Supplementary Information (SI)

Activation and Electrochemical Reduction of Carbon Dioxide by Transition Metal Atom-Doped Copper Clusters

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Computational Details:

The DFT calculation for the slab model and CO_2RR are performed using the VASP code.[1,2] The projector-augmented wave (PAW) method is used to describe ion-electron interaction.[3] The generalized gradient approximation (GGA) due to Perdew-Burke-Ernzerhof (PBE) is used to treat the exchange-correlation interaction of electrons.[4] The cut-off energy is set to 500 eV. The convergence criteria for energy and force are set to 10^{-6} eV and 0.01 eV/Å, respectively. A vacuum space larger than 20 Å is used to avoid the interaction between adjacent layers. A 4-atomic thick layer of Cu (111) surface having 64 atoms is used to study the interaction between Cu-flat surface and CO_2. The bottom two layers of Cu (111) surface are fixed during structure relaxation and a fine k-mesh of 2×2×1 is used. The van der Waals (vdW) correction is treated using Grime's DFT-D3 method.[5] For CO_2 reduction a vacuum of 15 Å is used along all the directions for clusters. All clusters are relaxed using the criteria mentioned before.

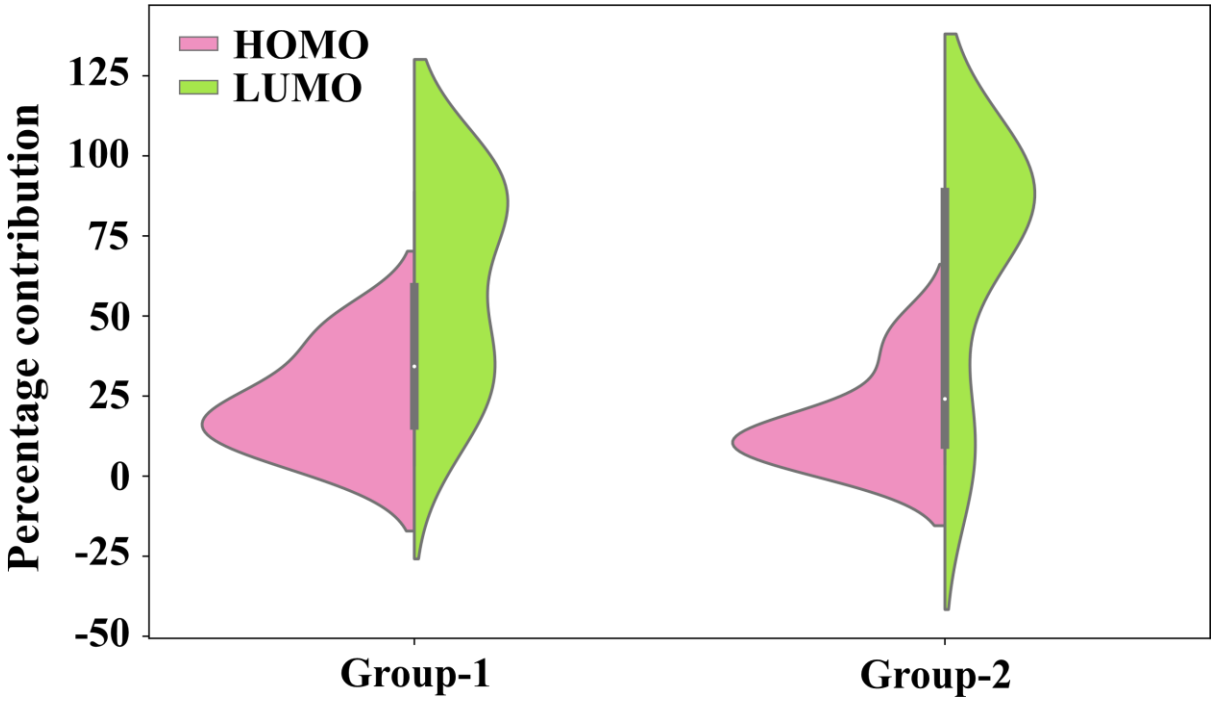

Figure S1 Percentage contribution of transition metal (X) atoms to HOMO and LUMO. Group-1 and 2 represent 3d and 4d metal atom doping.

