Atomistic – Continuum Modeling of Gas-Surface Interactions (Catalysis and Oxidation)

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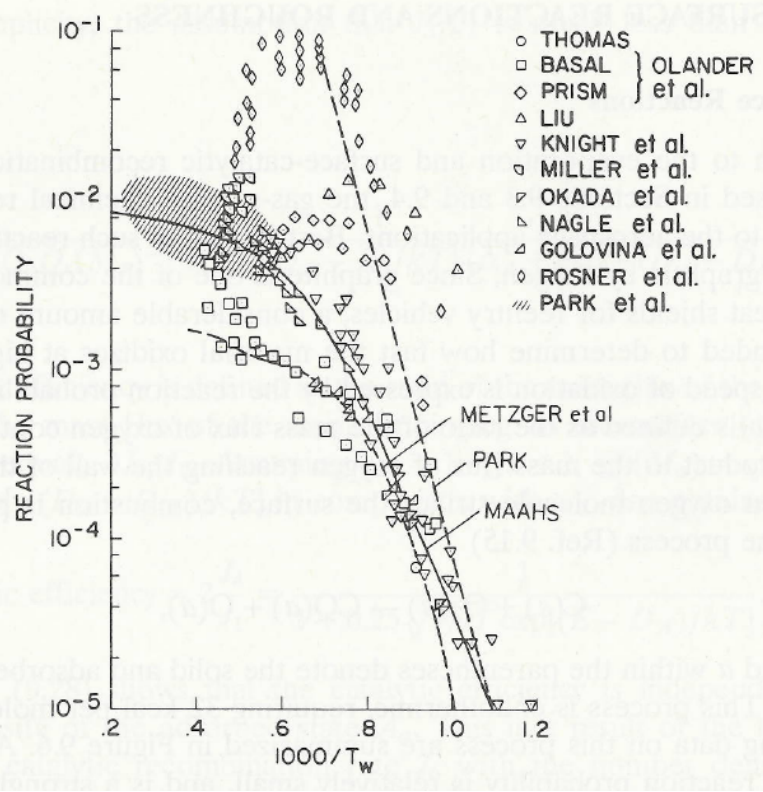
Mechanical and Nuclear Engineering, Penn State University

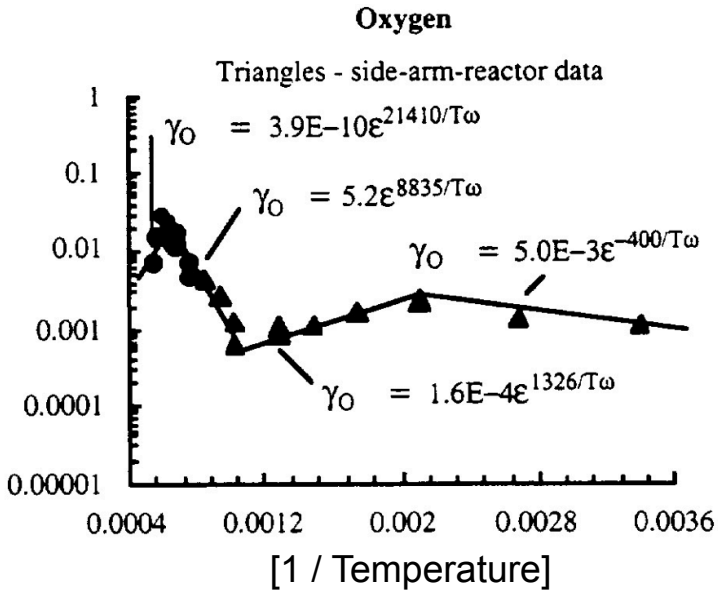
Fundamental Processes in High-Temperature Gas-Surface Interactions
[AFOSR FY2010 MURI #13]

Gas Surface Interaction Modeling (Motivation)

- Existing models for oxidation and catalysis exhibit large variations
- Precise mechanisms can not be inferred from experiment alone
- MURI team seeks to bridge physical chemistry ←→ macroscopic rates



Rate data for C(s) + O_2 → CO_2 on carbon and popular curve-fits used in current models.

