Supporting Information for:

Carbon Dioxide Hydrogenation on Copper and Nickel Catalysts via a Conformal Sampling Approach

Thantip Roongcharoen[1,*], and Alessandro Fortunelli[1,*]

[1] CNR-ICCOM, Consiglio Nazionale delle Ricerche, via Giuseppe Moruzzi 1, Pisa 56124, Italy

[*] Corresponding authors' email: thantip.roongcharoen@cnr.it, alessandro.fortunelli@cnr.it

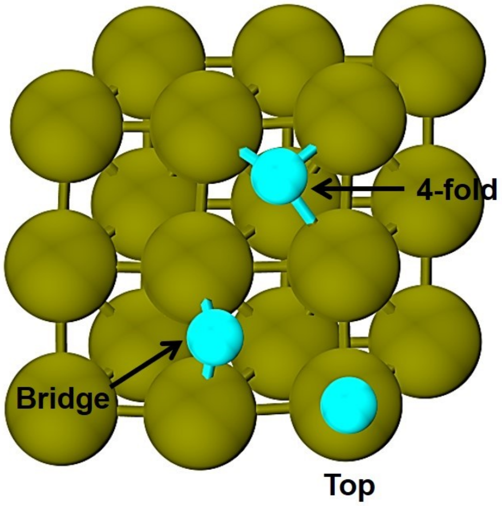

Figure S1. Three possible adsorption sites on a metal (100) surface: (1) top site on a surface atom, (2) bridge site, and (3) four-fold hollow site.

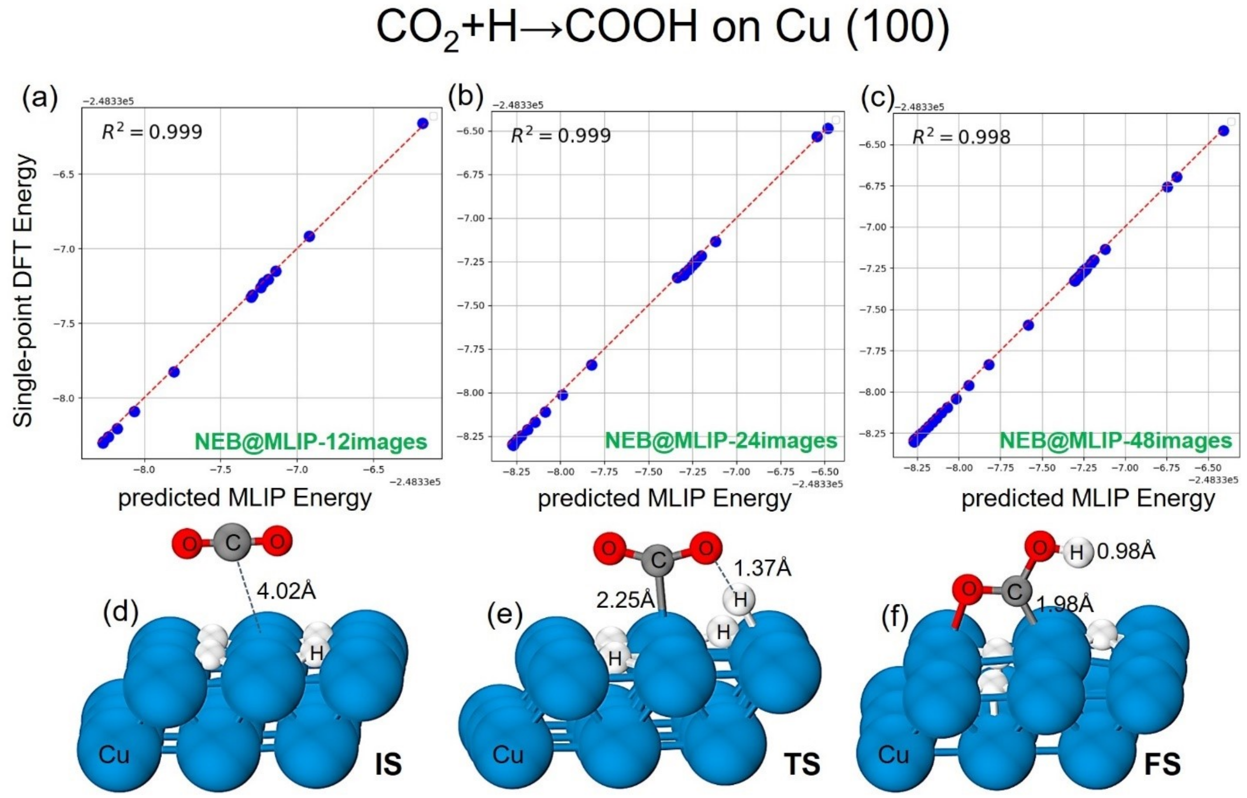

Figure S2. Parity plot comparing single-point DFT energies with NEB@MLIP-3 energies for coordinates along the reaction step of CO_2 + H → COOH on Cu (100), with the R² value shown in the panel. Panels (a), (b), and (c) present the parity plots for NEB coordinates generated with 12, 24, and 48 intermediate images, respectively.

