Supplementary Information for

Construction of BC_3−based TM Single−atom Catalyst for Efficient Reduction of CO_2 to CH_4: A Computational Study

Jianxin Ou,[a] Liying Pan,[a] and Xiangmei Duan*[a,b]

[a]*School of Physical Science and Technology, Ningbo University, Ningbo, 315211, China*

[b]*Laboratory of Clean Energy Storage and Conversion, Ningbo University, Ningbo,China*

*Corresponding author**s.**

E-mail address: duanxiangmei@nbu.edu.cn

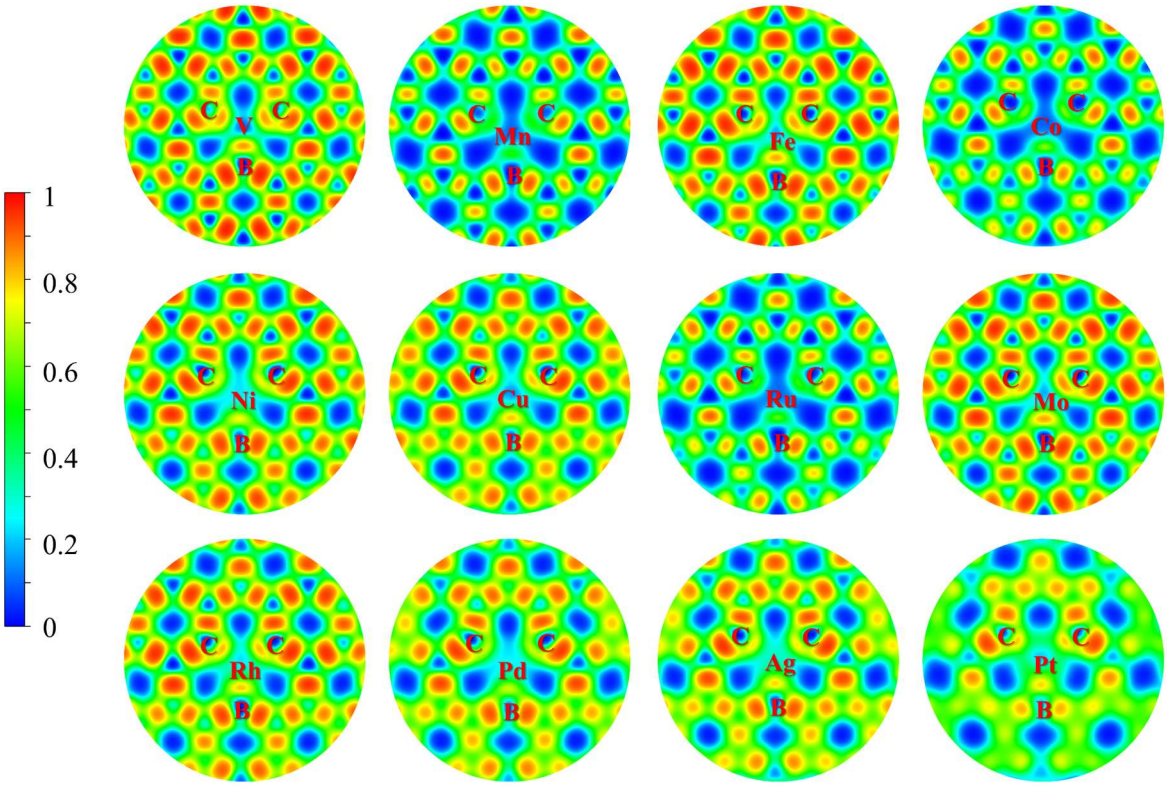

Fig. S1 The calculated electron localization function (ELF) for TM@BC_3.

