Supporting Information

Decreased Spin-resolved Anti-bonding States Filling to Accelerate CHO Conversion to CH_2O in Transitional Metals Doped Mo_2C Monolayer during CO_2 Reduction

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Table S1 The total energy (E_{DFT}, eV), zero-point energy (E_{ZPE}, eV) and entropy (TS, eV) of CO_2, H_2 and CO_2.

Species	E_{DFT} (eV)	E_{ZPE} (eV)	TS (eV)
CO_2	-23.02	0.31	0.65
H_2	-6.78	0.27	0.42
H_2O	-14.23	0.58	0.65

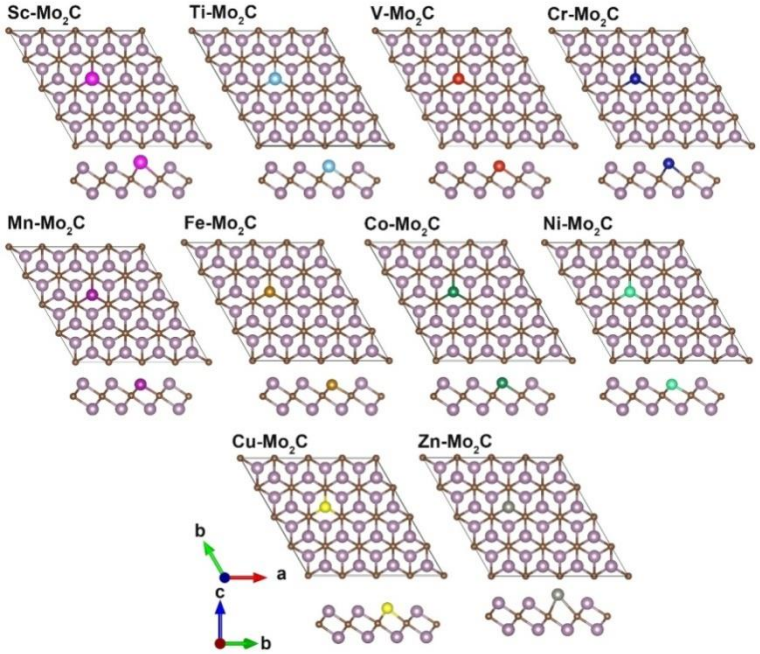

Fig. S1. Top and side views for optimized structures of TM-doped Mo_2C (TM=Tc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn).