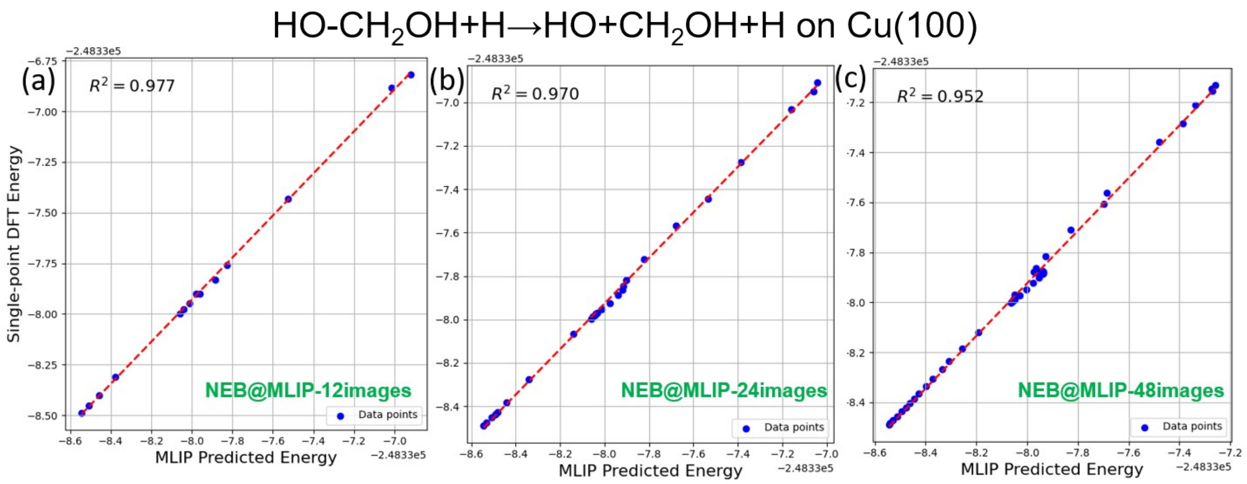

Figure S3. Parity plot comparing single-point DFT energies with NEB@MLIP-3' energies for coordinates along the reaction step of HO-CH_2OH+H→HO+CH_2OH+H on Cu (100) using MLIP-3′, with the R² value shown in the panel. Panels (a), (b), and (c) present the parity plots for NEB coordinates generated with 12, 24, and 48 intermediate images, respectively. Note that MLIP-3′ was trained using Database-D3 and additional structures generated from MLIP-3 as explained in the main text.

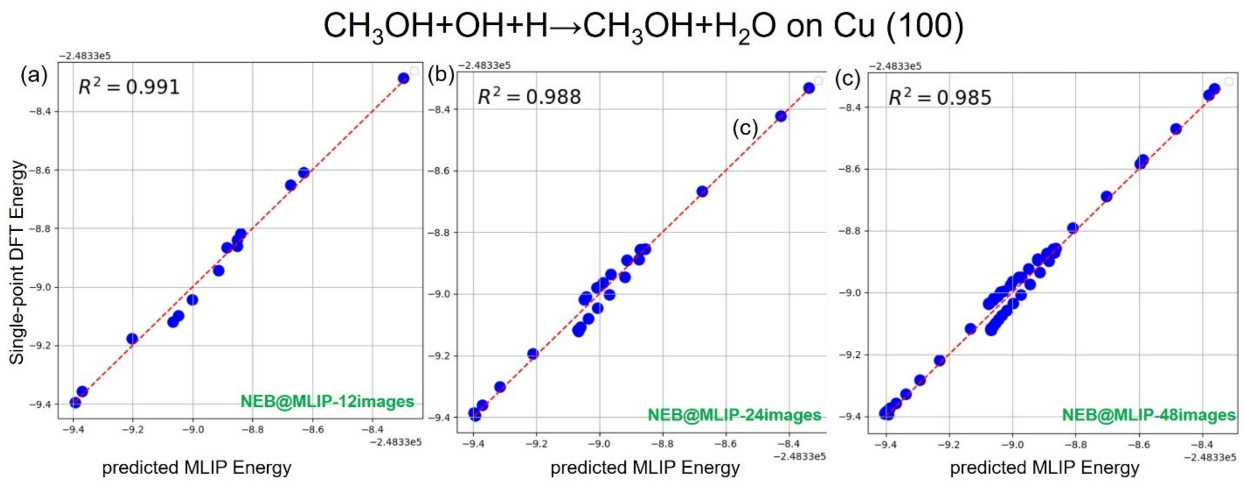

Figure S4. Parity plot comparing single-point DFT energies with NEB@MLIP-3 energies for coordinates along the reaction step of $CH_3OH+OH+H \rightarrow CH_3OH+H_2O$ on Cu (100), with the R^2 value shown in the panel. Panels (a), (b), and (c) present the parity plots for NEB coordinates generated with 12, 24, and 48 intermediate images, respectively.

