Supporting Information for

The catalytic oxidation of HCHO on metal single atom supported by defective graphene: Essential roles of *d*-electrons and radius of metal atom

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Supplementary Results

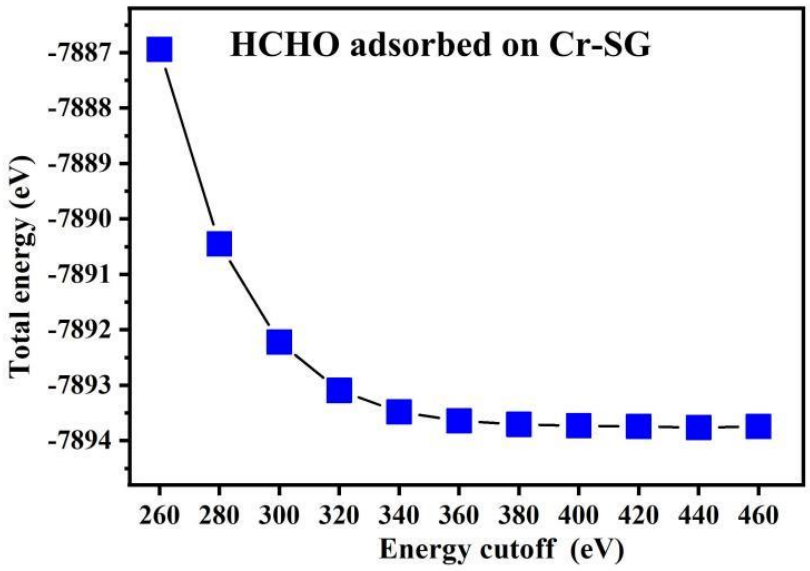

Fig. S1 Convergence test of the cutoff energy for the total energy of HCHO/Cr-SG system.

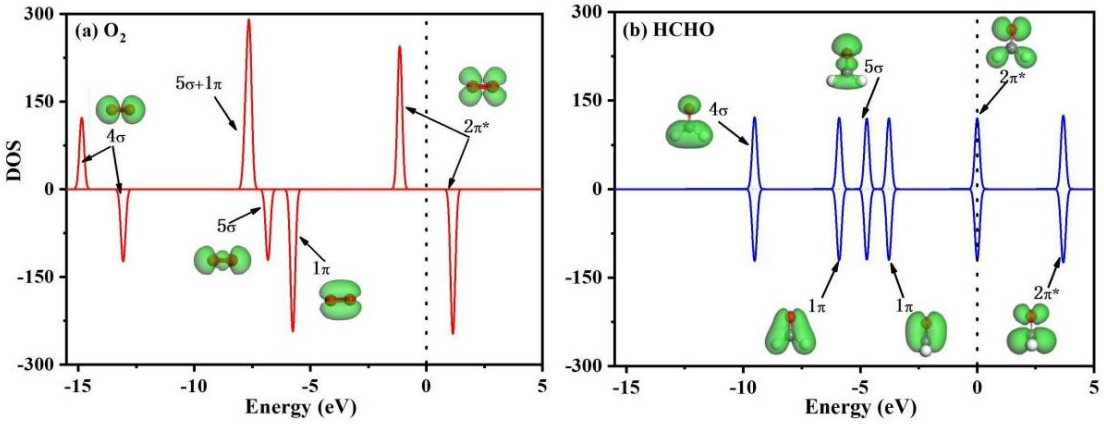

Fig. S2 PDOS of free O_2 molecule (a) and HCHO molecule (b), where the corresponding molecular orbitals are also shown.