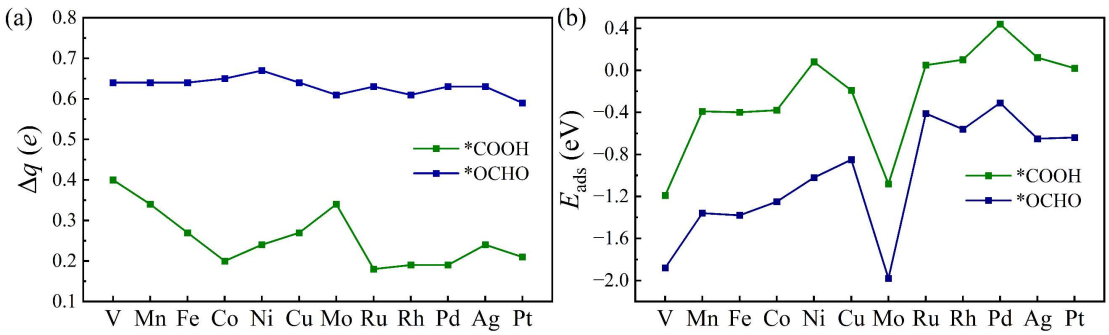

Fig. S2 (a) Charges obtained from the substrates and (b) the adsorption energies of *COOH and *OCHO.

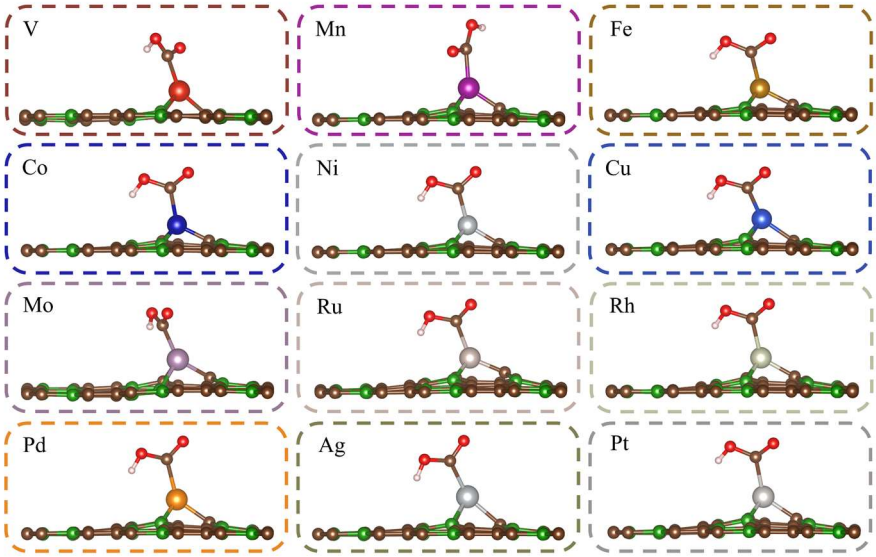

Fig. S3 The optimal structures for *COOH on TM@BC_3.

