Supporting Information for

Predicting CO_2 adsorption and reactivity on transition metal surfaces using popular density functional theory methods

Ojus Mohan[a], Quang Thang Trinh[b], Arghya Banerjee[c] and Samir H. Mushrif[d]*

[a]Energy Research Institute @NTU, Interdisciplinary Graduate School, Nanyang Technological University, Singapore; [b]Cambridge Centre for Advanced Research and Education in Singapore (CARES), Campus for Research Excellence and Technological Enterprise (CREATE), Singapore; [c]School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore; [d]Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Canada

*E-mail: mushrif@ualberta.ca

S1. Lattice constant optimization

Nickel has only one parameter of lattice constant since it has fcc crystal structure. The total energy of the primitive cell of bulk structure fcc Ni is plotted against different lattice constant values as shown in Fig. S1. The optimum lattice constant is the one that corresponds to the minimum energy of the fcc Ni. The optimized lattice constant calculated from Fig. S1 is tabulated in Table S1. Percentage error is calculated based on experimental lattice constant (formula 4.1)

$$\% \text{ Error} = \frac{|A_{func} - A_{exp}|}{A_{exp}} \quad (4.1)$$

where A_{func} is the optimized lattice parameter calculated using functional and A_{exp} is the experimental value of the lattice parameter. All functionals are predicting the lattice parameter within 3% error which is acceptable.

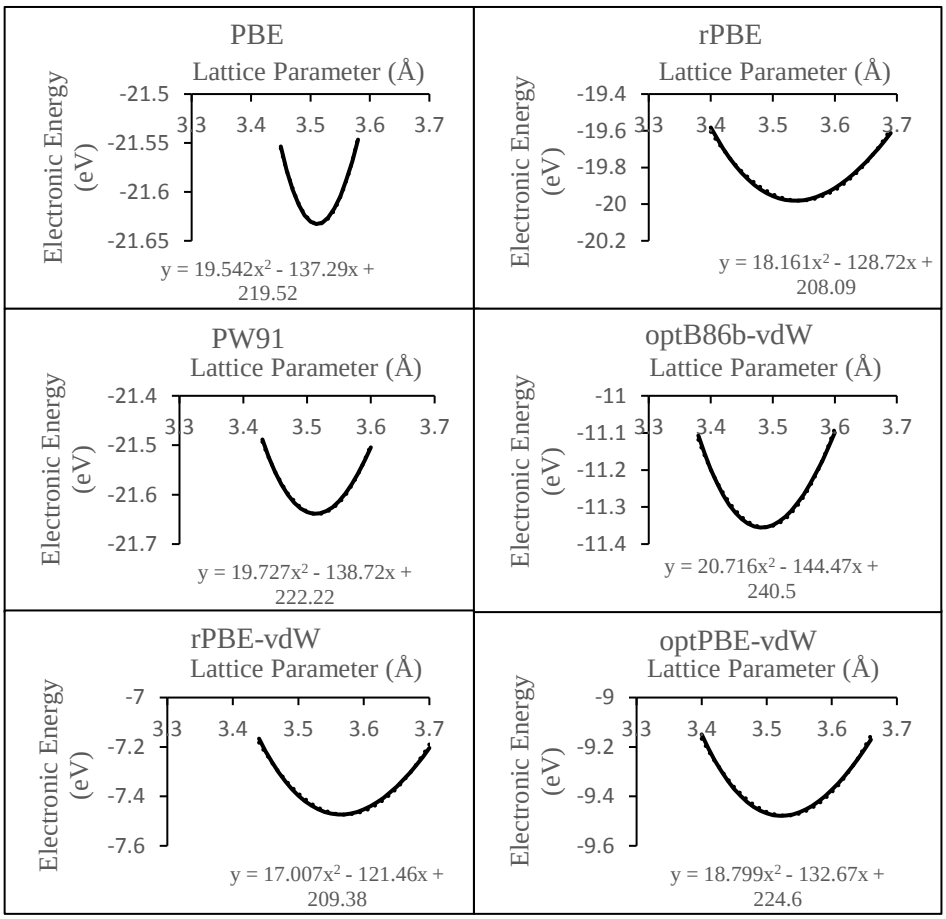

Fig. S1 Calculation of optimized lattice constant for Ni using different functionals. From lattice parameter-energy plot, lattice parameter corresponding to minimum energy is calculated