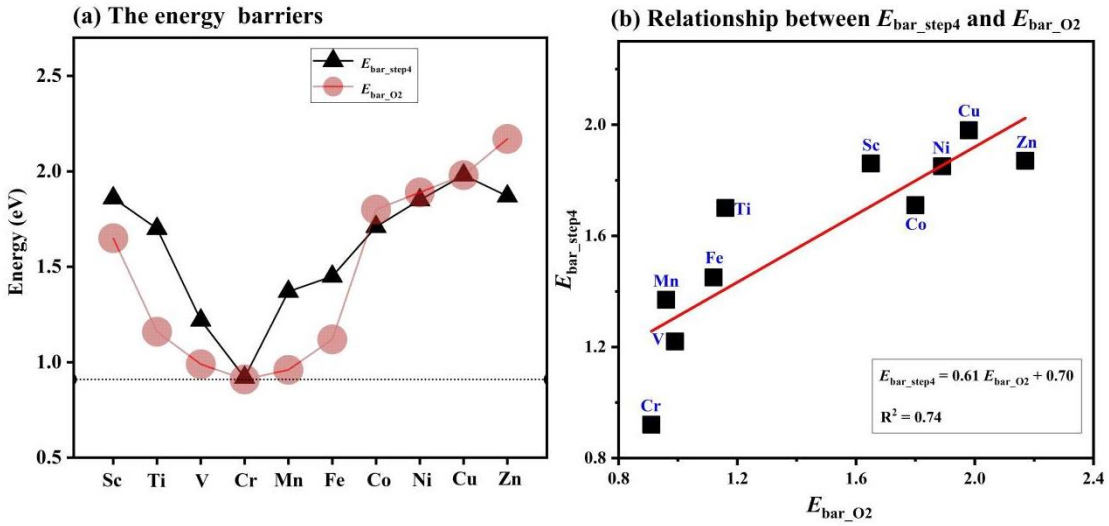

Fig. S3 The energy barriers E_{bar_step4} for HCHO oxidation and E_{bar_O2} for O_2 dissociation on M-SG. (b) The liner relationship between E_{bar_step4} and E_{bar_O2}.

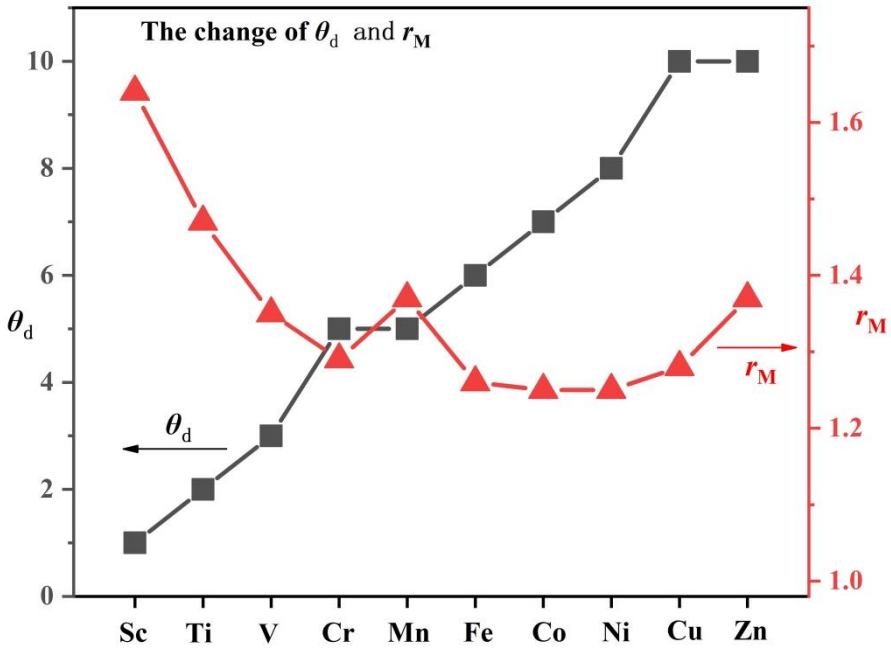

Fig. S4 The change of number of *d* electrons (θ_d) and atomic radius (r_M) for metal atoms form Sc to Zn.

Text S1 The correction of Gibbs free energy of along LH Path3

The correction of Gibbs free energy was considered to study the effect of temperature, which is defined by the following equation:

$$G = E + E_{ZPE} - TS \quad (1)$$

where E, E_{ZPE} and S indicate the DFT calculated total energy, zero-point vibration energy and entropy, respectively. Therefore, the Gibbs free energy barrier (G_{bar}) and reaction energy (G_r) of each reaction step are calculated as:

$$G_{bar} = G_{TS} - G_R \quad (2)$$

$$G_r = G_P - G_R \quad (3)$$

where G_R, G_{TS} and G_P represent the Gibbs free energies of the initial state, transition state,and final state for each reaction step, respectively.

Table S1 Gibbs free energy barrier (G_{bar}) and reaction energy (ΔG) of each step along LH Path3 at 298.15 K.