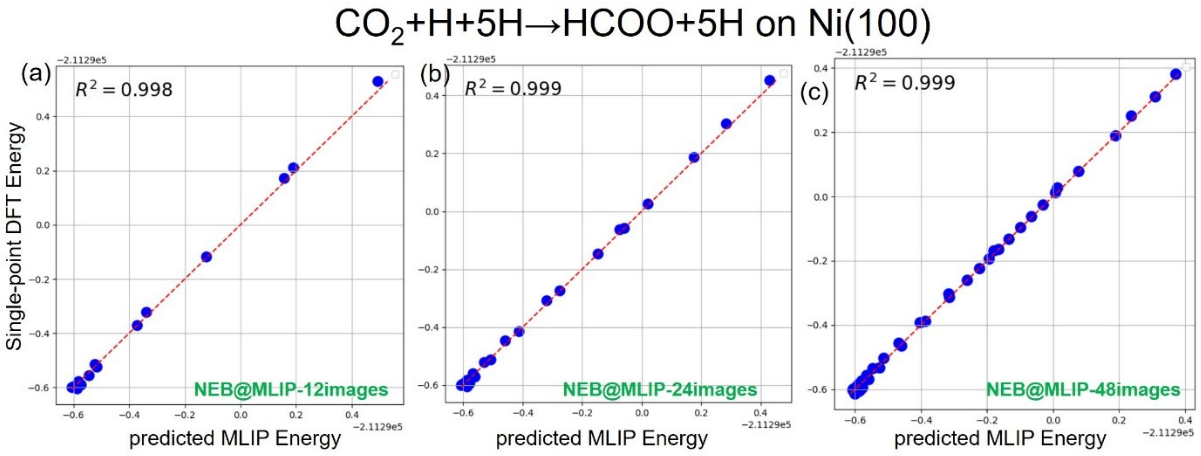

Figure S5. Parity plot comparing single-point DFT energies with NEB@MLIP-3 energies for coordinates along the reaction step of CO_2+H+5H→HCOO+5H on Ni (100), with the R^2 value shown in the panel. Panels (a), (b), and (c) present the parity plots for NEB coordinates generated with 12, 24, and 48 intermediate images, respectively.

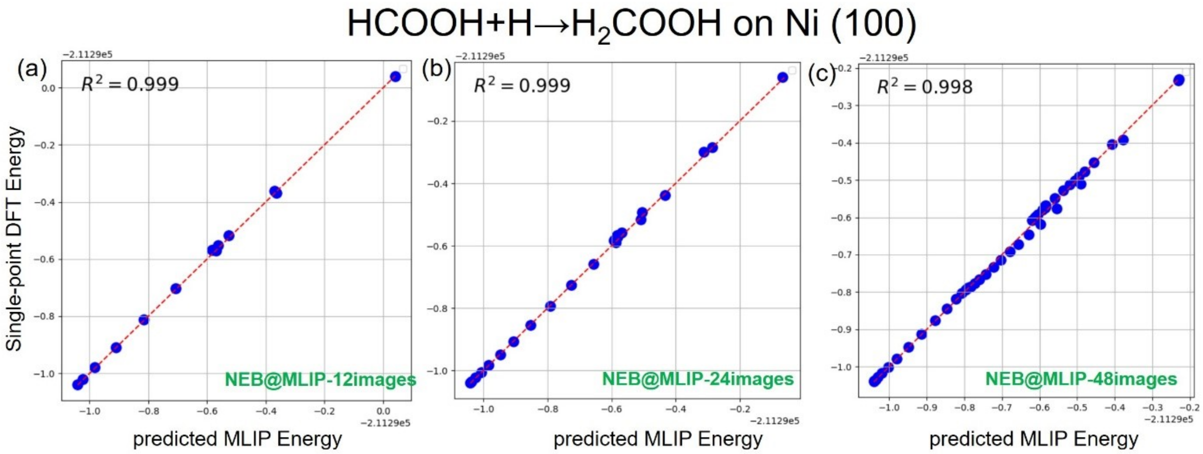

Figure S6. Parity plot comparing single-point DFT energies with NEB@MLIP-3 energies for coordinates along the reaction step of HCOOH+H→H_2COOH on Ni (100), with the R² value shown in the panel. Panels (a), (b), and (c) present the parity plots for NEB coordinates generated with 12, 24, and 48 intermediate images, respectively.

