

Toward Computational Materials Design

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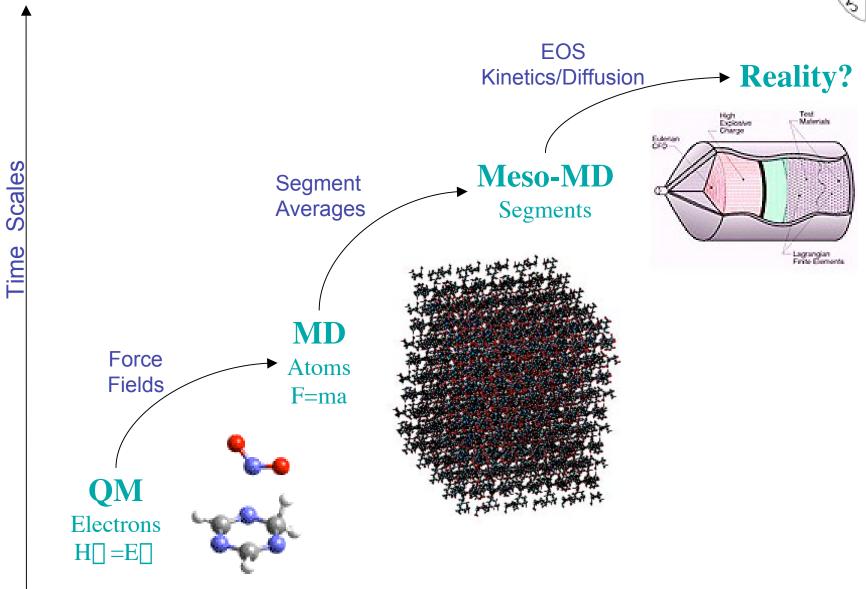
Computational Materials Design



- Develop tools to design new materials rather than merely understanding existing ones.
- Incorporate combinatorial-ish rapid scans of multiple structures, elements, etc.
- Getting close to materials design
 - QM and MM methods still have to get better
 - Design process is not combinatorial
 - Beginning to develop the approaches to use for the design process
 - In 20 years...

Multiscale Modeling





Rapid Prototyping Strategy



- 1. Determine mechanism/behavior of material in question.
- 2. Determine bottlenecks and critical points in the behavior above.
- 3. Formulate new materials and test against critical points in 2.
 - Lather, rinse, repeat
- 4. Validate against experiment, higher level theory, etc.

QM-RP Application: Methane Activation



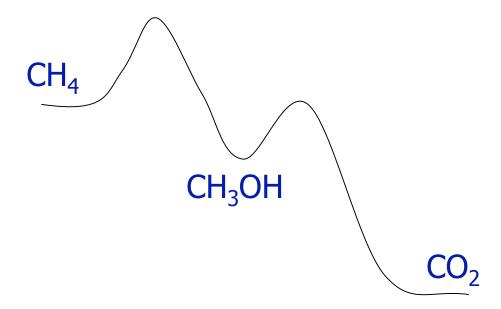
Methane

- Produced in large quantities at oil wells
- Gaseous: Need to convert to liquid to transport
- Most of this methane goes wasted
- Syngas/Fisher-Tropsch
 - Convert methane to Syngas (CO/H₂) (not efficient)
 - Syngas to alkanes via Fischer-Tropsch (not efficient)
- Ideal situation
 - Convert methane to methanol via low-temperature catalytic process.