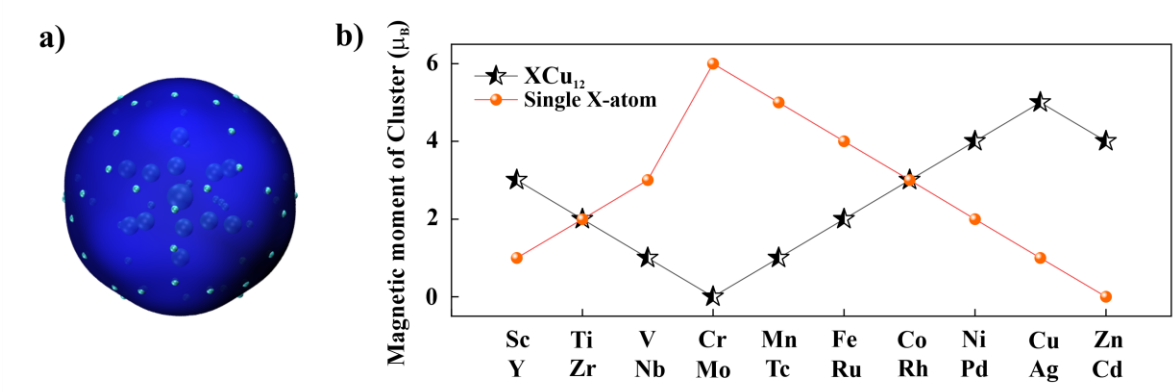

Figure S2 (a) Molecular surface map of average local ionization energy ($\bar{I}$); blue colour highlights the regions having relatively low $\bar{I}$ value indicating favourable sites for an electrophilic attack, (b) magnetic moment of XCu_{12} clusters (black curve) and isolated single TM of both 3d and 4d elements (orange curve).

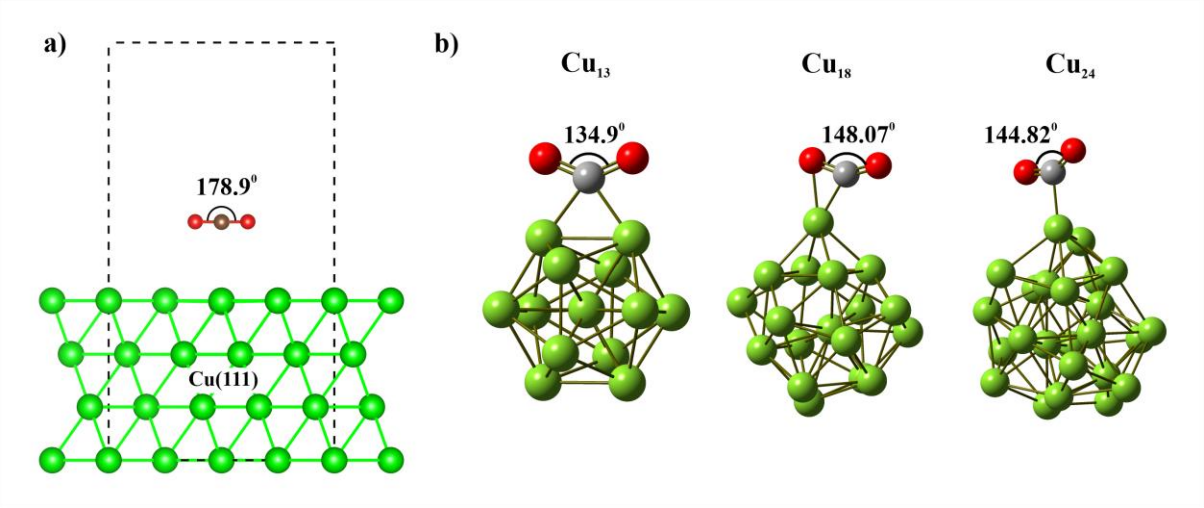

Figure S3 Interaction of CO_2 (a) with the Cu (111) surface where the four atomic layers are configured with the bottom two layers fixed at their bulk positions and the top two layers relaxed; (b) with various pure copper clusters.