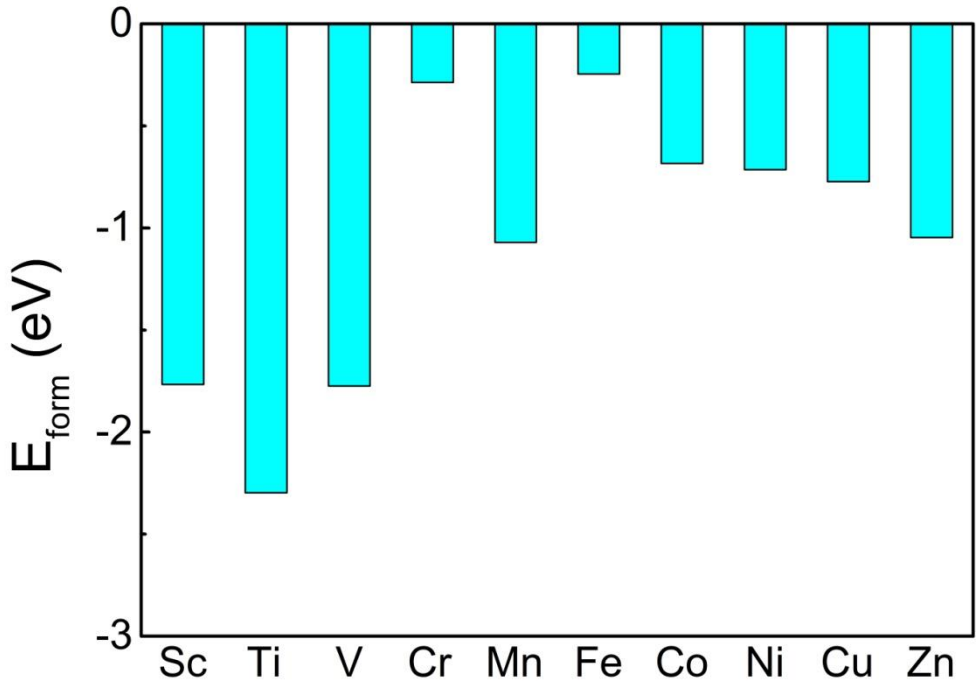

Fig. S2. The formation energies of TM-doped Mo_2C (TM=Tc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn).

Table S2 The lattice parameters (a=b), bond length of Mo-C/TM-C (d_{Mo-C}/d_{TM-C}) and the magnetic moments of TM and TM-Mo_2C (TM=Tc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn).

TM-Mo_2C	Sc	Ti	V	Cr	Mn
$a=b$ (Å)	12.12	12.10	12.10	12.10	12.07
d_{Mo-C} (Å)	2.09	2.09	2.09	2.09	2.10
d_{TM-C} (Å)	2.34	2.13	2.13	2.24	1.97
TM (μ_B)	0	-0.061	1.992	-0.247	-0.102
Magnetic moment (μ_B)	2.88	2.40	5.54	3.73	4.34
TM-Mo_2C	Fe	Co	Ni	Cu	Zn
$a=b$ (Å)	12.07	12.07	12.07	12.07	12.04
d_{Mo-C1} (Å)	2.09	2.10	2.10	2.09	2.07
d_{TM-C1} (Å)	1.96	2.05	1.96	2.17	2.57
TM	-0.57	1.91	0.02	-0.004	-0.001
Magnetic moment (μ_B)	2.83	4.55	2.69	1.97	1.82

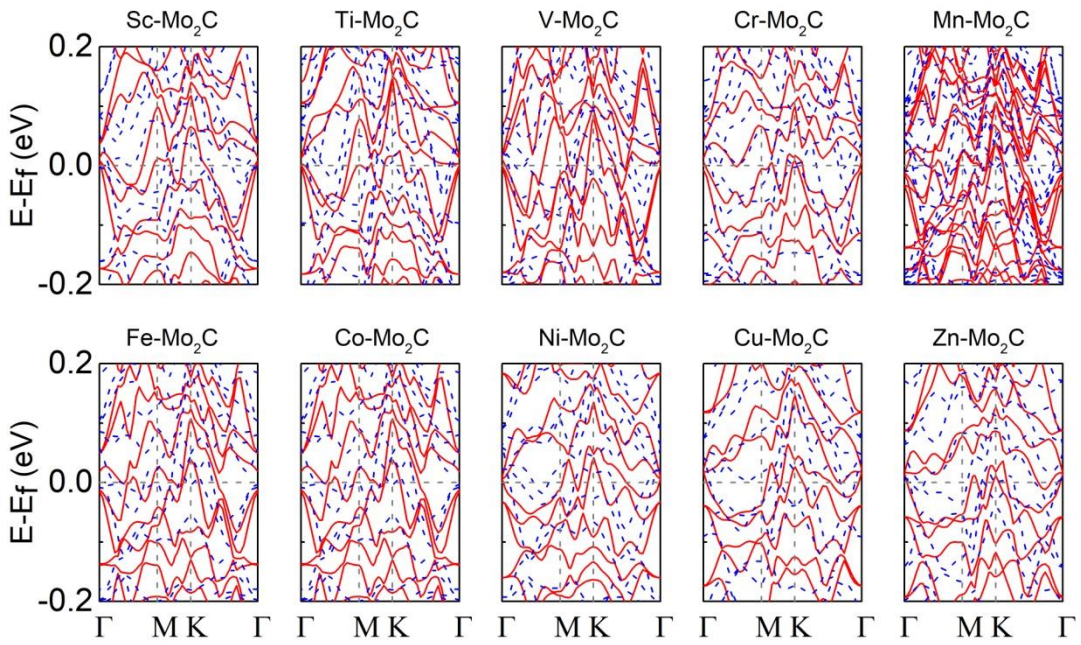

Fig. S3. The band st the energy of isolated TM atom (TM=Tc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn).

