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

Supporting Information

CO_2 Electroreduction on Single Atom Catalysts: Role of the DFT Functional

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S1 Working equations

The Gibbs free energy of each chemical species was calculated from DFT energies and adding thermodynamic correction following the approach of Norskov and co-workers:[1]

$$\Delta G = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S$$

ΔE_{ads} is related to the DFT energy, ΔE_{ZPE} and ΔS are the zero-point energy correction and entropy, respectively. The entropic contribution of gas phase molecules was taken from the NIST database,[2,3] and that of solid-state species was neglected. The zero-point energy correction term was taken from the literature. The working equations are reported below:

$$\Delta G^{CO_2} = \Delta E_{ads}^{CO_2} + 0.68\ eV$$

$$\Delta G^{H2O} = \Delta E_{ads}^{H2O} + 0.58\ eV$$

$$\Delta G^{COOH} = \Delta E_{ads}^{COOH} + 1.03\ eV$$

$$\Delta G^{OCHO} = \Delta E_{ads}^{OCHO} + 1.01\ eV.$$

S2 Supporting Figures and Tables

Table S1: Calculated TM binding energies to the support and atomic magnetization obtained at PBE and PBE+*U* levels.

TM	U^{4-6} / eV	PBE		PBE+U	
		B.E. (eV)	μ_d	B.E. (eV)	μ_d
Sc	2.11	-8.43	0.00	-8.56	0.00
Ti	2.58	-8.50	0.88	-7.40	1.01
V	2.72	-7.86	2.09	-7.02	2.31
Cr	2.79	-7.20	3.25	-6.22	3.46
Mn	3.06	-6.80	2.94	-5.41	3.17
Fe	3.29	-7.39	1.86	-6.27	1.97
Co	3.42	-7.79	0.76	-6.69	1.02
Ni	3.40	-7.78	0.00	-7.09	0.00
Cu	4.18	-5.36	0.54	-5.18	0.58
Mo	2.30	-6.51	2.36	-5.57	2.76
Ru	2.79	-8.52	1.16	-6.93	1.55
Rh	3.04	-7.81	0.00	-6.16	0.68
Pd	3.33	-6.03	0.00	-5.43	0.00
Ag	1.87	-2.31	0.27	-2.13	0.44
W	2.08	-8.28	1.49	-7.31	1.81
Os	2.51	-8.02	0.00	-6.34	1.83
Ir	2.74	-8.62	0.00	-7.32	0.75
Pt	2.95	-7.99	0.00	-7.97	0.00
Au	3.17	-3.31	0.00	-2.92	0.00

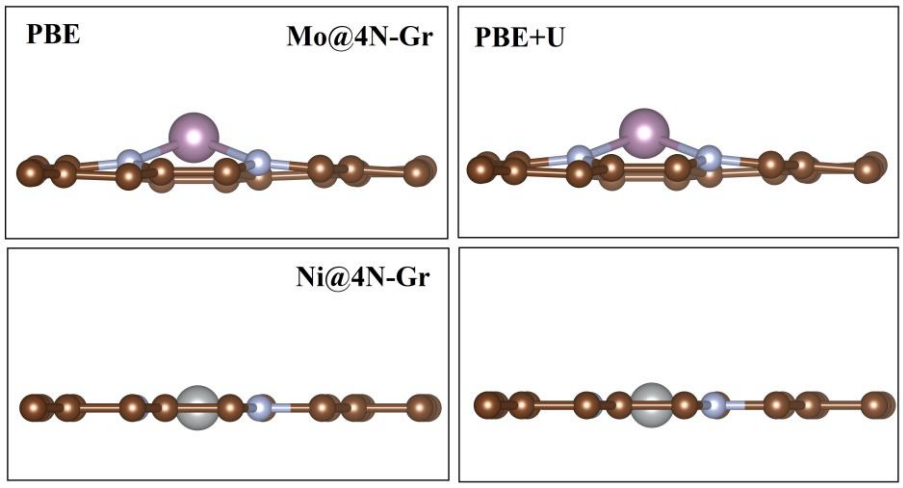

Figure S1: Structure of TMs anchored on 4N-Gr support with PBE and PBE+*U* frameworks.