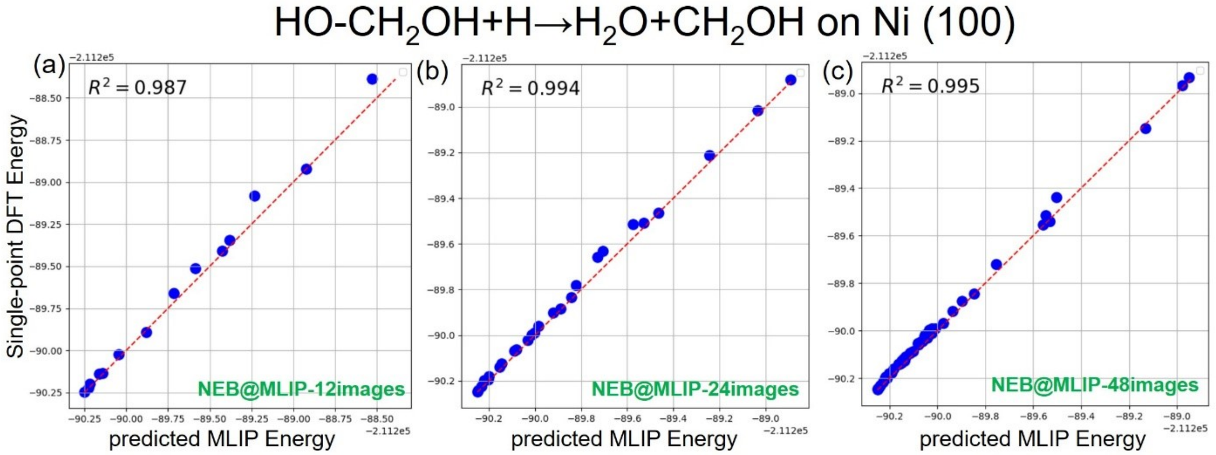

Figure S7. Parity plot comparing single-point DFT energies with NEB@MLIP-3 energies for coordinates along the reaction step of HO-CH$_2$OH+H → H$_2$O+CH$_2$OH on Ni (100), with the R² value shown in the panel. Panels (a), (b), and (c) present the parity plots for NEB coordinates generated with 12, 24, and 48 intermediate images, respectively.