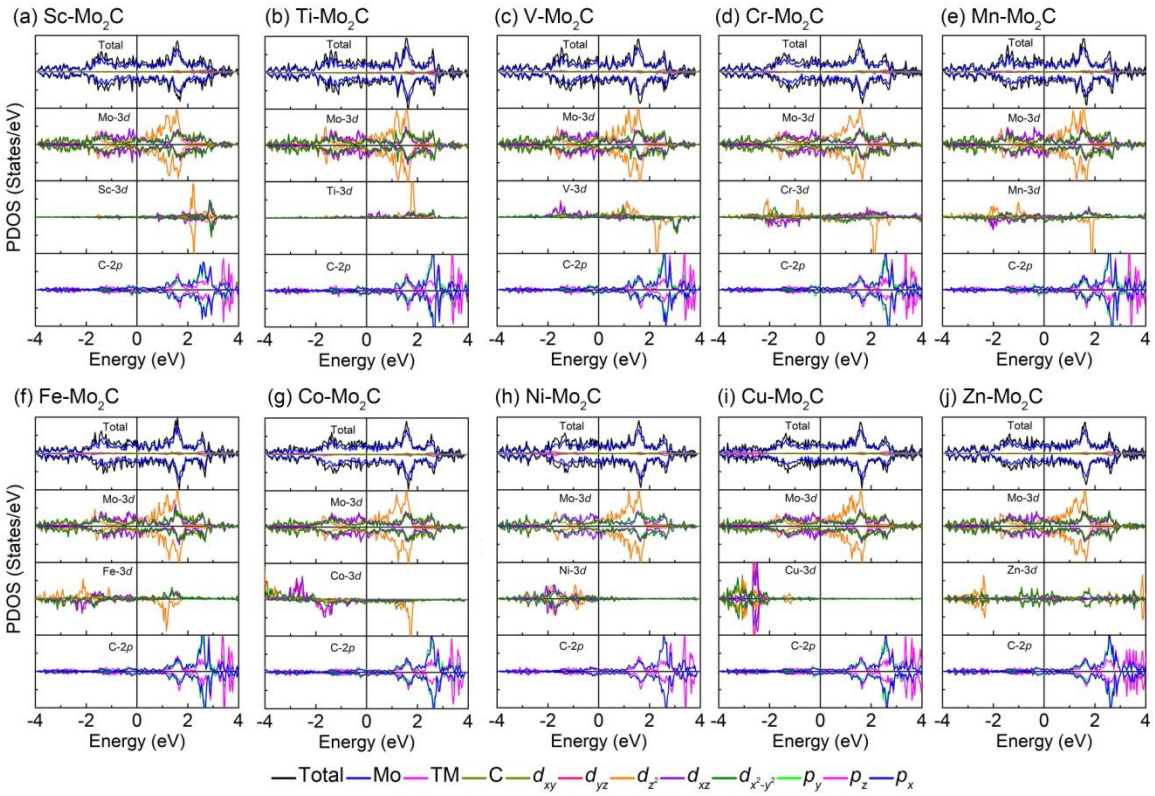

Fig. S4. The partial density of states of TM-doped Mo_2C (TM=Tc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn).

