
S-C_3N_6-N2-O_2-V	-592.37	-583.58	-9.86	0.00	1.06
S-C_3N_6-N2-O_2-p	-592.23	-583.58	-9.86	0.00	1.20
S-C_3N_6-N2-H_2O-V	-597.65	-583.58	-14.22	0.00	0.15
S-C_3N_6-N2-H_2O-P	-597.65	-583.58	-14.22	0.00	0.15
S-C_3N_6-Hf-CO_2	-617.64	-594.55	-22.96	0.00	-0.13
S-C_3N_6-Hf-H_2O-P	-609.84	-594.55	-14.22	0.00	-1.07
S-C_3N_6-Hf-H_2O-V	-609.87	-594.55	-14.22	0.00	-1.10
S-C_3N_6-Hf-HCHO@H_2O	-635.25	-594.55	-14.22	-22.14	-4.34
S-C_3N_6-Hf-HCHO@O_2	-632.92	-594.55	-9.86	-22.14	-6.37
S-C_3N_6-Hf-O_2-P	-608.53	-594.55	-9.86	0.00	-4.13
S-C_3N_6-Hf-O_2-V	-606.89	-594.55	-9.86	0.00	-2.49
S-C_3N_6-Hf-HCHO	-620.41	-594.55	0.00	-22.14	-3.72
S-C_3N_6-Zr-CO_2	-616.63	-593.29	-22.96	0.00	-0.39
S-C_3N_6-Zr-H_2O-P	-608.89	-593.29	-14.22	0.00	-1.39
S-C_3N_6-Zr-H_2O-V	-608.91	-593.29	-14.22	0.00	-1.40
S-C_3N_6-Zr-HCHO@O_2	-631.07	-593.29	-9.86	-22.14	-5.79
S-C_3N_6-Zr-HCHO@H_2O	-634.06	-593.29	-14.22	-22.14	-4.42
S-C_3N_6-Zr-O_2-V	-605.83	-593.29	-9.86	0.00	-2.69
S-C_3N_6-Zr-O_2-P	-607.32	-593.29	-9.86	0.00	-4.17
S-C_3N_6-Zr-HCHO	-619.15	-593.29	0.00	-22.14	-3.72