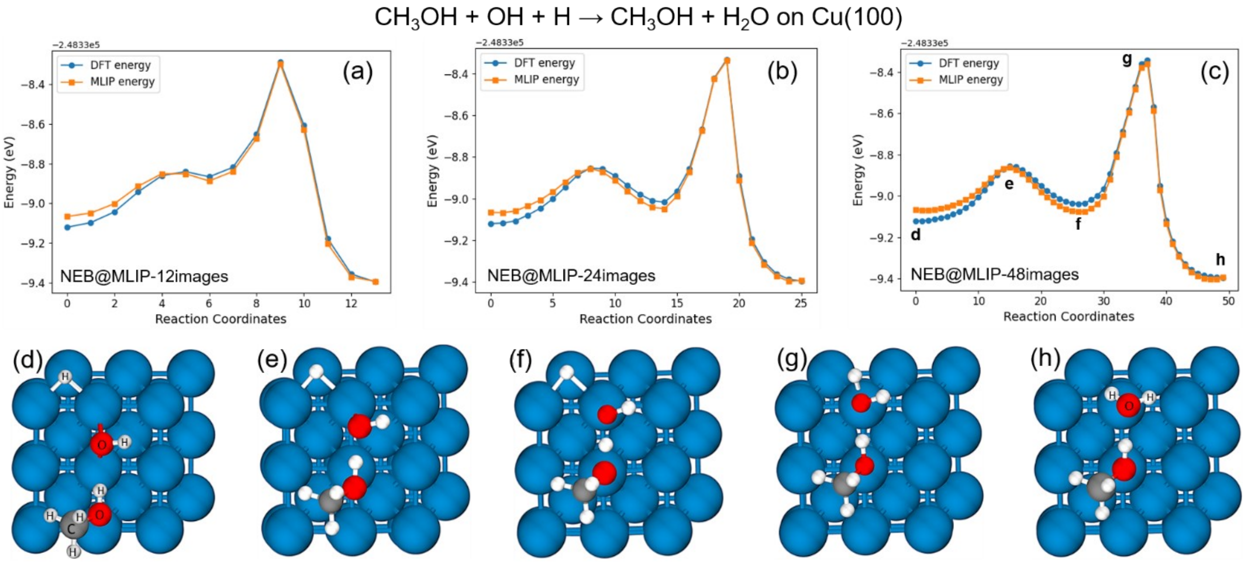

Figure S8. (a-c) Reaction energies for H2O formation on Cu(100) with CH$_3$OH spectator species (CH$_3$OH + OH + H → CH$_3$OH + H$_2$O) as a function of the reaction coordinate, simulated using NEB@MLIP-3 with 12, 24, and 48 intermediate images, respectively. The MLIP energies are shown by the orange line, while the DFT energies, computed from single-point calculations on the same set of reaction coordinates, are shown by the blue line. Panels (d-h) show selected frames extracted from the NEB@MLIP-3 calculation using 48 intermediate images shown in (c).

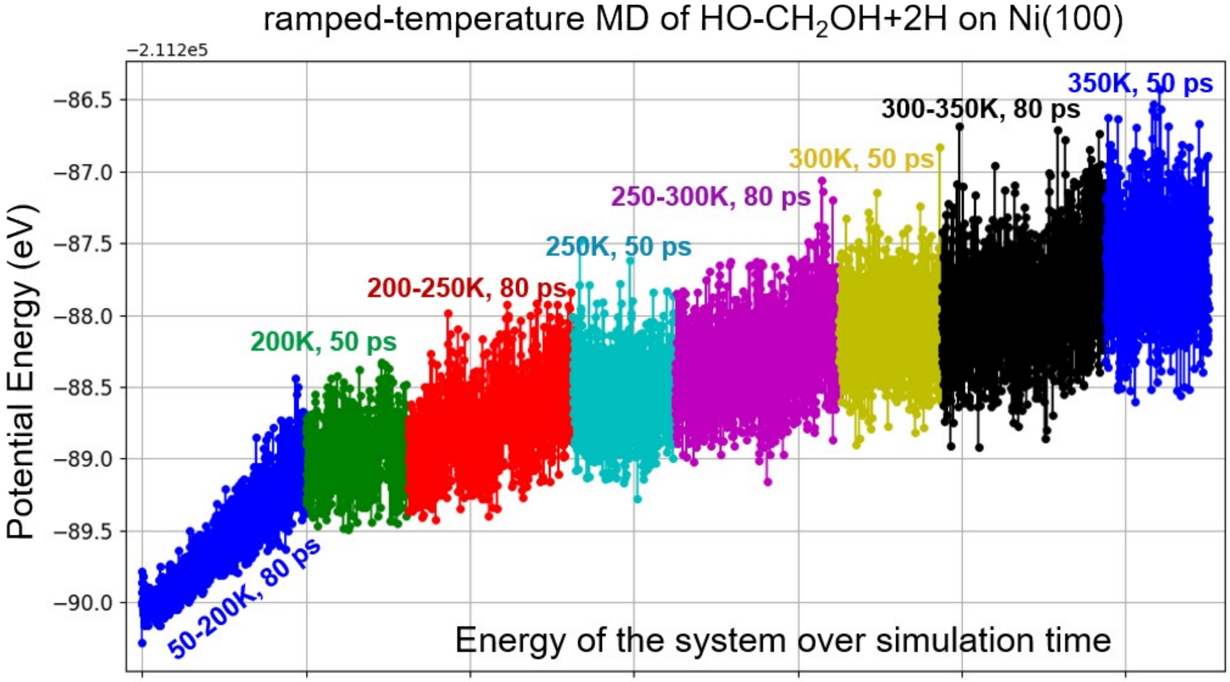

Figure S9. Ramped-temperature molecular dynamics simulation of the HO-CH$_2$OH + 2H system on Ni(100) using MLIP-3, showing the potential energy as a function of simulation time. Further details of the ramped-temperature procedure are described in the main text, and the input parameters for the MD simulations using the MLIP potential are provided in Section S3 of the Supporting Information.

Table S1. The MACE parameters for MLIP parametrization

Parameter	
--hidden_irreps	128x0e + 128x1o
--r_max	5.0
--batch_size	10
--max_num_epochs	300
--start_swa	200

Table S2. The reaction energy from NEB@DFT and NEB@MLIP simulations for all elementary steps of CO2 hydrogenation on Ni(100). ΔE denotes the energy difference between the two computed energies.