Table S3 The total energies of *H-Mo_2C, *OH-Mo_2C, *H_2O-Mo_2C and *CO_2-Mo_2C E_{total} (eV), the adsorption energies of H, OH, H_2O and CO_2 E_{ads} (eV) and the gibbs free energies of *H, *OH, *H_2O and CO_2 ΔG (eV)

	E_{total}	E_{ads}	ΔG
*H-Mo_2C	-371.19	-1.75	-1.79
*OH-Mo_2C	-379.01	-2.12	-1.72
*H_2O-Mo_2C	-381.94	-1.66	-1.21
*CO_2-Mo_2C	-391.14	0.43	0.90

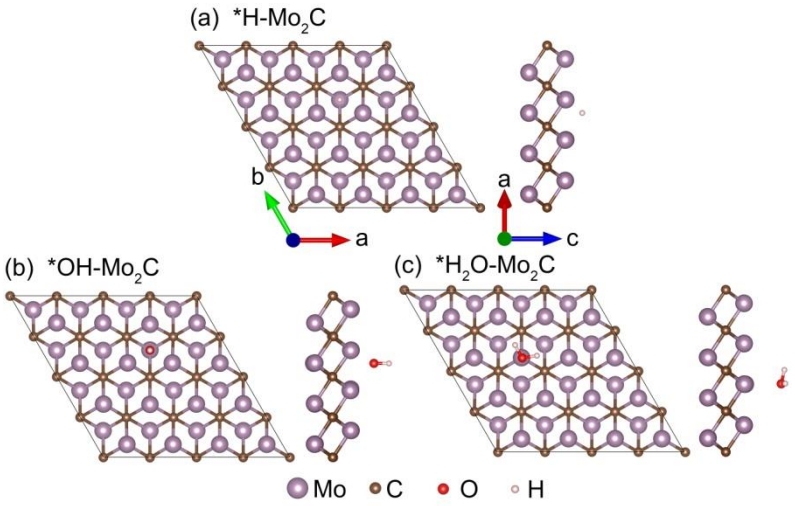

Fig. S5. Top and side views of optimized structure for (a) H, (b) OH and (c) H_2O adsorbed on the bridge sites of pure Mo_2C.

Table S4 The charge transfer of each element for pure Mo_2C and TM-Mo_2C (TM= Cr, Mn, Fe, Co, Ni, and Cu) with CO_2 adsorbed over the bridge active sites.

Charge Transfer	Mo_2C	Cr-Mo_2C	Mn-Mo_2C	Fe-Mo_2C	Co-Mo_2C	Ni-Mo_2C	Cu-Mo_2C
Mo	0.72	-1.08	-1.09	-1.12	-1.12	-1.14	-1.13
TM	-0.75	-1.03	-1.02	-0.41	-0.39	-0.27	-0.22
				-1.12	-1.12	-1.14	-1.23
C	-1.21	-1.22	-1.24	-1.23	-1.22	-1.08	-1.22
O1	1.08	1.12	1.14	1.09	1.09	1.08	1.08
O2	1.08	1.06	1.06	1.09	1.09	1.07	1.08

Table S5 The gibbs free energy (Δ*G*, eV), adsorbed energy (ΔE_{DFT}, eV), entropy (*ΔTS*, eV) and zero-point energy (ΔE_{ZPE}, eV) corrections in determining the free energy of intermediates adsorbed on pure Mo_2C and TM-Mo_2C (TM= Cr, Mn, Fe, Co, Ni, and Cu).

		Path way	*ΔG*	*ΔE_{DFT}*	*ΔE_{ZPE}*	*ΔTS*
Mo_2C	1	*H	0.90	0.43	-0.01	-0.48
	2	*CO_2→*COOH	0.19	-0.16	0.16	-0.19
	3	*COOH→*CO	-0.45	-0.07	0.02	0.40
	4	*CO→*CHO	0.16	-0.23	0.15	-0.25
	4	*CO→*COH	0.46	0.13	0.14	-0.19
	5	*CHO→*CHOH	1.36	1.00	0.16	-0.20
		CHO→CH_2O	3.00	2.86	-0.02	-0.16
	6	*CHOH→*CH_2OH	-0.28	-0.65	0.19	-0.18
		CH_2O→CH_2OH	-1.91	-2.50	0.38	-0.21
	7	*CH_2OH→*CH_2	-4.48	-4.08	-0.05	0.35
	8	*CH_2→*CH_3	-0.17	-0.51	0.15	-0.19
	9	*CH_3→*CH_4	0.51	0.27	0.20	-0.04

