Nanostructures and adsorption on metallic surfaces:

Dehydrogenation of cyclohexaphenylene on Cu(111): possible reaction pathways from ab initio simulations

C.A. Pignedoli

In collaboration with:

1Empa, Swiss Federal Laboratories for Materials Testing and Research
2Physical Chemistry Institute, University of Zurich (present address: IBM Zurich Research Laboratory)
3Max-Planck Institute for Polymer Research, 55128 Mainz, Germany
4Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland
Motivation: processing of individual sheets of graphene

• No easy-to-handle method for large-scale processing of individual sheets of graphene

• Large range of chemically tailored “nanographene” flakes can be synthesized by chemical routes

• 470 K: well below other thermal cyclodehydrogenation routes such as flash vacuum pyrolysis (>1000 K)
Cyclohexaphenylene undergoes dehydrogenation on Cu(111) at ~470 K

Initial state

RT deposition

450 K annealing

Final state

470 K annealing

$V_s = -0.6 \, V$, $I = 50 \, \text{pA}$, $T = 5\, \text{K}$
Motivation: understanding surface induced cyclodehydrogenation


Molecule in vacuum, constrained MD

```plaintext
&SUBSYS
&COLVAR
&DISTANCE
  ATOMS 49 50
&END
&END

[...]
&MOTION
&CONSTRAINT
  SHAKE_TOL 1.0E-5
  ROLL_TOL 1.0E-5
&COLLECTIVE
  COLVAR 1
  INTERMOLECULAR T
  TARGET [angstrom] 3.72
  TARGET_GROWTH [angstrom*fs^-1] -0.001
&END
&END

[...]
```
Inclusion of the Cu(111) substrate

PROLOGUE

&MULTIPLE_FORCE_EVALS
FORCE_EVAL_ORDER 2 3
MULTIPLE_SUBSYS T
&END
&FORCE_EVAL
METHOD MIXED
&MIXED
[....]
&MAPPING
 &FORCE_EVAL_MIXED
    &FRAGMENT 1
       1 56
    &END
 &FRAGMENT 2
    57 2936
    &END
 &END
 &FORCE_EVAL 1
    DEFINE_FRAGMENTS 1 2
 &END
 &FORCE_EVAL 2
    DEFINE_FRAGMENTS 1
 &END
Inclusion of the Cu(111) substrate

FORCE FIELD

&FORCE_EVAL
METHOD FIST
&MM
&FORCEFIELD
[...]
&CHARGE
ATOM Cu
CHARGE 0.0
&END CHARGE
[...]
&NONBONDED
&GENPOT
atoms Cu C
FUNCTION A*exp(-av*r)+B*exp(-ac*r)-C/(r^6)
VARIABLES r
PARAMETERS A av B ac C
VALUES 4.13 1.33 115.82 2.20 75.40
RCUT 15
&END GENPOT
[...]
&LENNARD-JONES
atoms C H
EPSILON 0.0
SIGMA 3.166
RCUT 15
&END LENNARD-JONES
[...]
&EAM
atoms Cu Cu
PARM_FILE_NAME CU.pot
&END EAM
&END NONBONDED

\[ E_i = F_{\alpha} \left( \sum_{i \neq j} \rho_{\beta}(r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{\alpha\beta}(r_{ij}) \]
Inclusion of the Cu(111) substrate

DFT

&FORCE_EVAL
  METHOD Quickstep
  &DFT
    &XS
      METHOD PM6
    

[...]

MD, GEO_OPT,BAND...
Insights on the dehydrogenation reaction from DFT

Two distinct approaches:

-hybrid empirical potentials/DFT approach
  molecule within standard DFT or empirical DFT (PM6)
  Cu(111) modeled with embedded atom model (EAM)
  van der Waals interactions included with potential fitted from large scale DFT simulations
  😊 simple and fast, allows for complex MD simulations
  😞 catalytic effects not included

-full ab initio approach, Grimme corrections
  😊 both catalytic effects and dispersive interactions considered
  😞 computational demanding, complex MD simulations impossible
Cyclohexaphenylene undergoes dehydrogenation on Cu(111) at ~470 K

Metadynamics in 3D CV space: PM6, 450 K (gbussi thermostat), multiple walkers

\[ V_G(C(x), t) = \sum_{t' < t, t' = \tau_G, 2\tau_G, ...} \exp \left( -\frac{(C(x) - c(t'))^2}{2\delta_s^2} \right) \]

CV\(_1\) = d(H\(_1\), C\(_3\))
CV\(_2\) = d(C\(_1\), C\(_2\))
CV\(_3\) = d(H\(_2\), C\(_1\))

Movie from G.Bussi
Cyclohexaphenylene undergoes dehydrogenation on Cu(111) at ~470 K

Metadynamics in 3D CV space: PM6, 450 K (gbussi thermostat), multiple walkers

\[ CV_1 = d(H_1, C_3) \]

\[ CV_2 = d(C_1, C_2) \]

\[ CV_3 = d(H_2, C_1) \]

Movie from G.Bussi
A possible non-catalytic reaction pathway...