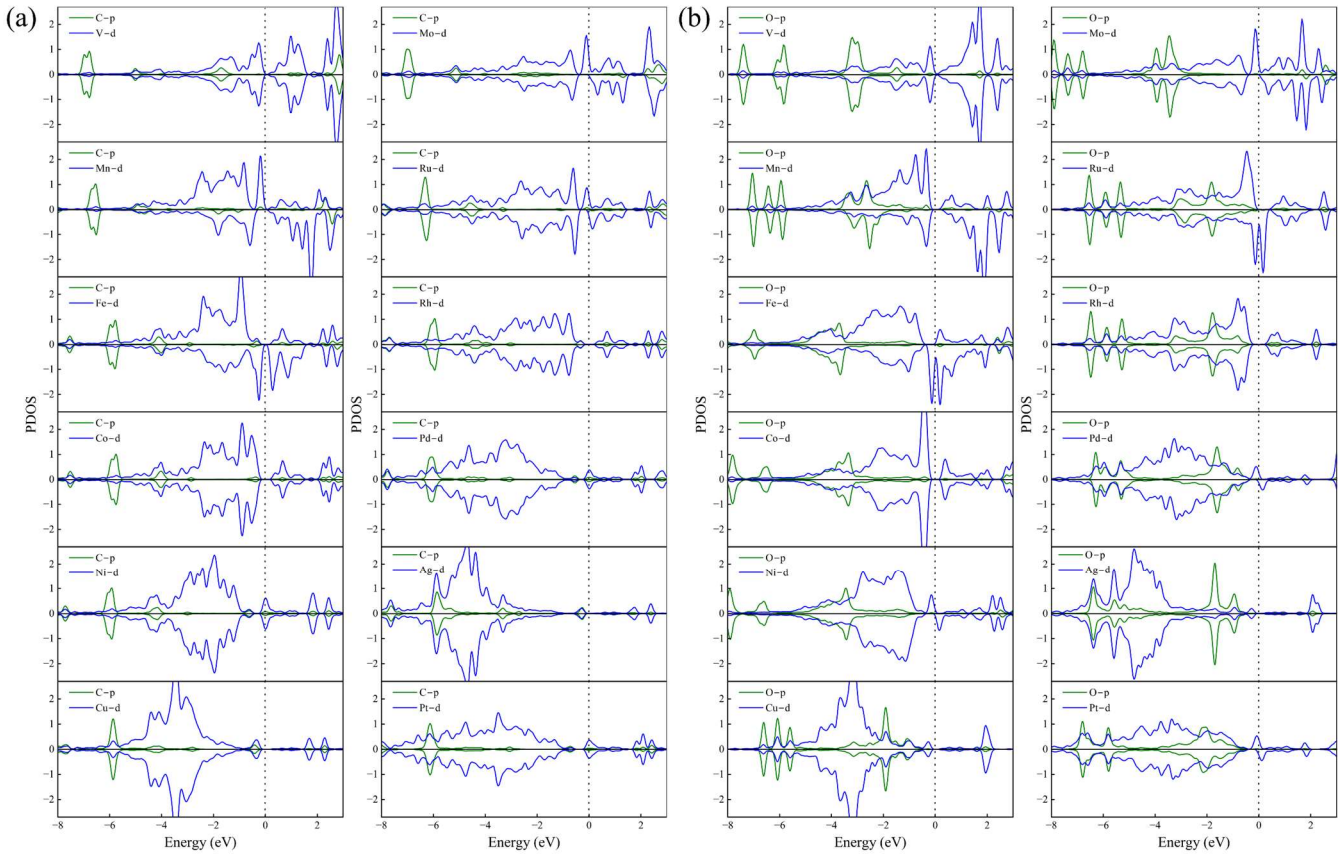

Fig. S4 PDOS of (a) *COOH and (b) *OCHO on 12 substrates.

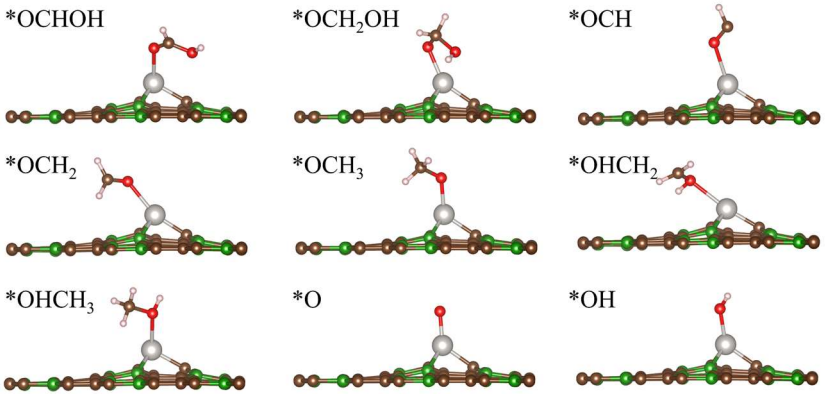

Fig. S5 The optimal structures of the intermediates on Pt@BC_3.