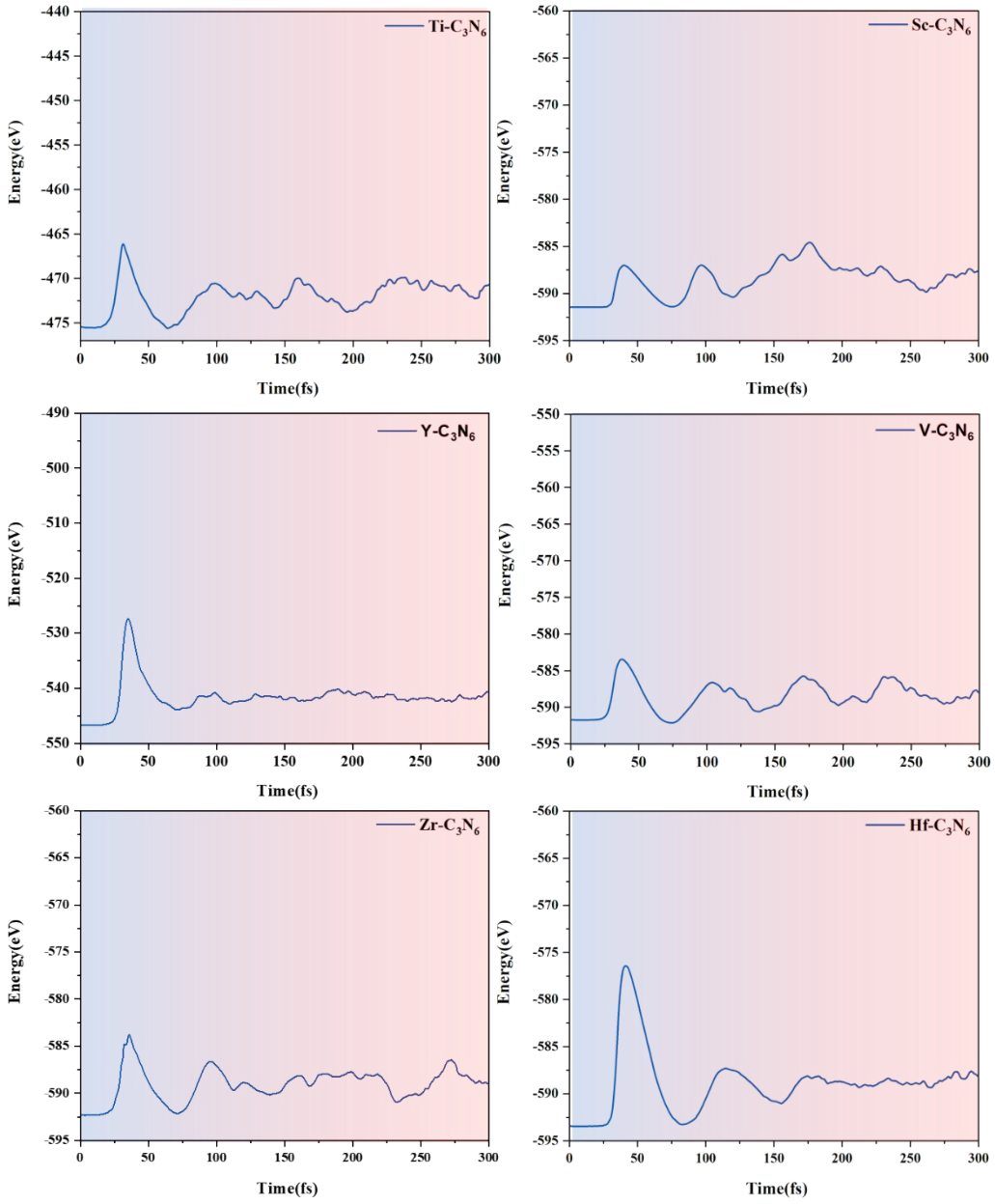


Fig S2 AIMD diagram of the TM-C_3N_6(Ti,Sc,Y,V,Zr,Hf)