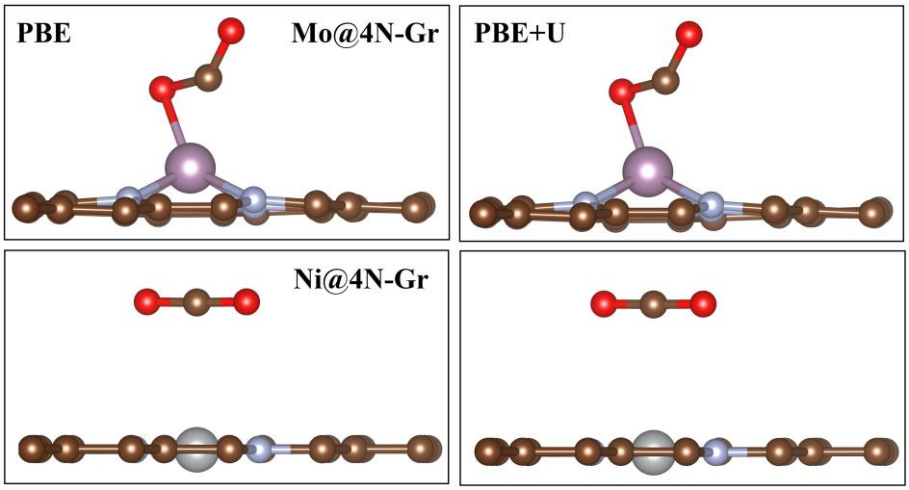

Figure S2: Structure of CO_2 adsorbed on TM@4N-Gr support with PBE (left) and PBE+*U* (right) approaches.

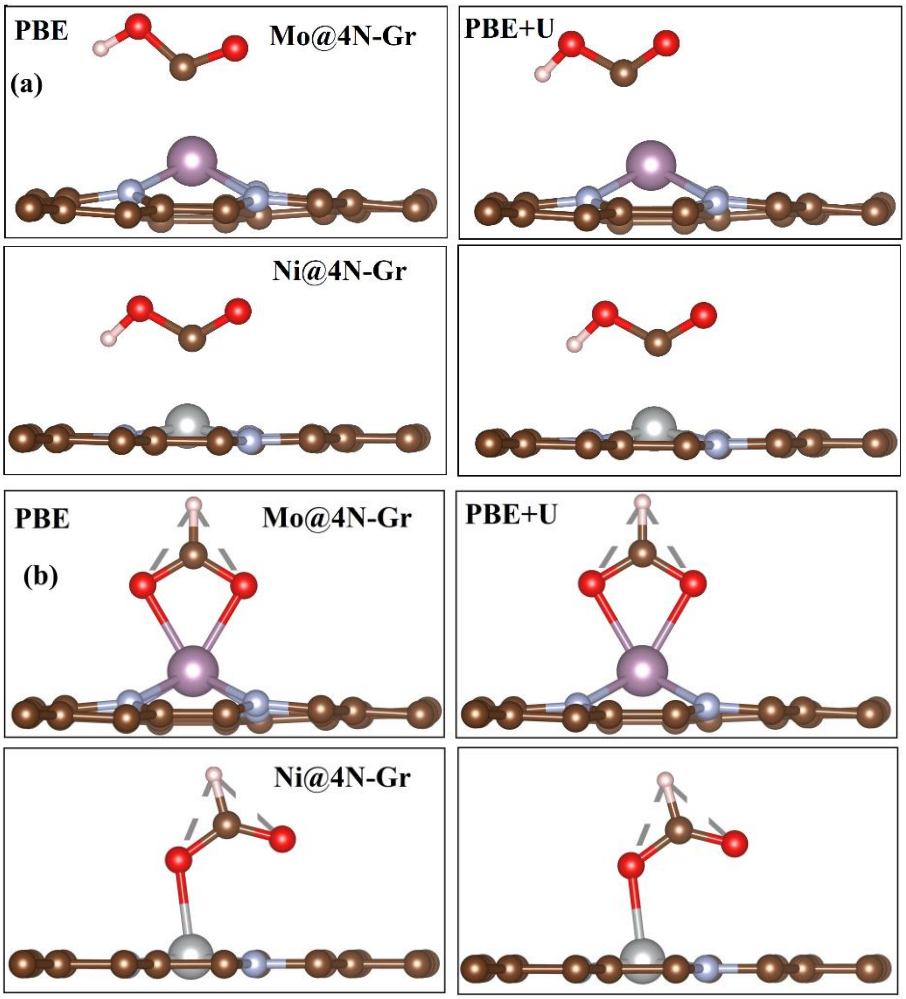

Figure S3: Structure of (a) *COOH and (b) *OCHO adsorbed on TM@4N-Gr support with PBE (left) and PBE+*U* (right) approaches.