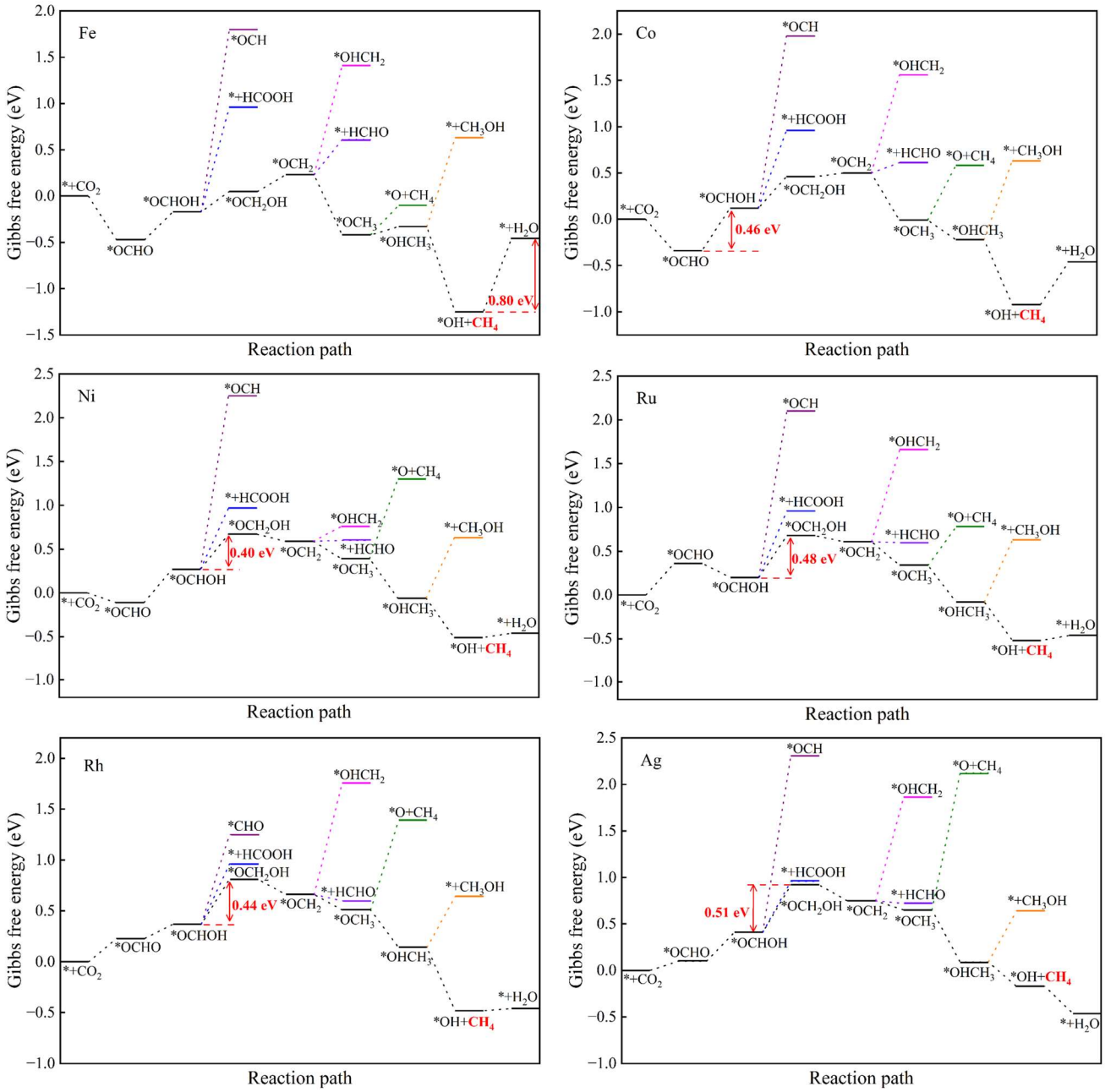

Fig. S6 The Gibbs free energy diagrams of CO_2RR on TM@BC_3 (TM=Fe, Co, Ni, Ru, Rh, and Ag).