Why CH₄ CH₃OH is hard

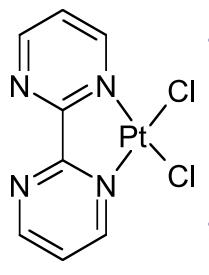


- CH bonds are stronger in CH₄ than in CH₃OH
 - 114 vs 103 kcal/mol
 - Thus, any catalyst that converts CH₄ to CH₃OH will probably continue on to CO₂



Periana Pt Catalyst





Pros

- 72% conversion to mixture of CH₃OH + CH₃OSO₃H in 2.5 hrs at 220 C
- Relatively low temperature
- Cons
 - Conc. Sulfuric Acid
 - SO₃ oxidizing agent
 - Separation/hydrolysis of CH₃OSO₃H
- Desire
 - Reaction that works in water

Periana Catalytic Cycle



Functionalization

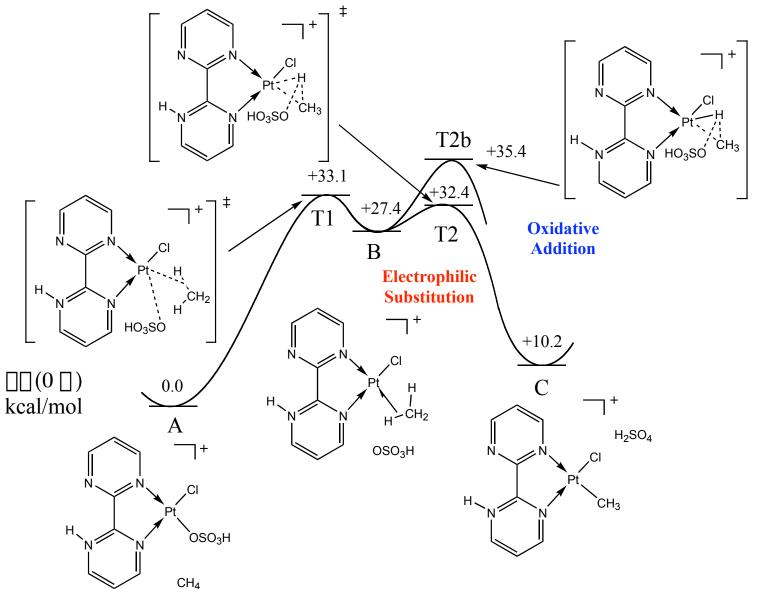
$$\begin{array}{c}
CH_{3}OSO_{3}H \\
HN
\end{array}$$

$$\begin{array}{c}
CH_{4}OSO_{3}H \\
HN
\end{array}$$

$$\begin{array}{c}
CH_{4}OSO_{4}H \\
HN
\end{array}$$

Mechanism of the C-H Activation Step





Water Poisoning

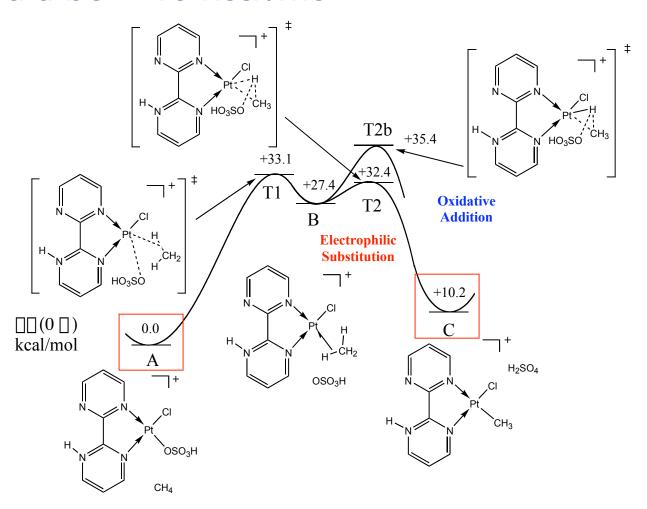


H N Pt CI
$$H(0 \text{ K}) = -6.8 \text{ kcal/mol}$$

$$H$$
 N
 N
 N
 OH_2
 $+ HSO_4^- (at ∞)$



 Compute the energy of the M-CH₃ compound; should be < 10 kcal/mol.

