Supporting Information

Mechanistic insights into positional and skeletal isomerization of cyclohexene in the H-BEA zeolite

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Table S1. Detailed parameters for coordination numbers.

cn	*p*	*q*	d_0
cn(C2-H_B)	6	6	1.6
cn(C1-H_B)	6	6	1.6
cn(O_{Al1}-H_B)	6	6	1.3
cn(O_{Al2}-H_{61})	6	6	1.3
cn(C6-H_{61})	6	6	1.6
cn(C-C)	6	6	1.7

Input file for the cp2k/Quickstep in the ab initio molecular dynamic simulations.

```
&FORCE_EVAL
    METHOD Quickstep
    &DFT
     LSD
     BASIS_SET_FILE_NAME      ./BASIS
     POTENTIAL_FILE_NAME      ./GTH_POTENTIALS
     WFN_RESTART_FILE_NAME ZSM-5-cyho-RESTART.wfn
     &MGRID
        CUTOFF 360
     &END MGRID
     &QS
        WF_INTERPOLATION ASPC
        EXTRAPOLATION_ORDER 2
     &END QS
     &SCF
      EPS_SCF 1.E-6
      SCF_GUESS RESTART
      MAX_SCF 1000
      &OT
          PRECONDITIONER    FULL_SINGLE_INVERSE
          MINIMIZER DIIS
          N_DIIS 7
      &END OT
     &END SCF
     &XC
       &XC_FUNCTIONAL PBE
       &END XC_FUNCTIONAL
      &VDW_POTENTIAL
          DISPERSION_FUNCTIONAL PAIR_POTENTIAL
          &PAIR_POTENTIAL
              TYPE DFTD3
              REFERENCE_FUNCTIONAL PBE
              PARAMETER_FILE_NAME            ./dftd3.dat
              R_CUTOFF 4.0
          &END PAIR_POTENTIAL
       &END VDW_POTENTIAL
     &END XC
    &END DFT
   &SUBSYS
```

```
    &CELL
      ABC                              12.6614      12.6614      26.4061
      ALPHA_BETA_GAMMA    90.0000      90.0000      90.0000
    &END CELL
    &TOPOLOGY
      COORD_FILE_NAME    ./bea-t9-cyclo.xyz
      COORD_FILE_FORMAT XYZ
    &END
    &KIND O
      BASIS_SET DZVP-MOLOPT-SR-GTH-q6
      POTENTIAL GTH-PBE-q6
    &END KIND
    &KIND H
      BASIS_SET DZVP-MOLOPT-SR-GTH-q1
      POTENTIAL GTH-PBE-q1
    &END KIND
    &KIND C
      BASIS_SET DZVP-MOLOPT-SR-GTH-q4
      POTENTIAL GTH-PBE-q4
    &END KIND
    &KIND Si
      BASIS_SET DZVP-MOLOPT-SR-GTH-q4
      POTENTIAL GTH-PBE-q4
    &END KIND
    &KIND Al
      BASIS_SET DZVP-MOLOPT-SR-GTH-q3
      POTENTIAL GTH-PBE-q3
    &END KIND
    &END SUBSYS
&END FORCE_EVAL
&GLOBAL
  PROJECT ZSM-5-cyho
    RUN_TYPE    MD
    PRINT_LEVEL    LOW
&END GLOBAL
&MOTION
    &MD
    ENSEMBLE NVT
    STEPS        5000
    TIMESTEP 0.5
    TEMPERATURE    413.0
    &THERMOSTAT
```

```
        &NOSE
          TIMECON    200
        &END NOSE
      &END THERMOSTAT
    &END MD
&END MOTION
```

Input file for plumed in the metadynamics studying the conformational isomerization of cyclohexene.

```
RESTART

UNITS LENGTH=A TIME=fs ENERGY=kcal/mol
MOLINFO STRUCTURE=../bea-t9-cyclo-select.pdb

cv1: PUCKERING ATOMS=1,2,4,6,5,3
UPPER_WALLS ARG=cv1.theta AT=3.5    KAPPA=900 LABEL=uwall
LOWER_WALLS ARG=cv1.theta AT=-0.5 KAPPA=900 LABEL=lwall

METAD ...
  LABEL=mwmtd
     ARG=cv1.theta,cv1.phi
     HEIGHT=0.4
     SIGMA=0.3,0.5
     PACE=30
     BIASFACTOR=8
     TEMP=413
     WALKERS_ID=0
     WALKERS_N=4
     WALKERS_DIR=../walkers_exchange
     WALKERS_RSTRIDE=50
... METAD

PRINT    STRIDE=1 ARG=cv1.theta,cv1.phi FILE=BIAS
```