		Path way	*ΔG*	*ΔE_{DFT}*	*ΔE_{ZPE}*	*ΔTS*
Fe-Mo_2C	1	*CO_2	-0.86	-1.35	0.00	-0.49
	2	*CO_2→*COOH	0.66	0.32	0.17	-0.17
	3	*COOH→*CO	-0.77	-0.44	0.03	0.36
	4	*CO→*CHO	0.41	0.09	0.09	-0.23
	5	*CHO→*CHOH	0.43	0.05	0.19	-0.19
		CHO→CH_2O	-1.40	-1.76	0.17	-0.19
	6	*CHOH→*CH_2OH	-0.15	-0.51	0.17	-0.19
		CH_2O→CH_2OH	1.68	1.30	0.19	-0.18
	7	*CH_2OH→*CH_2	-0.72	-0.33	-0.02	0.37
	8	*CH_2→*CH_3	-0.19	-0.56	0.17	-0.20
	9	*CH_3→*CH_4	0.58	0.32	0.18	-0.08

		Path way	ΔG	ΔE_{DFT}	ΔE_{ZPE}	ΔTS
Co-Mo_2C	1	$*CO_2$	-0.91	-1.39	0.00	-0.48
	2	$*CO_2 \rightarrow *COOH$	0.58	0.23	0.17	-0.18
	3	$*COOH \rightarrow *CO$	-0.56	-0.24	0.03	0.35
	4	$*CO \rightarrow *CHO$	0.36	0.14	0.06	-0.16
	5	$*CHO \rightarrow *CHOH$	0.85	0.44	0.19	-0.21
		$*CHO \rightarrow *CH_2O$	-0.33	-0.78	0.20	-0.25
	6	$*CHOH \rightarrow *CH_2OH$	-0.60	-0.98	0.18	-0.20
		$*CH_2O \rightarrow *CH_2OH$	0.57	0.24	0.17	-0.16
	7	$*CH_2OH \rightarrow *CH_2$	-0.64	-0.30	-0.01	0.33
	8	$*CH_2 \rightarrow *CH_3$	-0.31	-0.68	0.18	-0.19
	9	$*CH_3 \rightarrow *CH_4$	0.50	0.34	0.19	0.03

		Path way	ΔG	ΔE_{DFT}	ΔE_{ZPE}	ΔTS
Cu-Mo_2C	1	$*CO_2$	-0.87	-1.36	0.00	-0.49
	2	$*CO_2 \rightarrow *COOH$	0.57	0.25	0.16	-0.16
	3	$*COOH \rightarrow *CO$	-0.54	-0.23	0.03	0.34
	4	$*CO \rightarrow *CHO$	0.36	0.13	0.06	-0.17
	5	$*CHO \rightarrow *CHOH$	1.10	0.76	0.17	-0.17
		$*CHO \rightarrow *CH_2O$	0.02	-0.43	0.22	-0.23
	6	$*CHOH \rightarrow *CH_2OH$	-0.38	-0.84	0.22	-0.24
		$*CH_2O \rightarrow *CH_2OH$	0.69	0.35	0.17	-0.17
	7	$*CH_2OH \rightarrow *CH_2$	-0.74	-0.39	-0.01	0.34
	8	$*CH_2 \rightarrow *CH_3$	-0.14	-0.47	0.16	-0.17
	9	$*CH_3 \rightarrow *CH_4$	-0.07	-0.29	0.18	-0.04