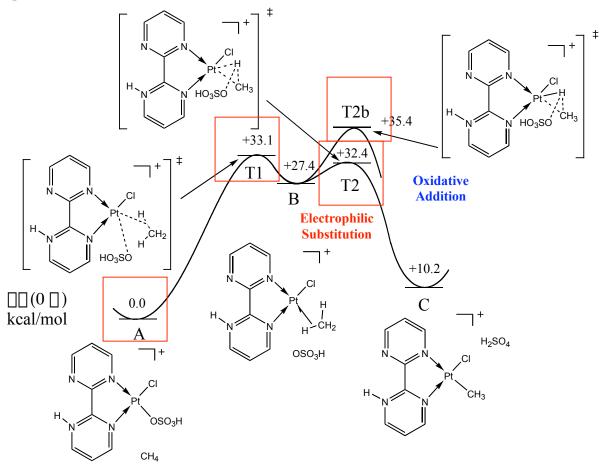




 For candiates that pass test 1, compute the reaction with a single water; new candidates should be stable (□E_{H2O} > 0).

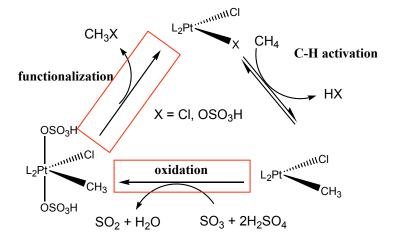
Holds at
$$\infty$$
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 For candidates that pass tests 1-3, compute energetics for oxidation and functionalization steps.

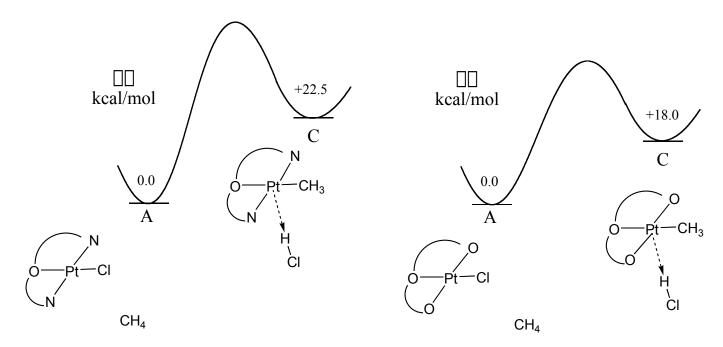


 Candidates that pass all tests are candidates for experimental validation.

Catalyst Candidates #1



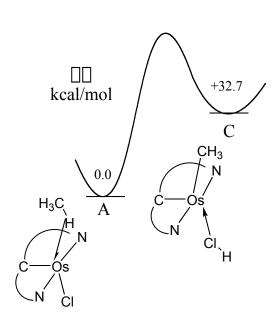
(a)
$$\sum_{N=1}^{\infty} \sum_{N=1}^{\infty} \sum_{N=1}^{\infty}$$



• Pt(II), 16 electron complexes with N,O,N (a) and O,O,O (b) coordinating atoms. Again, as the □E(A-C) energies are 22.5 and 18.0 kcal/mol, respectively, these systems do not pass QM-RP test 1, and are not pursued further.

Catalyst Candidates #2

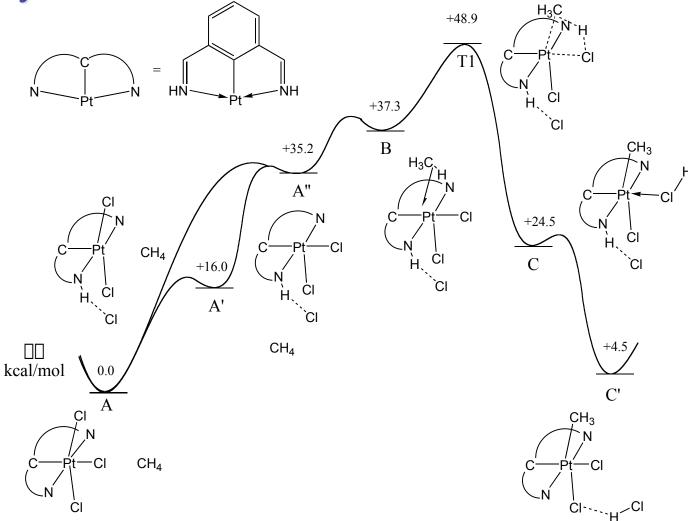




• NCN structures with (a) Os(II) (14 electrons) and (b) Pt(II) (18 electrons). Structure (a) has a □E(A-C) of 32.7 kcal/mol, which does not pass QM-RP test 1, but structure (b) has □E(A-C), which does pass QM-RP test 1.