	Reaction barrier		Reaction energy	
	E_{bar}(eV)	G_{bar}(eV)	E_r(eV)	G_r(eV)
IS→ MS_1	0.15	0.19	-0.47	-0.27
MS_1→ MS_2	0.28	0.20	-2.70	-2.81
MS_2→ MS_3	0.10	0.14	0	-0.06
MS_3→ MS_4	0.92	0.87	0.11	0.05
MS_{4+O2}→ FS_2	0.26	0.27	-1.52	-1.48

Text S2 Comparative study of the dissociation barriers of O_2 and HCO_2 on Cr-SG

For O_2 molecule adsorbed on Cr-SG (see IS in Fig. 1), the binding energy E_{bind_O2} between O_2 and Cr-SG is calculated by using the following equation,

$$E_{bind\_O2} = E_{O2/Cr\text{-}SG} - (E'_{Cr\text{-}SG} + E'_{O2}) \quad (4)$$

where $E_{O2/Cr\text{-}SG}$ refers to the total energy of the O_2/Cr-SG system, while $E'_{Cr\text{-}SG}$ and E'_{O2} refer to the total energies of the Cr-SG and O_2 in the O_2/Cr-SG configuration, respectively. For example, $E'_{Cr\text{-}SG}$ is obtained by calculated the single point energy of Cr-SG through deleting the O_2 in the O_2/Cr-SG configuration. It is worth noting that $E_{Cr\text{-}SG}$ and E_{O2} refer to the total energy of the freestanding Cr-SG and isolated O_2 after sufficient geometric optimization for the calculation of the adsorption energy of O_2 molecule on Cr-SG in the main text.

Therefore, the total energy of the O_2/Cr-SG system (see IS in Fig. 1) is calculated by using the following equation,

$$E_{O2/Cr\text{-}SG} = E_{bind\_O2} + E'_{Cr\text{-}SG} + E'_{O2} \quad (5)$$

At TS state, the O-O bond is elongated to 1.825 Å (see TS in Fig. 1), where the two O atoms is labeled as OO species, and the binding energy E_{ad_OO} for OO species on Cr-SG and the total energy $E_{OO/Cr\text{-}SG}$ of the TS state are separately calculated by using the following equation,

$$E_{bind\_OO} = E_{OO/Cr\text{-}SG} - (E''_{Cr\text{-}SG} + E_{OO}) \quad (6)$$

$$E_{OO/Cr\text{-}SG} = E_{bind\_OO} + E''_{Cr\text{-}SG} + E_{OO} \quad (7)$$

The dissociation barrier E_{bar} for O_2 on Cr-SG is the energy difference between TS and IS states (see Fig. 1), which is calculated by using the following equation,

$$E_{bar} = E_{OO/Cr\text{-}SG} - E_{O2/Cr\text{-}SG} = (E_{bind\_OO} - E_{bind\_O2}) + (E''_{Cr\text{-}SG} - E'_{Cr\text{-}SG}) + (E_{OO} - E'_{O2}) \quad (8)$$

Based on the DFT calculations, $E_{bind\_OO} - E_{bind\_O2}$ = -6.81 eV – (-3.49 eV) = -3.32 eV, $E''_{Cr\text{-}SG} - E'_{Cr\text{-}SG}$ = 0.40 eV, and $E_{OO} - E'_{O2}$= 3.83 eV. Therefore, the energy barrier for the dissociation of O2 on Cr-SAC is composed of the following parts,

$$E_{bar} = -3.32 \text{ eV} + 0.40 \text{ eV} + 3.83 \text{ eV} = 0.91 \text{ eV} \quad (9)$$

For HCO_2 species adsorbed on Cr-SG pre-adsorbed with OH group (Cr-SG-OH), the binding energy E_{bind_HCO2} between HCO_2 and Cr-SG-OH (see MS_3 in Fig. 5) is calculated by using the following equation,

$$E_{bind\_HCO2} = E_{HCO2/Cr\text{-}SG\text{-}OH} - (E'_{Cr\text{-}SG\text{-}OH} + E_{HCO2}) \quad (10)$$

Therefore, the total energy of HCO_2/Cr-SG-OH system is calculated by using the following equation,

$$E_{HCO2/Cr\text{-}SG\text{-}OH} = E_{bind\_HCO2} + E'_{Cr\text{-}SG\text{-}OH} + E_{HCO2} \quad (11)$$