Input file for plumed in the metadynamics studying the protonation of cyclohexene.

```
RESTART

UNITS LENGTH=A TIME=fs ENERGY=kcal/mol
MOLINFO STRUCTURE=../bea-cyclohexene-pt.pdb

cn_bhc1:    COORDINATION GROUPA=193 GROUPB=195 R_0=1.6 NN=6 MM=12
cn_bhc2:    COORDINATION GROUPA=193 GROUPB=197 R_0=1.6 NN=6 MM=12
cn_bhbo:    COORDINATION GROUPA=193 GROUPB=166 R_0=1.3 NN=6 MM=12

cn_comb:    COMBINE          ARG=cn_bhbo,cn_bhc1,cn_bhc2 COEFFICIENTS=1.0,-1.0,-1.0    PERIODIC=NO
cn_diff:    COMBINE          ARG=cn_bhc1,cn_bhc2                COEFFICIENTS=1.0,-1.0          PERIODIC=NO

METAD ...
    LABEL=mwmtd
    ARG=cn_comb,cn_diff
    HEIGHT=0.4
    SIGMA=0.2,0.2
    PACE=30
    BIASFACTOR=8
    TEMP=413
    WALKERS_ID=0
    WALKERS_N=4
    WALKERS_DIR=../walkers_exchange
    WALKERS_RSTRIDE=50
... METAD
```

Input file for plumed in the metadynamics studying the positional isomerization of alkene with cyclohexene.

```
RESTART

UNITS LENGTH=A TIME=fs ENERGY=kcal/mol
MOLINFO STRUCTURE=../bea-cyhex-h-transfer.pdb

cn_hboal1:      COORDINATION GROUPA=193 GROUPB=91              R_0=1.3 NN=6 MM=12
cn_hbc2:        COORDINATION GROUPA=193 GROUPB=197             R_0=1.6 NN=6 MM=12

cn_hc61oal2:    COORDINATION GROUPA=200 GROUPB=166             R_0=1.3 NN=6 MM=12
cn_hc61c6:      COORDINATION GROUPA=200 GROUPB=194             R_0=1.6 NN=6 MM=12

cn_diff1:       COMBINE        ARG=cn_hboal1,cn_hbc2           COEFFICIENTS=1.0,-1.0 PERIODIC=NO
cn_diff2:       COMBINE        ARG=cn_hc61oal2,cn_hc61c6       COEFFICIENTS=1.0,-1.0 PERIODIC=NO

METAD ...
    LABEL=mwmtd
    ARG=cn_diff1,cn_diff2
    HEIGHT=0.3
    SIGMA=0.2,0.2
    PACE=30
    BIASFACTOR=8
    TEMP=413
    WALKERS_ID=0
    WALKERS_N=4
    WALKERS_DIR=../walkers_exchange
    WALKERS_RSTRIDE=50
... METAD
```

Input file for plumed in the metadynamics studying the ring contraction of cyclohexene.

```
RESTART

UNITS LENGTH=A TIME=fs ENERGY=kcal/mol
MOLINFO STRUCTURE=../ht-b12.pdb

cn_hboal1:    COORDINATION GROUPA=193 GROUPB=166      R_0=1.3   NN=6 MM=12
cn_hbc1:      COORDINATION GROUPA=193 GROUPB=195      R_0=1.6   NN=6 MM=12
cn_c3c4:      COORDINATION GROUPA=198 GROUPB=199      R_0=1.7   NN=6 MM=12
cn_c2c4:      COORDINATION GROUPA=197 GROUPB=198      R_0=1.7   NN=6 MM=12

cn_hc41c4:    COORDINATION GROUPA=206 GROUPB=198      R_0=1.6   NN=6 MM=12
cn_hc41c3:    COORDINATION GROUPA=206 GROUPB=199      R_0=1.6   NN=6 MM=12

cn_hc21c4:    COORDINATION GROUPA=205 GROUPB=198      R_0=1.6   NN=6 MM=12
cn_hc21c2:    COORDINATION GROUPA=205 GROUPB=197      R_0=1.6   NN=6 MM=12

cn_diff1:     COMBINE      ARG=cn_hboal1,cn_hbc1      COEFFICIENTS=1.0,-1.0 PERIODIC=NO
cn_diff2:     COMBINE      ARG=cn_c3c4,cn_c2c4        COEFFICIENTS=1.0,-1.0 PERIODIC=NO
cn_diff3:     COMBINE      ARG=cn_hc41c4,cn_hc41c3    COEFFICIENTS=1.0,-1.0 PERIODIC=NO
cn_diff4:     COMBINE      ARG=cn_hc21c4,cn_hc21c2    COEFFICIENTS=1.0,-1.0 PERIODIC=NO

METAD ...
    LABEL=mwmtd
    ARG=cn_diff1,cn_diff2,cn_diff3,cn_diff4
    HEIGHT=0.5
    SIGMA=0.2,0.2,0.2,0.2
    PACE=30
    BIASFACTOR=8
    TEMP=413
    WALKERS_ID=0
    WALKERS_N=4
    WALKERS_DIR=../walkers_exchange
    WALKERS_RSTRIDE=50
... METAD
```