Reaction step	**NEB@DFT**	**NEB@MLIP**	**ΔE**
CO_2+H→HCOO (1)	0.018	-0.006	-0.02
HCOO+H→H_2COO (2)	0.478	0.469	-0.01
H_2COO+H→H_2COOH (3)	0.571	0.573	0.00
H_2COOH+H→ HO-H_2C-OH(4)	0.611	0.604	-0.01
CO_2+H→COOH (9) R2 done	0.877	0.879	0.00
COOH+H→HCOOH (10)	0.883	0.847	-0.04
HCOOH+H→H_2COOH (11)	0.458	0.472	0.01
H_2COOH→CH_2O+OH(12)	0.705	0.725	0.02
CH_2O+OH→CH_3O+OH (13)	-0.223	-0.182	0.04
CH_3O+OH→CH_3OH+OH (14)	0.411	0.393	-0.02
HCOO+H→HCOOH (15)	0.598	0.587	-0.01
HCOOH+H→ H_2COOH(16)	0.420	0.412	-0.01
HO-CH_2OH→ OH+CH_2OH (17)	-0.213	-0.120	0.09
CH_3OH+OH+H→CH_3OH+H_2O	0.521	0.460	0.06
COOH+H→ HO-COH (20)	0.681	0.693	0.01
HO-COH+H→HO-CHOH (21)	0.679	0.702	0.02
HCOOH+H→HO-CHOH (25)	0.802	0.790	-0.01
H_2COOH+H→HO-CH_2OH (26)	0.720	0.701	-0.02
HO+CH_2O+H→CH_2OH+OH	0.260	0.242	0.02
HO-COH→HO+COH (28)	-0.584	-0.558	0.03
HO+COH→OH+CHOH (29)	1.159	1.170	0.01
OH+CHOH+H→ OH+CH_2OH (30)	0.066	0.064	0.00
OH-CHOH→OH+CHOH (31)	-0.739	-0.726	0.01
HO-CH_2OH→ H_2O+CH_2OH (32) R2	0.031	0.048	0.02
HCOOH→HCO+OH (33)	0.681	0.693	0.01
HCO+OH→ HCOH+OH (34)	0.547	0.550	0.00

$CH_2OH+OH\rightarrow CH_2OH+H_2O$ (35)	0.215	0.200	-0.02
$CH_2OH+H_2O\rightarrow CH_3OH+H_2O$ (36)	-0.510	-0.454	0.06
$CH_3O+OH\rightarrow CH_3O+H_2O$ (37)	0.283	0.274	-0.01
$H_2O+CH_3O+H\rightarrow CH_3OH+H_2O$ (38)	0.080	0.088	0.01

S1. The DFT input parameters

In this work, we employed density functional theory (DFT) to generate a database for Cu(100) and Ni(100) systems. Three types of calculations were performed: (1) geometry optimization, (2) single-point energy calculation, and (3) Nudged Elastic Nand (NEB) simulation.

S1.1 input parameters for optimization and singles-point calculations

The input parameters for optimization and single-point calculations are listed below. The main difference between the two methods is the calculation tag:

For geometry optimization: calculation = 'relax'

For single-point calculations: calculation = 'SCF'

```
&CONTROL
   calculation      = 'relax'
   restart_mode     = 'from_scratch'
   wf_collect       = .true.
   nstep            = 300
   tprnfor          = .true.
   outdir           = './scr/'
   pseudo_dir       = '/dir/'
   tefield          = .true.
   dipfield         = .true.
/
&SYSTEM
   ibrav            = 0
   ecutwfc          = 40.0
   ecutrho          = 200.0
   occupations      = 'smearing'
   degauss          = 0.005
   nspin            = 2
   edir             = 3
   starting_magnetization(1) = 0.3
   starting_magnetization(2) = 0.0
   starting_magnetization(3) = 0.0
   starting_magnetization(4) = 0.0
```

```
  ntyp            = 4
  nat             = 54
/
&ELECTRONS
  electron_maxstep = 300
  conv_thr        = 1e-06
  mixing_mode     = 'plain'
  mixing_beta     = 0.1
  diagonalization  = 'david'
/
&IONS
/
&CELL
/
ATOMIC_SPECIES
Ni  58.6934 ni_pbe_v1.4.uspp.F.UPF
O  15.999 o_pbe_v1.2.uspp.F.UPF
C  12.011 c_pbe_v1.2.uspp.F.UPF
H  1.008 h_pbe_v1.4.uspp.F.UPF
K_POINTS automatic
3 3 1  0 0 0
CELL_PARAMETERS angstrom
7.46251011562500 0.00000000000000 0.00000000000000
0.00000000000000 7.46251011562500 0.00000000000000
0.00000000000000 0.00000000000000 20.43194971250000
ATOMIC_POSITIONS angstrom
Ni          0.0934231620       0.0864249619        0.0116127745
Ni          1.3302847500       1.3300101200       -1.7580667000    0   0   0
Ni          0.0865055100       0.0862308900       -3.5169960500    0   0   0
Ni          1.3491482835       1.3315732004        1.8128555245
…..         ………                   …………                  …………..
```