Catalyst Candidates: Barrier Tests

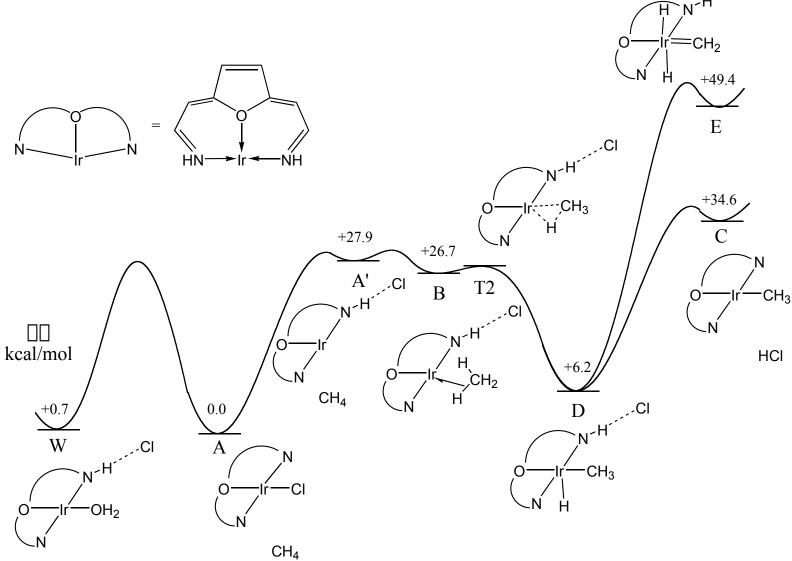




• Transition state for C-H bond activation for the structure from the previous slide. The barrier is 48.9 kcal/mol, and thus does not pass QM-RP test 2.

Best QM-RP Catalyst Candidate

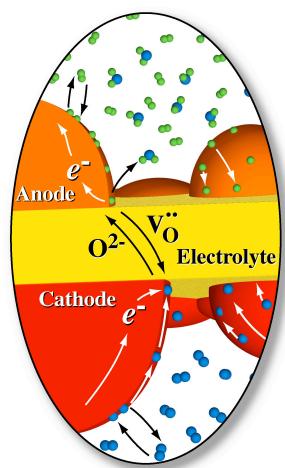




Catalysis-RP Future Directions



- Continue work on CH₄
 - Roy looking at a few structures
- Move on to fuel cell design
 - High T DECO Fuel Cells
 - Optimize Catalyst to prevent coking
 - Understand behavior of TPB



CMDF Energetic Materials Simulation



- Predictive simulation of HE
 - Integrate software tools across multiple physical scales
 - First principles based simulation
 - Validate against existing experiments
 - Predict behavior of novel materials