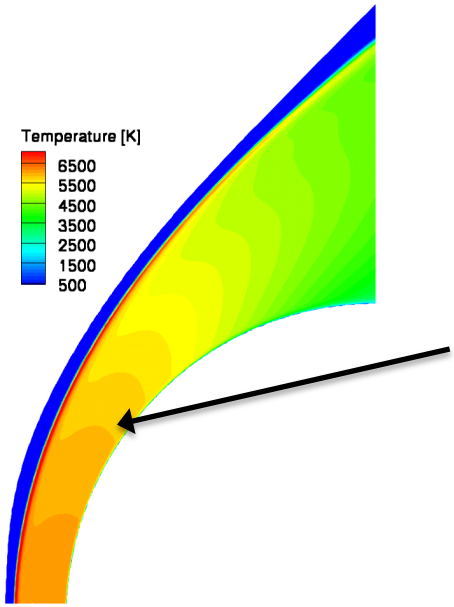


Oxygen recombination efficiencies on RCG (silica-based) tiles, taken from:

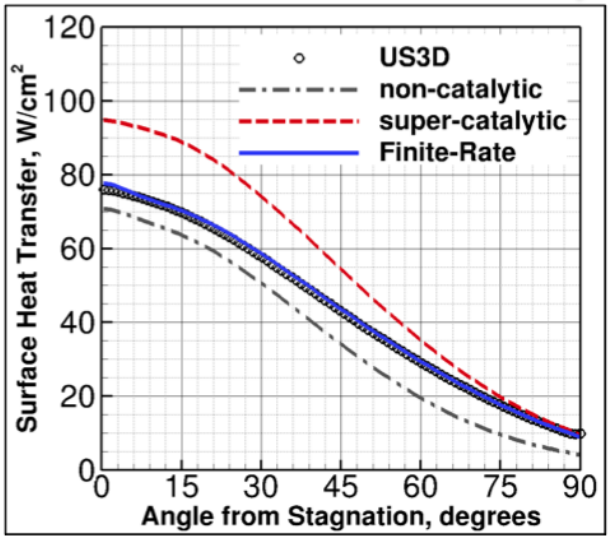
Stewart, D.A., "Surface Catalysis and Characterization of Proposed Candidate TPS for Access-to-Space Vehicles", *NASA Technical Memorandum 112206*, July 1997, Ames Research Center.

Finite-Rate Models for Gas-Surface Chemistry

- Surface reactions now modeled similar to gas-phase; this is required for nonequilibrium vehicle trajectories
- Surface catalysis chosen as a preliminary study (now complete)
- US3D – DPLR code-code validation complete; finite rate model naturally results in temperature *and pressure-dependent* catalytic efficiency
- Model requires activation energies and steric factors for each rate (parameters are now directly linked to physical chemistry)
- What are the mechanisms? What are their rate parameters?



(1) $O + [s] \rightarrow O_s$
(2) $N + [s] \rightarrow N_s$
(3) $O + O_s \rightarrow O_2 + [s]$
(4) $N + N_s \rightarrow N_2 + [s]$
(5) $O + N_s \rightarrow NO + [s]$
(6) $N + O_s \rightarrow NO + [s]$
(7) $O_{s,m} + O_s \rightarrow O_2 + 2[s]$
(8) $N_{s,m} + N_s \rightarrow N_2 + 2[s]$
(9) $O_{s,m} + N_s \rightarrow NO + 2[s]$
(10) $N_{s,m} + O_s \rightarrow NO + 2[s]$
(11) $O_s \rightarrow O + [s]$
(12) $N_s \rightarrow N + [s]$

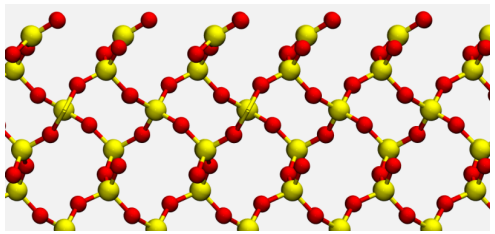


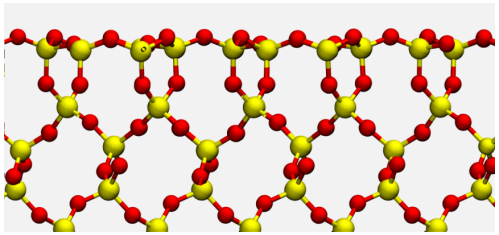
(c) $T_W = 2250$ K

Atomistic Simulation of Real Silica Surfaces

- Silica is a main component in non-ablative/ablative TPS and SiO_2 oxide layers form on many TPS materials (i.e. SiC and UHTCs)
- Start with the state-of-the-art $ReaxFF_{SiO}$ interatomic potential [1]
- Experimental validation of $ReaxFF_{SiO}$ with bulk silica polymorphs [2], surface reconstructions [3], and amorphous structure (*a*-SiO_2) [4]