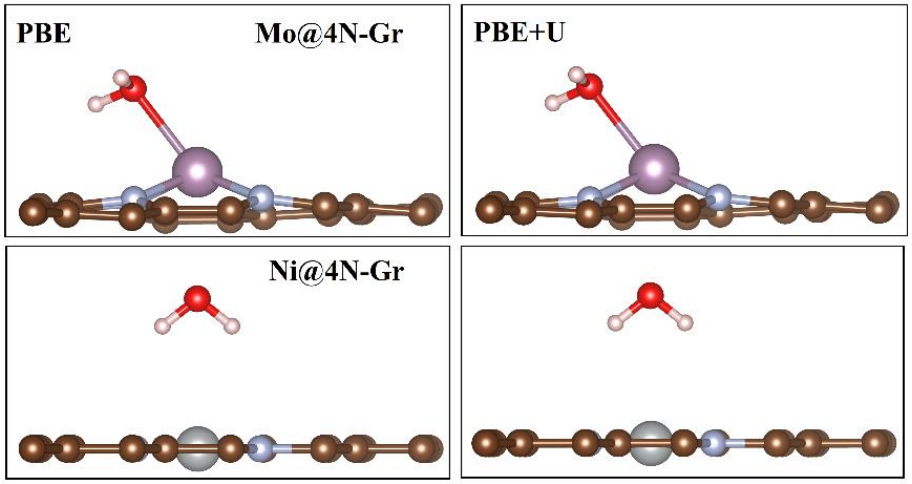

Figure S4: Structure of *H_2O adsorbed on TM@4N-Gr support with PBE (left) and PBE+*U* (right) approaches.

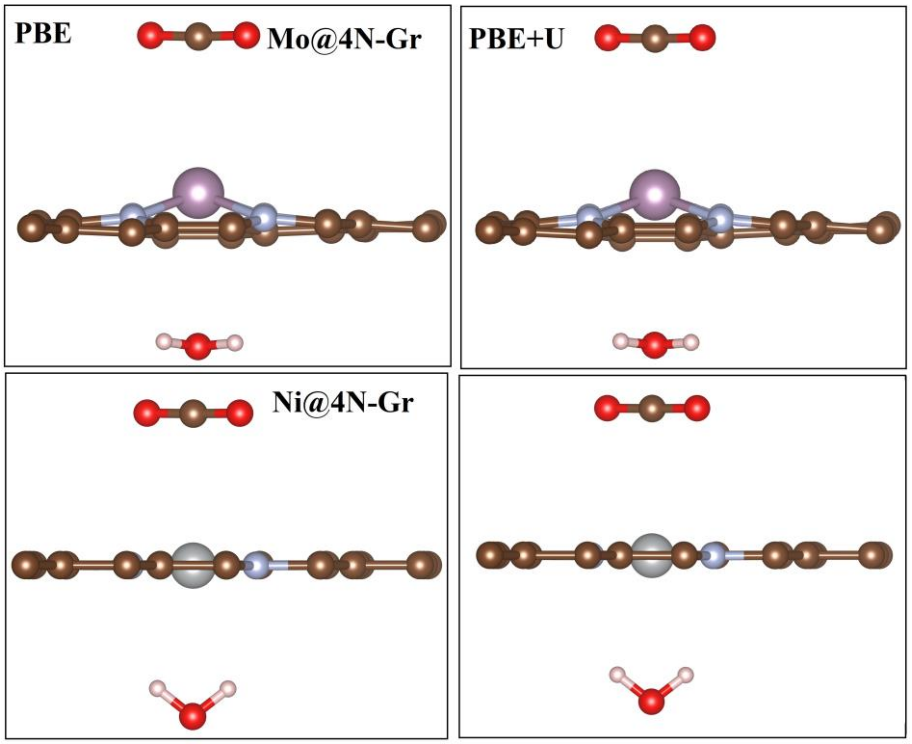

Figure S5: Structure of *CO_2 adsorbed on TM@4N-Gr support in the presence of *H_2O with PBE (left) and PBE+*U* (right) approaches.

References

1 J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, Trends in the Exchange Current for Hydrogen Evolution, *J Electrochem Soc*, 2005, **152**, J23.

2 Y. Yang, J. Li, C. Zhang, Z. Yang, P. Sun, S. Liu and Q. Cao, Theoretical Insights into Nitrogen-Doped Graphene-Supported Fe, Co, and Ni as Single-Atom Catalysts for CO ₂ Reduction Reaction, *The Journal of Physical Chemistry C*, 2022, **126**, 4338–4346.

3 D. Misra, G. Di Liberto and G. Pacchioni, CO2 electroreduction on single atom catalysts: Is water just a solvent?, *J Catal*, 2023, **422**, 1–11.

4 G. Di Liberto, L. A. Cipriano and G. Pacchioni, Universal Principles for the Rational Design of Single Atom Electrocatalysts? Handle with Care, *ACS Catal*, 2022, 5846–5856.

5 I. Barlocco, G. Di Liberto and G. Pacchioni, Hydrogen and oxygen evolution reactions on single atom catalysts stabilized by a covalent organic framework, *Energy Advances*, , DOI:10.1039/D3YA00162H.

6 I. Barlocco, L. A. Cipriano, G. Di Liberto and G. Pacchioni, Modeling Hydrogen and Oxygen Evolution Reactions on Single Atom Catalysts with Density Functional Theory: Role of the Functional, *Adv Theory Simul*, 2022, 2200513.