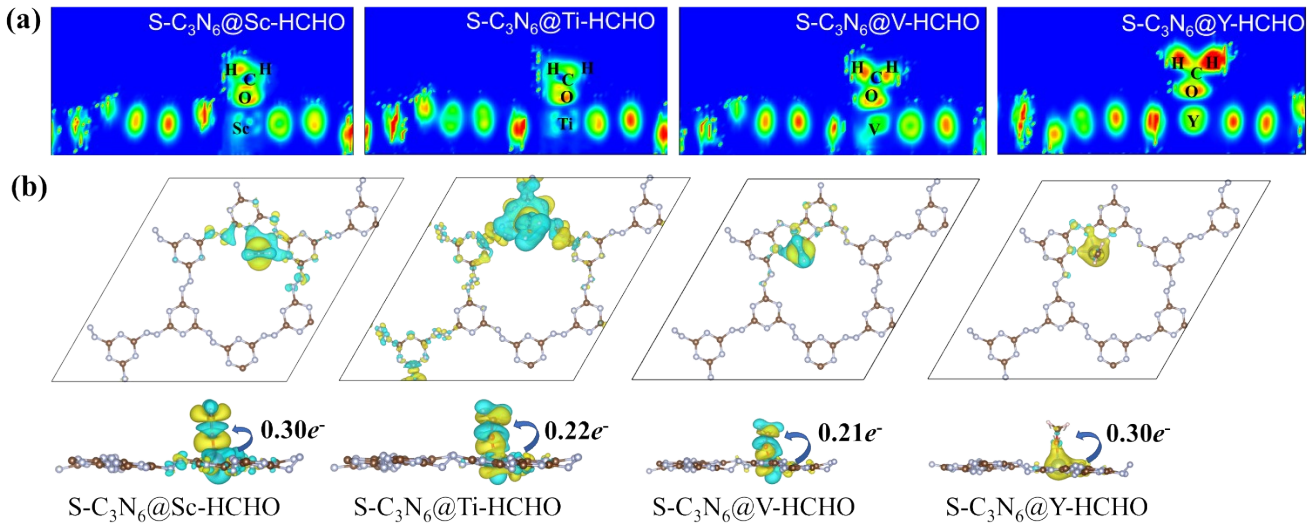


Figure S3. (a) ELF of HCHO adsorbed on TM-C3N6 (Sc, Ti, V, Y), respectively; (b) Differential charge density and charge transfer for HCHO adsorption by Sc, Ti, V, Y-embedded C_3N_6, respectively.

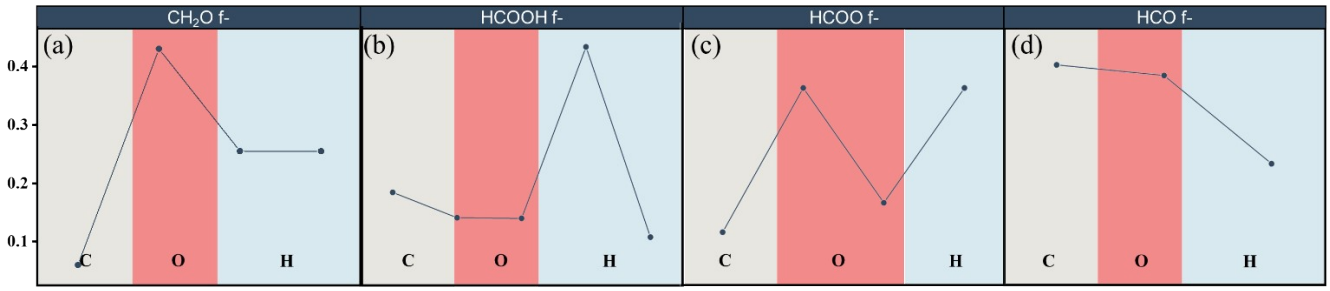


Figure S4. (a-d) Fukui functions (f^-) of intermediates from HCHO degradation into CO_2.

Gibbs free energy calculation：

***OH is involved in the degradation of formaldehyde:**

$$G = H - TS = U + PV - TS = E_{DFT} + E_{ZPE} + nRT - TS \quad (n=1$$

$$\Delta G[OH^*] = G[HCHO] + G[OH^*] + G\left[H^+ + e^-\right] - \left(G[^*] + G[HCHO] + G[H_2O]\right)$$

$$\Delta G[HCOOH^*] = G[HCOOH^*] + 2G\left[H^+ + e^-\right] - \left(G[^*] + G[HCHO] + G[H_2O]\right)$$

$$\Delta G[HCOO^*] = G[HCOO^*] + 3G\left[H^+ + e^-\right] - \left(G[^*] + G[HCHO] + G[H_2O]\right)$$

$$\Delta G[CO_2^*] = G[CO_2^*] + 4G\left[H^+ + e^-\right] - \left(G[^*] + G[HCHO] + G[H_2O]\right)$$

$$G\left[H^+ + e^-\right] = 1/2G[H_2] - eU$$

***O is involved in the degradation of formaldehyde:**

$$\Delta G[O^*] = G[HCHO] + G[O^*] - (G[^*] + G[HCHO] + G[O_2])$$

$$\Delta G[HCHOO^*] = G[HCHOO^*] + G[O] - (G[^*] + G[HCHO] + G[O_2])$$

$$\Delta G[HCOO^*] = G[HCOO^*] + G[OH] - (G[^*] + G[HCHO] + G[O_2])$$

$$\Delta G[CO_2^*] = G[CO_2^*] + G[H2O] - (G[^*] + G[HCHO] + G[O_2])$$

$$G[O] = 1/2G[O_2] - eU$$

Direct degradation of formaldehyde:

$$\Delta G[CHO^*] = G[CHO^*] + G[H] - (G[^*] + G[HCHO])$$

$$\Delta G[CO^*] = G[CO^*] + G[H2O] - (G[^*] + G[HCHO])$$