$$O_2N$$
 O_2N
 O_2N

Detailed Nitramine Reaction Mechanism



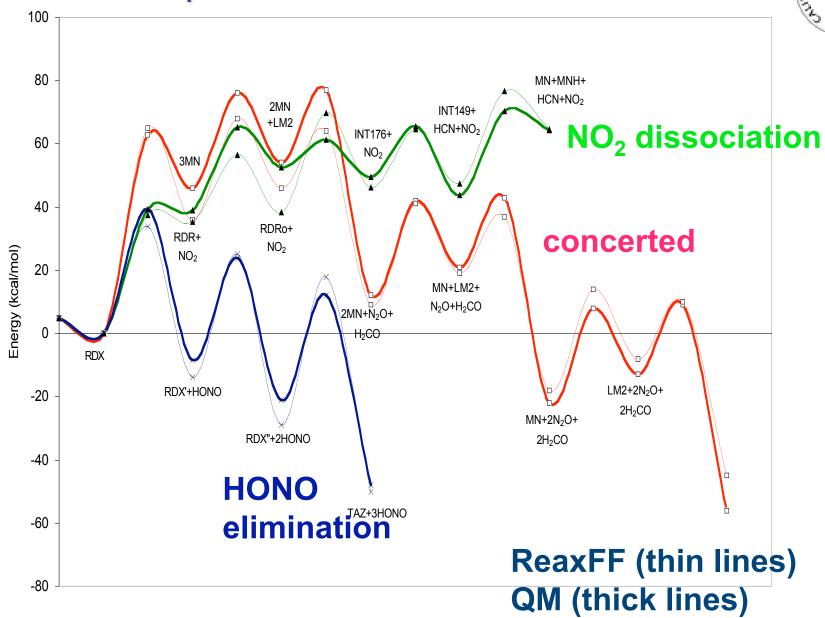
ReaxFF: QM-honest Classical FF



- Classical FF accurately describes QM results
 - TS and Pathways
 - Automatically fit to QM structures, energies
- E = Eval + Ecoul + Evdw
- Bonds can break and reform
 - Bond-order-dependent valence terms
- Charge equilibration for long-range charge transfer
- Generic: every O is the same, regardless of CH₂O or Al₂O₃

ReaxFF Reproduces RDX QM Data

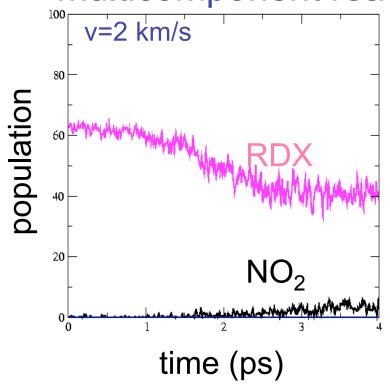


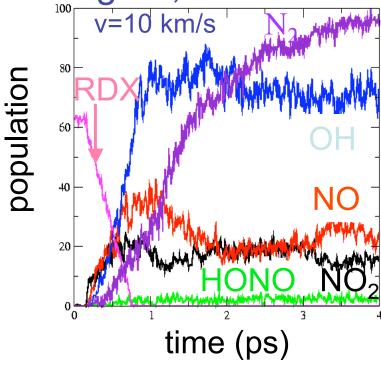


Species Profiles from ReaxFF

- Can use ReaxFF for shock or cook-off
- Every product in the simulation is also observed experimentally

 ReaxFF can simulate complicated multicomponent reactions at high T,P





Move from Simulation to Design



- Detailed reaction mechanisms too expensive
 - Too many man hours to work for arbitrary new materials
- Use ReaxFF to simulate reaction chemistry
 - Validate against quantum chemistry
- Distill multiple ReaxFF trajectories to reduced reaction mechanism
- Use reduced mechanism in Cantera flame simulation
 - Also need transport and thermochemistry parameters
 - Collaboration with Dave Goodwin, Caltech

CMDF Sample Code for HE



```
RDX = load_bgf("rdx_uc.bgf")
RDX444 = periodic supercell(RDX, (4,4,4))
for T in [100,500,1000]:
  RDX444.set_temperature(T)
  Traj[T]=RunDynamics(material=RDX444,time=10)
Species = AnalyzeFragments(Traj)
Mech1D = SimpleMech(Species, reactant="rdx",
                      product="n2")
for frag in Species:
  Thermo[frag] = SimThermo(frag)
  Transport[frag] = SimTransport(frag)
CanteralDFlame(Mech1D, Thermo, Transport,
                MoleFrac=("rdx",1))
```