Table S1 Optimized lattice constant for Ni with different functionals

Functional	Lattice parameter (Å)	Percentage error (%)
PBE	3.513	0.31
rPBE	3.544	0.56
PW91	3.516	0.22
vdW-DF2	3.606	2.32
PBE D2	3.516	0.23
opt86b-vdW	3.497	0.76
rPBE-vdW	3.571	1.33
optPBE-vdW	3.529	0.14
Experiment	3.524	**-**

S2. Computational Parameter optimization

The number of slab layers, vacuum and the density of K point grids were chosen to ensure the adsorption energies were well converged within 5 kJ/mol with respect to the computational setup discussed in this study and are tabulated from Table S2a to Table S2c.

Table S2a. Number of slab layers optimization

Number of layers	Binding energy of CO_2 (kJ/mol)
4	-46.16
5	-33.25
6	-41.35
7	-41.26

Table S2b. K-points optimization

K-points	Binding energy of CO_2 (kJ/mol)
3x3x1	-41.35
4x4x1	-40.8
5x5x1	-40.35
6x6x1	-41.02

Table S2c. Vacuum Thickness optimization

Vacuum Thickness (Å)	Binding energy of CO_2 (kJ/mol)
12	-41.35
15	-39.12
20	-39.6

S3. Adsorption configuration of CO_2 and CO on Ni (110)

Four different configurations are identified for CO_2 adsorption on Ni (110) surface. The different adsorption configurations are shown in Fig. S3a-d and adsorption energies and geometric parameters are tabulated in Table S3a. All the calculations are performed using PBE functional and configuration (a) corresponds to the most stable configuration.

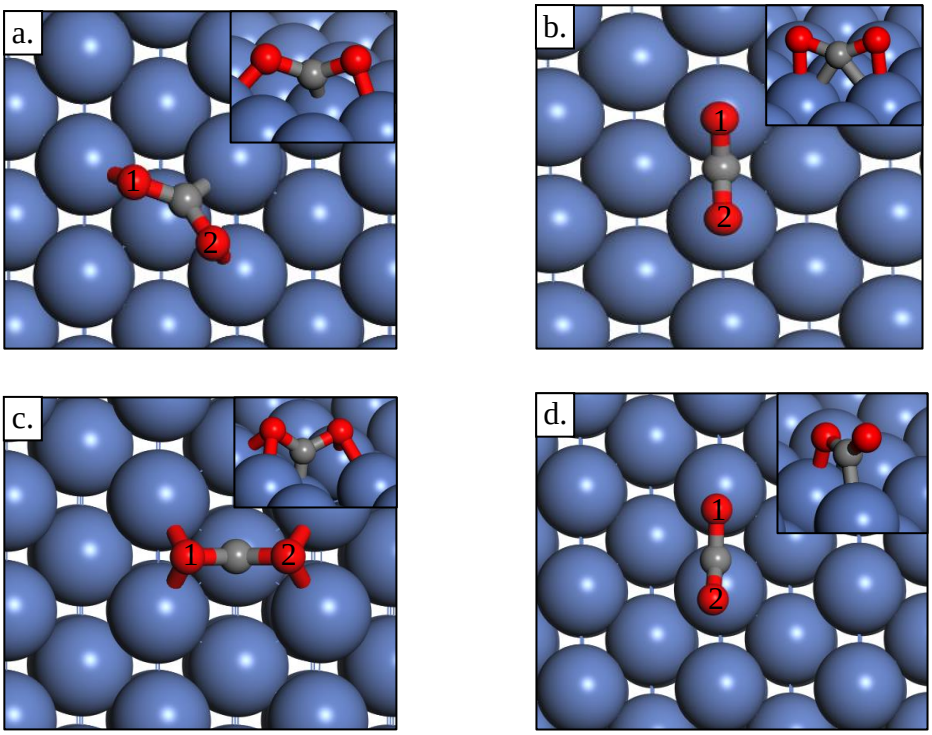

Fig. S3 a-d shows different adsorption configuration of CO_2 on Ni (110). Blue balls represent Ni atoms, red balls represent oxygen atoms, and the grey ball represents carbon atom.