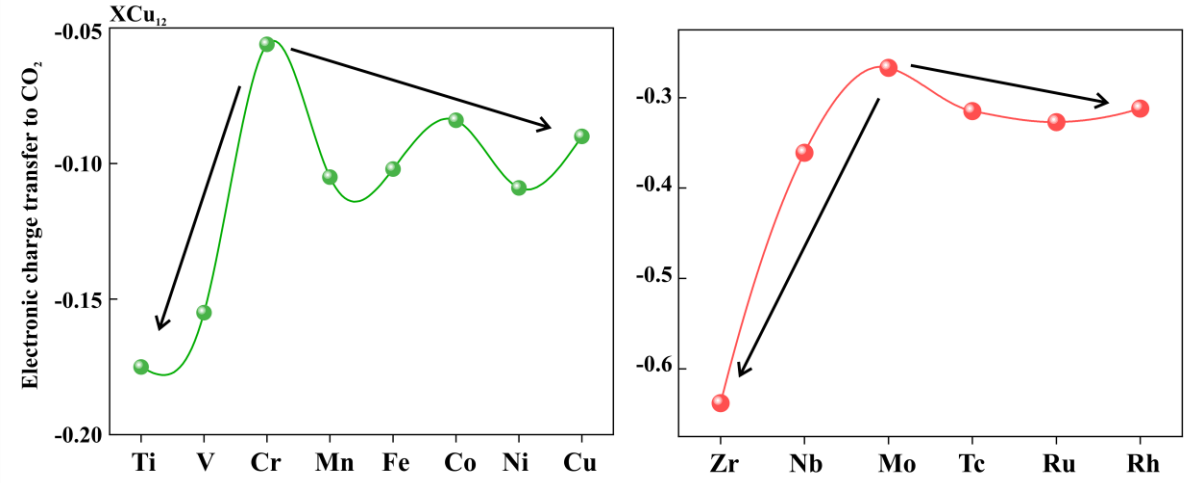

Figure S4 Electronic charge transfer to CO_2 molecule

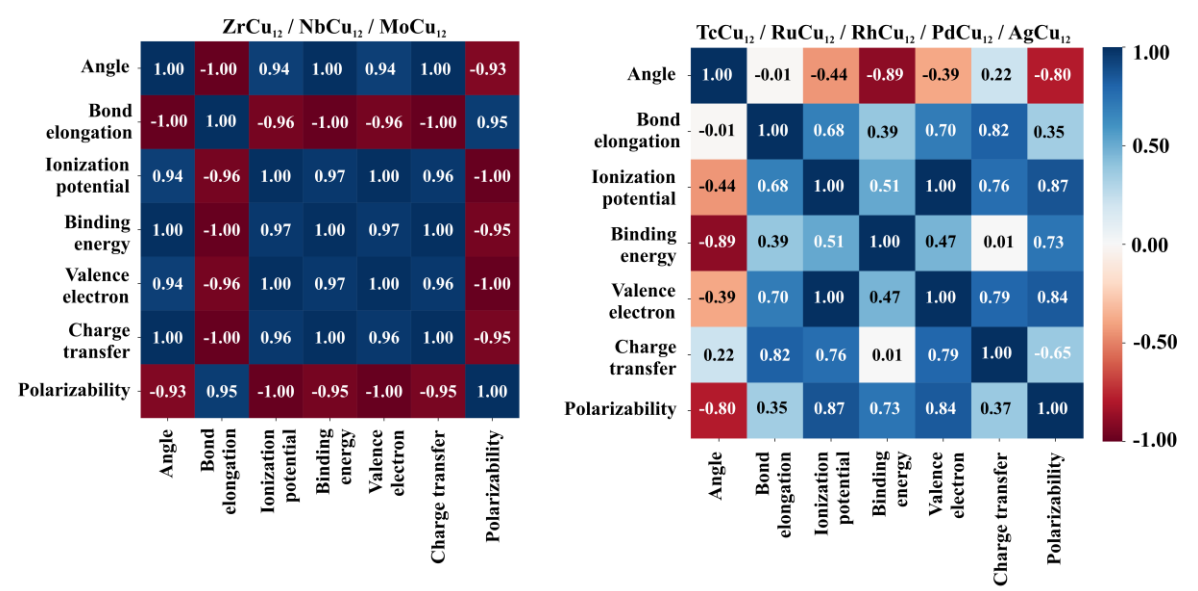

Figure S5 Pearson correlation plot; angle refers to O=C=O bond angle, bond length refers to the percentage change in C-O bond length.