S1.2 The parameter inputs for NEB calculation

```
BEGIN
BEGIN_PATH_INPUT
&PATH
string_method ='neb',
restart_mode ='from_scratch',
!restart_mode ='restart',
nstep_path =500,
num_of_images = 18,
opt_scheme="broyden",
CI_scheme = 'auto',
first_last_opt = .false.
path_thr =0.10D0,
/
END_PATH_INPUT
BEGIN_ENGINE_INPUT
&control
   restart_mode='from_scratch',
   calculation='relax',
   title='cuoinsio',
   nstep = 500
   verbosity='low',
   prefix='cuoinsio'
   pseudo_dir = ' /new-PP/',
   outdir='./scr/'
   tprnfor = .true.
   dipfield=.true.
   tefield=.true.
   wf_collect=.true.
 /
 &system
```

```
    edir=3
    ibrav=0,
    nat=54
    ntyp=4,
    ecutwfc =  40.0,
    ecutrho = 200.0,
    nspin = 2
    starting_magnetization(1) = 0.01,
    occupations='smearing',
    smearing='gauss',
    degauss=0.005,
 /
 &electrons
    conv_thr =  1.0d-6,
    electron_maxstep = 1000,
    diagonalization='david',
    mixing_mode='plain',
    mixing_beta = 0.1,
 /
 &ions
 /
ATOMIC_SPECIES
Cu 63.546 cu_pbe_v1.2.uspp.F.UPF
C  12.011 c_pbe_v1.2.uspp.F.UPF
O  15.999 o_pbe_v1.2.uspp.F.UPF
H  1.008 h_pbe_v1.4.uspp.F.UPF
CELL_PARAMETERS (angstrom)
7.67848353314501 0.00000000000000 0.00000000000000
0.00000000000000 7.67848353314501 0.00000000000000
0.00000000000000 0.00000000000000 21.02327327564026
K_POINTS automatic
```

```
 3 3 1 0 0 0
BEGIN_POSITIONS
FIRST_IMAGE
ATOMIC_POSITIONS (angstrom)
   Cu     0.0054825896    -0.0043074487     0.0142065383
   Cu     1.2797728500     1.2797728500    -1.8098323900 0 0 0
   Cu     0.0000000000     0.0000000000    -3.6196632400 0 0 0
   Cu     1.3066809171     1.2821464075     1.8856265841
---------------        ---------------------  -------------------------
```

S2. NEB@MLIP parameters

The input files for NEB@MLIP simulations comprise eight files. Examples of each input file are shown below.

1. Odata file contains parameters for NEB calculations

```
DEBUG
LAMMPS
READMASS
FREEZE 2 3 6 7 10 11 14 15 18 19
FREEZE 22 23 26 27 30 31 34 35
NEWNEB 12 400 0.0005
NEBK 20
DUMPNEBXYZ 20
POINTS
```

2. data.lammps file

```
------------------------
54      atoms
4 atom types
0.0 7.462509909922475 xlo xhi
0.0 7.462509909922475 ylo yhi
0.0 20.4319491578326 zlo zhi
0.0 0.0 0.0 xy xz yz
Masses
1 1.008
2 12.011
3 15.999
4 58.6934
Atoms  ##coordinates of your system
1 4 0.09289079 0.08999324 0.01141003
2 4 1.33028475 1.33001012 -1.7580667
```

```
3 4 0.08650551 0.08623089 -3.51699605
4 4 1.35211456 1.34036236 1.80223853
5 4 2.57272921 0.08713511 0.01533452
6 4 3.81776861 1.33001012 -1.7580667
7 4 2.57398937 0.08623089 -3.51699605
8 4 3.79923088 1.34407972 1.77599965
9 4 5.06046547 0.08670446 0.0102728
```

----

3. in.lammp file contains parameter to perform MD with LAMMMP interfaces.

```
atom_modify     map yes #FONDAMENTALE PER LAMMPS+MACE
newton          on      #IDEM
units           metal
dimension       3
boundary        p p p
atom_style      atomic
read_data       data.lammps
pair_style      mace no_domain_decomposition           #USA MACE
pair_coeff      * * MACE_model_swa.model-lammps.pt H C O Ni    #MODELLO COMPILATO
PER LAMMPS
neighbor        2 bin
neigh_modify    every 1 delay 0 check yes
variable        dt equal 0.1
timestep        $(dt)
thermo          1
run             1
```

----

4. “masses” file contains atomic mass data of coordinates for NEB

```
58.6934  #Ni
58.6934 #Ni
58.6934 #Ni
58.6934 #Ni
15.999 #O
12.011 #C
1.008 #H
15.999 #C
1.008
1.008
1.008
1.008
1.008
```

5. “start” file contains 3 column data of XYZ coordinates of the initial structure for NEB@MLIP calculation