Table S3a Geometric parameters and calculated adsorption energy of CO_2 on Ni (110)

Parameter	Configuration			
	a	b	c	d
$d_{C\text{-}O1}$ (Å)	1.279	1.243	1.308	1.261
$d_{C\text{-}O2}$ (Å)	1.278	1.244	1.306	1.223
O1-C-O2 (deg)	126.704	139.036	121.323	139.200
E_{ads} (kJ/mol)	-41.35	-32.22	-31.57	-29.44

We found that CO prefers to sit on Ni with carbon bonded vertical configuration on all sites. The different adsorption configurations are shown in Fig. S3e-g and adsorption energies and geometric parameters are tabulated in Table S3b.

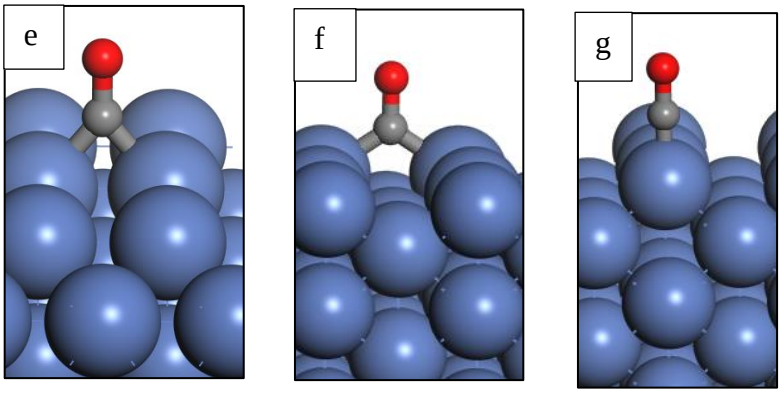

Fig. S3 e-g shows different adsorption configuration of CO on Ni (110). Color code for the atoms is the same as used in Fig. S2

Table S3b Geometric parameters and calculated adsorption energy of CO on Ni (110)

Parameter	**Configuration**		
	a	**b**	**c**
d_{C-O} (Å)	1.128	1.196	1.165
E_{ads} (kJ/mol)	-173.92	-134.15	-159.52

The most stable adsorption configuration was the one in which CO sits vertically in the bridge site between two-nickel atoms.

Table S3c. Bond angle and bond length of CO_2* calculated by different functionals

Parameter	**Functional**							
	PBE	**rPBE**	**PW91**	**vdWDF2**	**opt86b-vdW**	**PBE D2**	**rPBE-vdW**	**optPBE-vdW**
dC-O1 (Å)	1.279	1.281	1.276	1.280	1.283	1.282	1.279	1.282
dC-O2 (Å)	1.278	1.283	1.278	1.279	1.278	1.281	1.281	1.278
O1-C-O2 (deg)	126.704	126.416	127.713	127.782	125.896	126.283	126.913	126.239

S4. Zero-point energy and enthalpy corrections using different functionals

The zero-point energies calculated using different functionals for CO_2 are given in following Table S4

Table S4. ZPE and ΔH calculated using different functionals for CO_2

Functional	ZPE (kJ/mol)	Enthalpy correction, ΔH (kJ/mol)
PBE	27.733	5.197
rPBE	27.398	5.308
PW91	27.735	5.172
vdW-DF2	26.787	5.318
opt86b-vdW	27.734	5.113
PBE D2	27.566	5.159
rPBE-vdW	26.959	5.389
optPBE-vdW	27.342	5.277