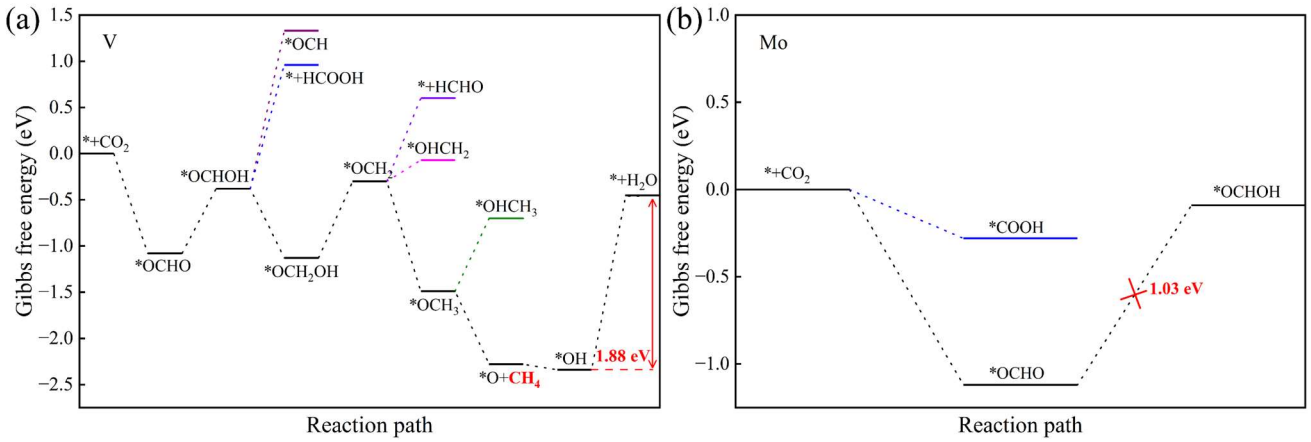

Fig. S7 The Gibbs free energy diagrams of CO_2RR on (a) $V@BC_3$ and (b) $Mo@BC_3$.

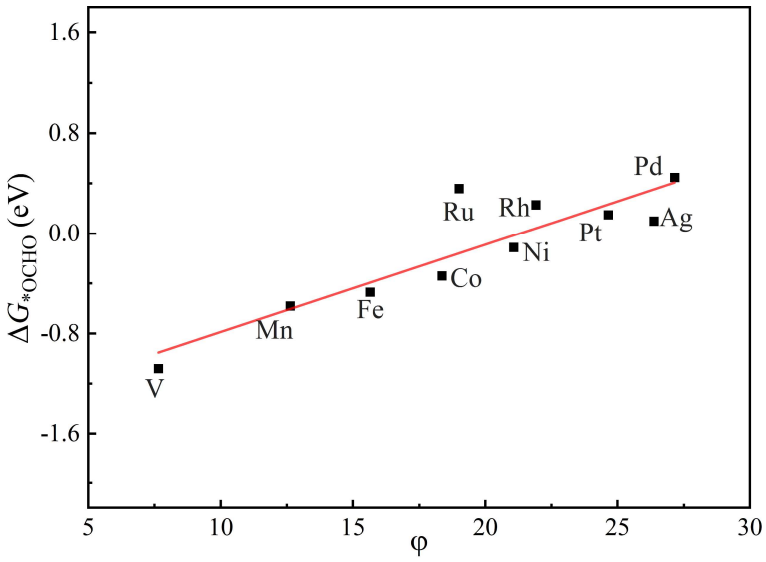

Fig. S8 Relationship between ΔG_{*OCHO} and descriptor φ.

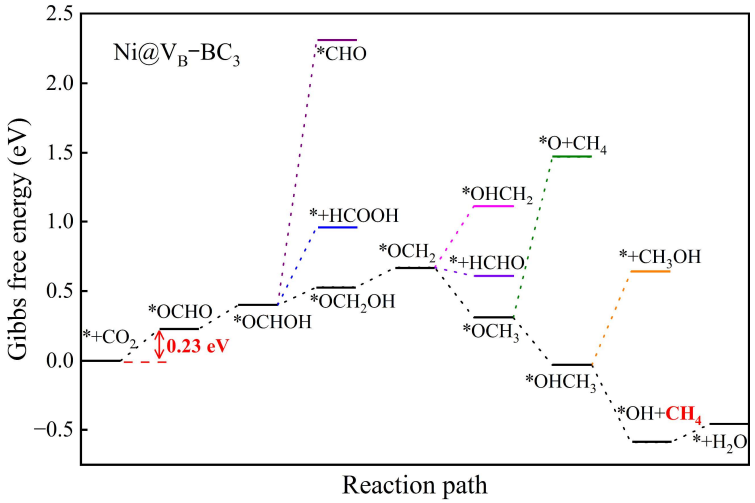

Fig. S9 The Gibbs free energy diagram of CO_2RR on $Ni@V_B{-}BC_3$.

Table S1. Binding energy E_b (in eV) of TM@BC_3 and the ratio of binding energy and cohesion energy (E_b/E_c)

TM@BC_3	E_b	E_b/E_c
V	−5.77	0.98
Mn	−4.79	1.19
Fe	−5.86	1.11
Co	−6.55	1.18
Ni	−6.39	1.23
Cu	−4.10	1.02
Mo	−5.84	0.93
Ru	−7.82	1.16
Rh	−7.33	1.22
Pd	−5.48	1.46
Ag	−2.70	1.07
Pt	−7.71	1.38