6. “finish” file contains 3 column data of XYZ coordinates of the final structure for NEB@MLIP calculation

7. Potential file obtained from MLIP-3 parametrization e.g. MACE_model_swa.model-lammps.pt

8. Script to submit the NEB@MLIP simulation

```
 #!/bin/bash
#SBATCH --job-name=job_name
#SBATCH --nodes=1                # Number of nodes
#SBATCH --ntasks-per-node=1      # Number of MPI ranks per node
#SBATCH --cpus-per-task=32       # number of  threads per task
#SBATCH --gres=gpu:4
##SBATCH --exclusive             # Number of requested gpus per node
##SBATCH --mem=230000MB          # Memory per node
#SBATCH --time 00:09:59          # Walltime, format: HH:MM:SS
#SBATCH --partition=boost_usr_prod
```

```
#SBATCH --account=X

module purge

source /home/cinprod/spack_setup.sh

module use /home/cinprod/spack/02/modules/BA/0.19/

module load intel-oneapi-mkl/2022.2.1--intel--2021.8.0-3x3

export PYTHONPATH="${PYTHONPATH}:/leonardo_scratch/fast/CNHPC_1457049/new_MACE/PACK_PY/"

/leonardo/Example /MACE_k/LMPOPTIM > out.min
```

S3. The input parameters for ramped-temperature molecular dynamic simulations

```
# ---------- Initialize Simulation ---------------------

units          metal

atom_style      atomic

atom_modify     map yes

newton          on

dimension       3

boundary        p p p

# ---------- Create Atoms ---------------------

read_data       system.data

# ---------- Define Interatomic Potential ---------------------

pair_style      mace no_domain_decomposition

pair_coeff      * * MACE_model_swa.model-lammps.pt H C O Ni

# ---------- Neighbor List ---------------------

neighbor        2.0 bin

neigh_modify    every 1 delay 0 check yes

# ---------- Define Fixed Region ---------------------

region fixed_slab block EDGE EDGE EDGE EDGE EDGE 6.8

group slab region fixed_slab
```

```
variable nslab equal count(slab)
print "Number of atoms in group 'slab' = ${nslab}"
# ---------- Energy Minimization --------------------
log            log.all
thermo_style   custom step cpu temp fmax fnorm pe ke density press pxx pyy pzz lx ly lz xlo xhi ylo yhi zlo zhi xy xz yz cella cellb cellc cellalpha cellbeta cellgamma
thermo         10
thermo_modify  norm no flush yes
dump           d01_opt all custom 1 dump_01_opt.lammps id type x y z fx fy fz
dump_modify    d01_opt sort id
min_style      cg
minimize       1.0e-6 1.0e-6 10000 10000
undump         d01_opt
write_data     data.after01_opt
write_restart  after01_opt.restart
reset_timestep 0
# ---------- Velocity Initialization --------------------
velocity       all create 50.0 11299259 mom yes rot no dist gaussian
velocity       slab set 0.0 0.0 0.0
# ---------- Common Settings --------------------
variable dt equal 0.0001
variable tdamp equal ${dt}*100
timestep       ${dt}
thermo         400
thermo_style   custom step temp press pe ke etotal vol
# ---------- Temperature Equilibration Setup ----------
variable teq index 50 200 250 300 350 400 450
variable tprod index 200 250 300 350 400 450 500
label          loop_start
# Set temperatures
```

```
variable teq_now equal ${teq}
variable tprod_now equal ${tprod}
# ---------- Equilibration Run ----------
log         log.eq_${tprod_now}K.lammps append
print       "### Starting Equilibration from ${teq_now} K to ${tprod_now} K ###"
reset_timestep  0
fix fNVT all nvt temp ${teq_now} ${tprod_now} ${tdamp}
fix fFreeze slab setforce 0.0 0.0 0.0
dump deq all custom 8000 dump_eq_${tprod_now}K.lammpstrj id element xu yu zu fx fy fz
dump_modify deq element H C O Ni
run 800000
unfix fNVT
unfix fFreeze
undump deq
# ---------- Production Run ----------
log         log.prod_${tprod_now}K.lammps append
print       "### Starting Production Run at ${tprod_now} K ###"
reset_timestep  0
fix fNVT all nvt temp ${tprod_now} ${tprod_now} ${tdamp}
fix fFreeze slab setforce 0.0 0.0 0.0
dump dprod all custom 5000 dump_prod_${tprod_now}K.lammpstrj id element xu yu zu
dump_modify dprod element H C O Ni
#restart 10000 PdCH2OH_${tprod_now}K.restart
run 500000
unfix fNVT
unfix fFreeze
undump dprod
next teq
next tprod
jump SELF loop_start
```