S5. Adsorption configuration of CO_2 and CO on different metals

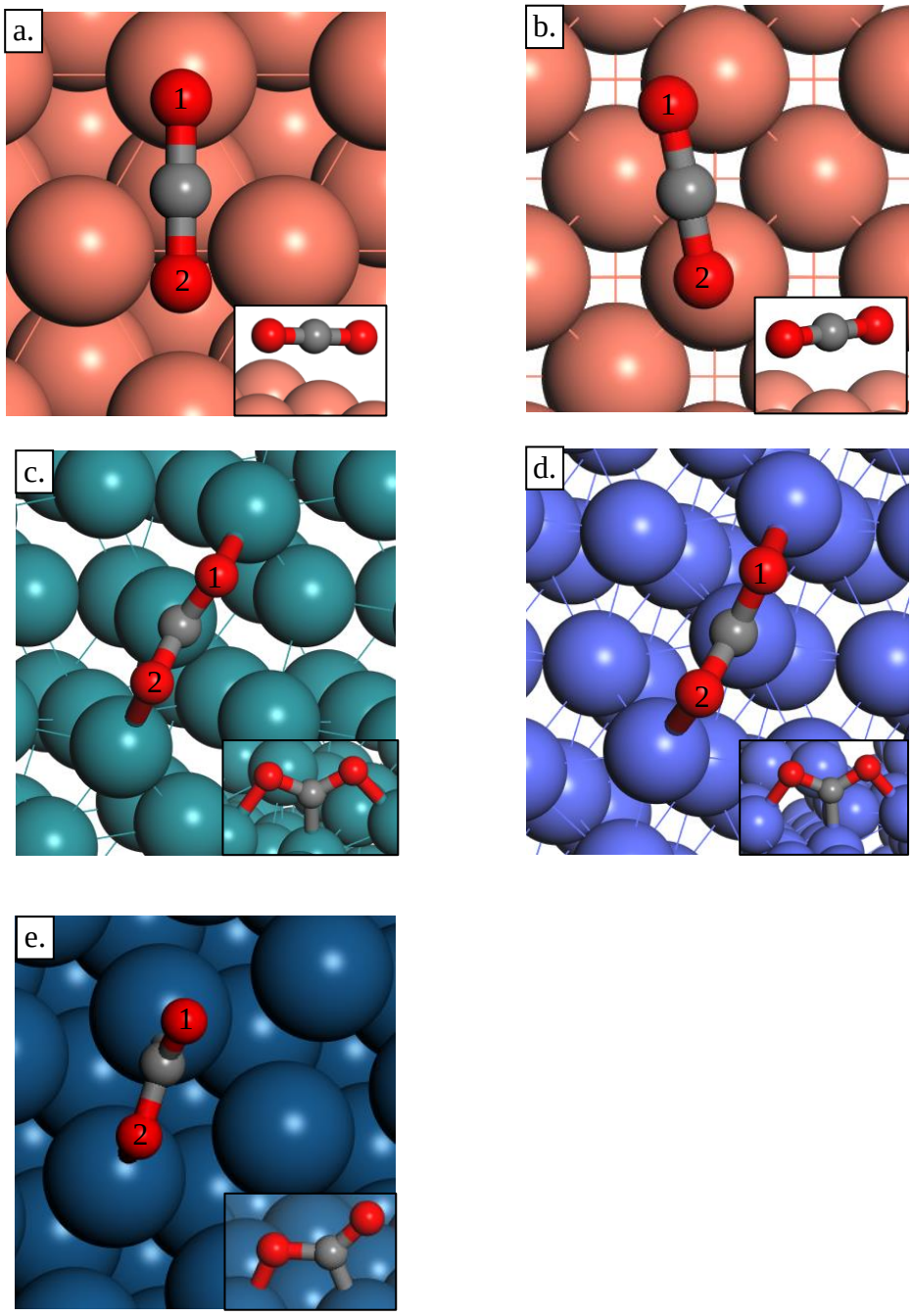

Fig. S5 the adsorption configuration of CO_2 on **a.** Cu (111), **b.** Cu (100), **c.** Ru (111), **d.** Co (111), **e.** Pt (111). Salmon balls represent Cu atoms, green balls represent Ru atoms, blue balls represent Co atoms, dark blue balls represent Pt atoms, red balls represent oxygen atoms, and the grey ball represents carbon atom.

Table S5 Geometric parameters CO_2 on Cu, Ru, Co, and Pt surfaces

Parameter	**Configuration**				
	Cu		**Ru**	**Co**	**Pt (111)**
	(111)	**(100)**	**(111)**	**(111)**	
$d_{C\text{-}O1}$ (Å)	1.18	1.180	1.296	1.289	1.214
$d_{C\text{-}O2}$ (Å)	1.181	1.182	1.300	1.290	1.295
O1-C-O2 (deg)	179.43	179.29	122.62	123.21	132.32