		Path way	ΔG	ΔE_{DFT}	ΔE_{ZPE}	ΔTS
Cr-Mo_2C	1	$*CO_2$	-0.73	-1.20	-0.01	-0.48
	2	$*CO_2 \rightarrow *COOH$	-1.40	-1.81	0.19	-0.22
	3	$*COOH \rightarrow *CO$	-0.36	0.03	0.00	0.39
	4	$*CO \rightarrow *CHO$	0.38	0.04	0.14	-0.20

	5	*CHO→*CHOH	0.36	-0.04	0.17	-0.23
		CHO→CH_2O	-0.07	-0.42	0.11	-0.24
	6	*CHOH→*CH_2OH	-0.08	-0.44	0.16	-0.20
		CH_2O→CH_2OH	0.34	-0.06	0.22	-0.18
	7	*CH_2OH→*CH_2	-0.86	-0.45	-0.03	0.38
	8	*CH_2→*CH_3	-0.07	-0.43	0.17	-0.19
	9	*CH_3→*CH_4	0.23	-0.06	0.21	-0.08

		Path way	*ΔG*	*ΔE_{DFT}*	*ΔE_{ZPE}*	*ΔTS*
Mn-Mo_2C	1	*CO_2	-2.50	-2.95	-0.01	-0.46
	2	*CO_2→*COOH	0.65	0.30	0.18	-0.17
	3	*COOH→*CO	-1.29	-1.05	-0.54	-0.30
	4	*CO→*CHO	0.23	-0.05	0.07	-0.21
	5	*CHO→*CHOH	0.58	0.22	0.17	-0.19
		CHO→CH_2O	0.12	-0.29	0.17	-0.24
	6	*CHOH→*CH_2OH	-0.01	-0.47	0.22	-0.24
		CH_2O→CH_2OH	0.45	0.05	0.22	-0.18
	7	*CH_2OH→*CH_2	-0.46	-0.04	-0.04	0.38
	8	*CH_2→*CH_3	-0.65	-1.02	0.18	-0.19
	9	*CH_3→*CH_4	0.67	0.38	0.20	-0.09

		Path way	*ΔG*	*ΔE_{DFT}*	*ΔE_{ZPE}*	*ΔTS*
Ni-Mo_2C	1	*CO_2	-0.67	-1.13	-0.03	-0.49
	2	*CO_2→*COOH	0.53	0.15	0.17	-0.21
	3	*COOH→*CO	-0.60	-0.44	0.24	0.40
	4	*CO→*CHO	0.17	0.11	-0.13	-0.19
	5	*CHO→*CHOH	0.435	-0.005	0.21	-0.23
		CHO→CH_2O	-0.30	-0.74	0.20	-0.24
	6	*CHOH→*CH_2OH	-0.23	-0.58	0.17	-0.18
		CH_2O→CH_2OH	0.51	0.15	0.18	-0.18

7	$*CH_2OH \rightarrow *CH_2$	-0.25	-0.25	0.44	0.44
8	$*CH_2 \rightarrow *CH_3$	-0.63	-0.61	-0.29	-0.27
9	$*CH_3 \rightarrow *CH_4$	0.61	0.35	0.18	-0.08

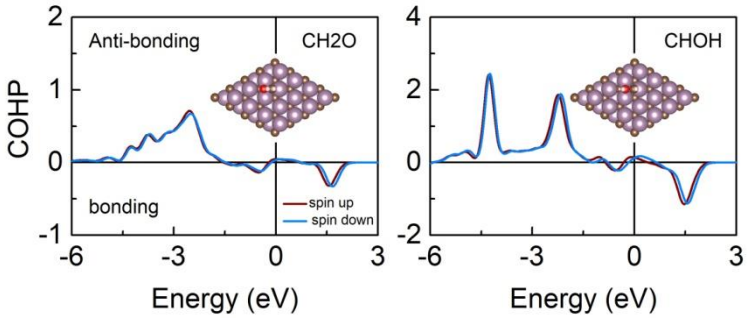

Fig. S6. The optimized structures and COHP of Mo_2C with CH_2O and CHOH intermediates adsorbed on Mo atoms.