Hybrid approach:
~3000 Cu atoms molecule with PM6

Metadynamics

Diagram: geometry optimization of the intermediates within standard DFT
...step by step
...step by step

CV1 = d(H2, C) + d(H3, C)
CV2 = d(H1, C)
CV3 = d(H2, H3).

b
...step by step
...step by step
...step by step

\textbf{FUNCTION CV1+CV2}
\begin{verbatim}
&SUBSYS
 &COLVAR
 &COMBINE_COLVAR
 &COLVAR
   &DISTANCE
   ATOMS 4 50
 &END
 &END COLVAR
 &COLVAR
   &DISTANCE
   ATOMS 7 49
 &END
 &END COLVAR
 FUNCTION CV1+CV2
 VARIABLES CV1 CV2
 ERROR_LIMIT 1.0E-8
 &END
 &COLVAR
   &DISTANCE
   ATOMS 49 50
 &END
 &END
\end{verbatim}

$CV1 = \quad + \quad d_{C2-H2}$

$CV2$
...step by step

&MOTION
&MD
ENSEMBLE NVT
[...]
&THERMOSTAT
TYPE CSVR
REGION MASSIVE
[...]
&END
&END MD
&FREE_ENERGY
&METADYN
DO_HILLS
NT_HILLS 50
WW 2.0e-3
&METAVAR
SCALE 0.1
COLVAR 1
&WALL
TYPE QUADRATIC
POSITION [angstrom] 5
&QUADRATIC
DIRECTION WALL_PLUS
K [kcalmol] 40.0
&END
&END
&WALL
“The” reaction pathway on Cu(111): full GPW, NEB

Cu(111) modeled with 4 Cu layers, 90 atoms per layer

1 Cu layer kept fix

Cell size ~23 x 23 Å²

30 Å of vaccum

Reaction pathway: NEB calculations with “climbing image”

guess from series of constrained geometry optimizations
The initial guess is important
"The" reaction pathway on Cu(111): full GPW, NEB

Why o-H detaches and p-H not?
"The" reaction pathway on Cu(111): full GPW, NEB

```
&XC
  &XC_FUNCTIONAL PBE
  &END XC_FUNCTIONAL
  &VDW_POTENTIAL
    DISPERSION_FUNCTIONAL PAIR_POTENTIAL
  &PAIR_POTENTIAL
    TYPE DFTD3
    CALCULATE_C9_TERM .TRUE.
    PARAMETER_FILE_NAME /scratch/rosa/cpi/CP2K_FILES/dftd3.dat
  &REFERENCE_FUNCTIONAL PBE
  R_CUTOFF 15
&END PAIR_POTENTIAL
&END VDW_POTENTIAL
&END XC
```
&MOTION

&MOTION

&REPLICA

COORD_FILE_NAME  ini_eq.xyz
&END

&REPLICA

COORD_FILE_NAME  two.xyz
&END

[...]

&END

&REPLICA

COORD_FILE_NAME  fin_eq.xyz
&END

&PROGRAM_RUN_INFO

INITIAL_CONFIGURATION_INFO
&END

&REPLICA

COORD_FILE_NAME  ini_eq.xyz
&END

&REPLICA

COORD_FILE_NAME  two.xyz
&END

[...]

&END
How many intermediates?

Why do we see only two intermediates from the experiments?
How many intermediates?

Why do we see only two intermediates from the experiments?

T. Laino Uni Irchel
Stepped Au(111) surfaces, interplay between step and reconstruction

FIG. 1. (Color online) (a) Atomic geometry of the stepped Au(677) surface including a kink in each unit cell (2 × 2 × 1 cells
Stepped Au(111) surfaces, interplay between step and reconstruction
Some other examples: porous graphene networks

Surface-promoted polymerization

Monomer deposition

300 K

Surface-promoted dehalogenation

575 K

Cyclohexa-m-phenylene (CHP)

[ M. Bieri et al., Chem. Commun., 6919 (2009) ]
Some other examples: porous graphene networks

Cu(111)  Au(111)  Ag(111)

dendritic  dendritic & 2D  2D

What determines the network morphology?
Some other examples: porous graphene networks
Some other examples: porous graphene networks as nanofilters
Conclusions

Simulations:

Don’t forget vdW contributions
Nor electronic ones…
A simple approach could give good ideas for accurate QM calculations

some References

cp2k http://cp2k.berlios.de