Table S1 Energy of clusters with different spin states			
System	Energy (Hartree)/ Spin multiplicity		
	1	3	5
CrCu12	**-20731.698548**	-20731.657193	-20731.619296
MoCu12	**-19755.336672**	-19755.204089	-19755.172644
TiCu12	-20536.498724	**-20536.503518**	-20536.439712
ZrCu12	-19734.105941	**-19734.111514**	-19734.036121
NiCu12	-21195.343461	-21195.350669	**-21195.363199**
PdCu12	-19814.938326	-19814.945291	**-19814.958796**
FeCu12	-20950.706185	**-20950.731620**	-20950.697409
RuCu12	-19781.991393	**-19782.001452**	-19781.885233
CdCu12	-19854.688203	-19854.694261	**-19854.705657**
ZnCu12	-21466.356516	-21466.363294	**-21466.373045**
	Energy (Hartree)/ Spin Multiplicity		
	2	4	6
ScCu12	-20447.702806	**-20447.706278**	-20447.639760
YCu12	-19725.235274	**-19725.239097**	-19725.158204
CoCu12	-21069.796764	**-21069.806252**	-21069.771549
RhCu12	-19797.644754	**-19797.649937**	-19797.543621
VCu12	**-20631.001801**	-20630.996782	-20630.939323
NbCu12	**-19744.096987**	-19744.022322	-19743.923174
MnCu12	**-20838.030001**	-20837.991075	-20837.954697
TcCu12	**-19767.919575**	-19767.841454	-19767.768779
Cu13	-21327.529145	-21327.532575	**-21327.541370**
AgCu12	-19833.954048	-19833.972613	**-19833.981938**

Table S2 List of different parameters used for Pearson correlation plot.

Name (XCu_{12})	Bending angle of O=C=O (degree)	% Increase in bond length	Ionization potential (eV)	Binding energy of CO_2 (eV)	Valence electron	Charge transfer to CO_2 (e)	Polarizability (a. u)
Sc	125.26	21.44	6.4	3.1	15	-0.198	301.78
Ti	126.49	20.05	6.42	2.94	16	-0.175	293.1
V	128.77	16.92	6.57	2.08	17	-0.155	291.59
Cr	136.63	7.41	7.45	1.37	18	-0.056	298.428
Mn	135.42	8.08	5.24	1.89	19	-0.105	297.925
Fe	135.04	8.44	5.38	1.9	20	-0.102	305.66
Co	135.74	8.06	5.57	1.8	21	-0.084	313.92
Ni	134.78	8.65	5.75	2.22	22	-0.109	321.35
Cu	134.91	8.736	6.1	2.185	23	-0.09	322.765
Zn	122.68	25.037	5.84	3.947	24	-0.255	329.481
Zr	115.22	25.82	6.52	3.58	16	-0.638	308.937
Nb	127.87	14.67	6.59	1.81	17	-0.361	298.90
Mo	130.82	11.21	6.66	1.17	18	-0.267	287.494
Tc	126.45	11	4.34	2.79	19	-0.315	325.746
Ru	119.17	13.3	4.83	4.32	20	-0.327	341.868
Rh	120.19	13.06	5.22	4.03	21	-0.312	348.908
Pd	120.47	11.14	5.6	3.62	22	-0.31	350.948
Ag	122.26	25.93	5.97	4.02	23	-0.289	348.609

Table S3 Binding energy of H_2O on clusters (H-O-H bond angle: 103.97 degree; H-O bond length: 0.968 Å)

	Binding Energy (eV)	H-O bond length (Å)	$\angle H-O-H$ (degree)
$CrCu_{12}$	0.59	0.974	106.19
$MnCu_{12}$	0.42	0.974	106.2
$FeCu_{12}$	0.68	0.977	105.48
$CoCu_{12}$	0.70	0.974	106.46
$NiCu_{12}$	0.69	0.974	106.45
Cu_{13}	0.57	0.975	106.54

Table S4 The number of d electrons (N_{TM}), atomic radius (r_{TM}) and periodic number (n) of transition metals and their corresponding descriptor (Φ)[6]				
	N_{TM}	r_{TM}/Å	n	Φ
Cr	5	1.66	3	1.00
Mn	5	1.61	3	1.04
Fe	6	1.56	3	1.28
Co	7	1.52	3	1.54
Ni	8	1.49	3	1.79
Cu	10	1.45	3	2.3

Table S5 Magnetic moment and Mulliken spin population analysis of TM-doped clusters			
Cluster	**Magnetic moment of cluster (μ_B)**	**Mulliken spin population analysis**	
		Spin population (a.u.) on central TM	**Avg. spin population (a.u.) on outer Cu**
$CrCu_{12}$	0	/	/
$MnCu_{12}$	1	2.57	-0.13
$FeCu_{12}$	2	2.041	-0.003
$CoCu_{12}$	3	1.051	0.16
$NiCu_{12}$	4	0.496	0.29
Cu_{13}	5	0.442	0.38

References:

1 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
2 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15–50.
3 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
4 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
5 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.
6 E. Clementi, D. L. Raimondi and W. P. Reinhardt, *J. Chem. Phys.*, 1967, **47**, 1300–1307.