At $TS_{4\text{-}2}$ state, the H-C bond is elongated to 1.385 Å (see $TS_{4\text{-}2}$ in Fig. 5), and the binding energy $E_{bind\_H\text{-}CO2}$ for H-CO_2 species on Cr-SG and the total energies of the $TS_{4\text{-}2}$ state are calculated by using the following equation,

$$E_{bind\_H\text{-}CO2} = E_{H\text{-}CO2/Cr\text{-}SG\text{-}OH} - (E''_{Cr\text{-}SG\text{-}OH} + E_{H\text{-}CO2}) \quad (12)$$

$$E_{H\text{-}CO2/Cr\text{-}SG\text{-}OH} = E_{bind\_H\text{-}CO2} + E''_{Cr\text{-}SG\text{-}OH} + E_{H\text{-}CO2} \quad (13)$$

The dissociation barrier E_{bar} for HCO_2 species on Cr-SG-OH is calculated by using the following equation,

$$E_{bar} = E_{H\text{-}CO2/Cr\text{-}SG\text{-}OH} - E_{HCO2/Cr\text{-}SG\text{-}OH} = (E_{bind\_H\text{-}CO2} - E_{bind\_HCO2}) + (E''_{Cr\text{-}SG\text{-}OH} - E'_{Cr\text{-}SG\text{-}OH}) + (E_{H\text{-}CO2} - E_{HCO2}) \quad (14)$$

Based on the DFT calculations, $E_{bind\_H\text{-}CO2} - E_{bind\_HCO2}$ = -2.08 eV – (-3.01 eV) = 0.93 eV, $E''_{Cr\text{-}SG\text{-}OH} - E'_{Cr\text{-}SG\text{-}OH}$ = -0.14 eV, and $E_{H\text{-}CO2} - E_{HCO2}$= 0.13 eV. Therefore, the

dissociation barrier E_{bar} for HCO_2 species on Cr-SG-OH is composed of the following parts,

$$E_{bar} = 0.93 \text{ eV} + (-0.14 \text{ eV}) + 0.13 \text{ eV} = 0.92 \text{ eV} \quad (15)$$

Table S2 The electronegativity (*E*), number of *d* electrons (θ_d), group number (*g*), atomic radius (r_M) for metal atoms.

No.	M-SG	E_M	θ_d	*g*	r_M	E_{bar_step4}
1	Sc-SG	1.36	1	3	1.64	1.86
2	Ti-SG	1.54	2	4	1.47	1.70
3	V-SG	1.63	3	5	1.35	1.22
4	Cr-SG	1.66	5	6	1.29	0.92
5	Mn-SG	1.55	5	7	1.37	1.37
6	Fe-SG	1.83	6	8	1.26	1.45
7	Co-SG	1.88	7	8	1.25	1.71
8	Ni-SG	1.91	8	8	1.25	1.85
9	Cu-SG	1.90	10	1	1.28	1.98
10	Zn-SG	1.65	10	2	1.37	1.87
11	Y-SG	1.22	1	3	1.82	2.20
12	Zr-SG	1.33	2	4	1.60	1.95
13	Nb-SG	1.60	4	5	1.47	1.50
14	Mo-SG	2.16	5	6	1.40	1.12
15	Tc-SG	1.90	5	7	1.35	0.98
16	Ru-SG	2.20	7	8	1.34	1.36
17	Rh-SG	2.28	8	8	1.34	1.62
18	Pd-SG	2.20	10	8	1.37	2.31
19	Ag-SG	1.93	10	1	1.44	2.14
20	Cd-SG	1.69	10	2	1.52	2.03
21	La-SG	1.10	1	3	1.88	2.10
22	Ce-SG	1.12	1	3	1.83	2.00
23	Pr-SG	1.13	0	3	1.82	2.06
24	Hf-SG	1.30	2	4	1.59	1.98
25	Ta-SG	1.50	3	5	1.47	1.54
26	W-SG	2.36	4	6	1.41	1.25
27	Re-SG	1.90	5	7	1.37	1.03
28	Os-SG	2.20	6	8	1.35	1.55
29	Ir-SG	2.20	7	8	1.36	1.61
30	Pt-SG	2.28	9	8	1.39	2.11
31	Au-SG	2.54	10	1	1.44	2.38
32	Hg-SG	2.00	10	2	1.55	2.17
33	Ac-SG	1.10	1	3	1.90	2.12
34	Th-SG	1.30	2	3	1.80	2.11
35	Pa-SG	1.50	1	3	1.61	2.10