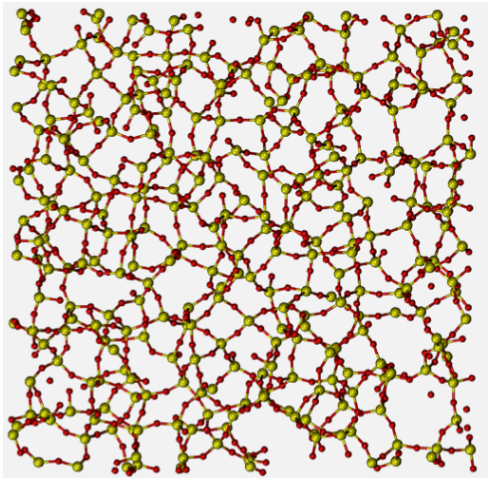
Cleaved (001) α-Quartz surface

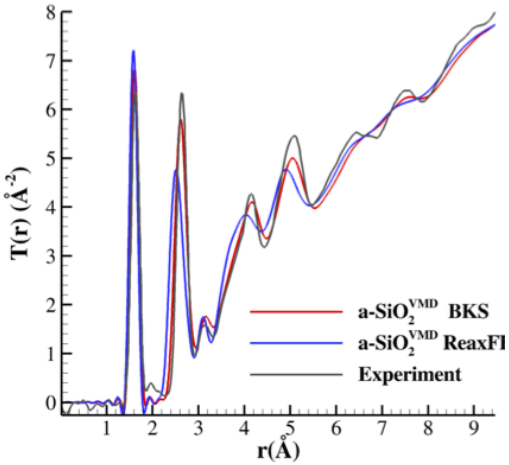




Reconstructed (001) α-Quartz surface

Bulk Amorphous *a*-SiO_2





Total Correlation Function (distribution of atomic distances)

[1] A. van Duin et al., "$ReaxFF_{SiO}$ Reactive Force Field for Silicon and Silicon Oxide Systems", *J. Phys. Chem. A*, l07, pp. 3803-3811, **2003.**

[2] T. Demuth et al. *J. Phys: Condensed Matter,* **1999.**

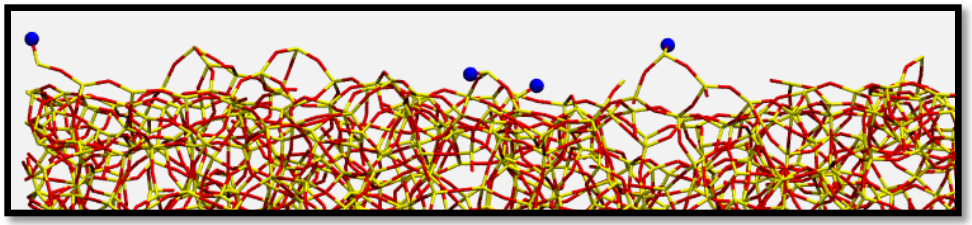
[3] Y. Chen et al. *Applied Physics Letters*. 93, pp. 181911, **2008**.

[4] Susman, S. et al., *Physical Review B.*, Vol. 43, No. 13, **1991.**

In-situ Surface Structure

- What are the *precise chemical structures* on realistic silica surfaces that gas-phase O and O_2 interact with under hypersonic conditions?
- Proper investigation requires multi-disciplinary collaboration (MURI)

Collaborative/Iterative Procedure:



- Validate predicted amorphous SiO_2 structure with experiment (stable reconstructions and defect structures observed)

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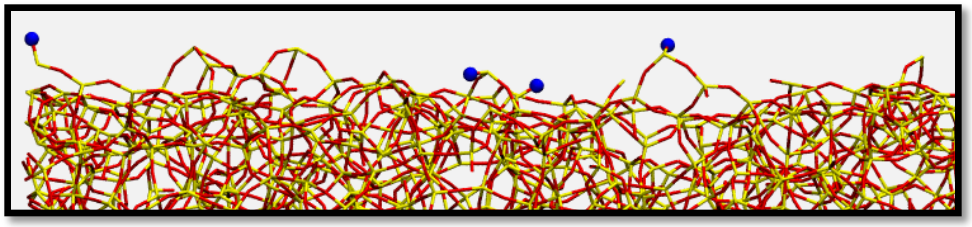

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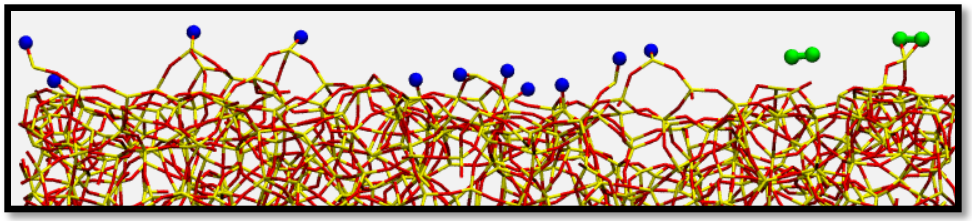

- Simulate exposure to dissociated oxygen at high temperature, observe *in-situ* surface structure and chemical defects

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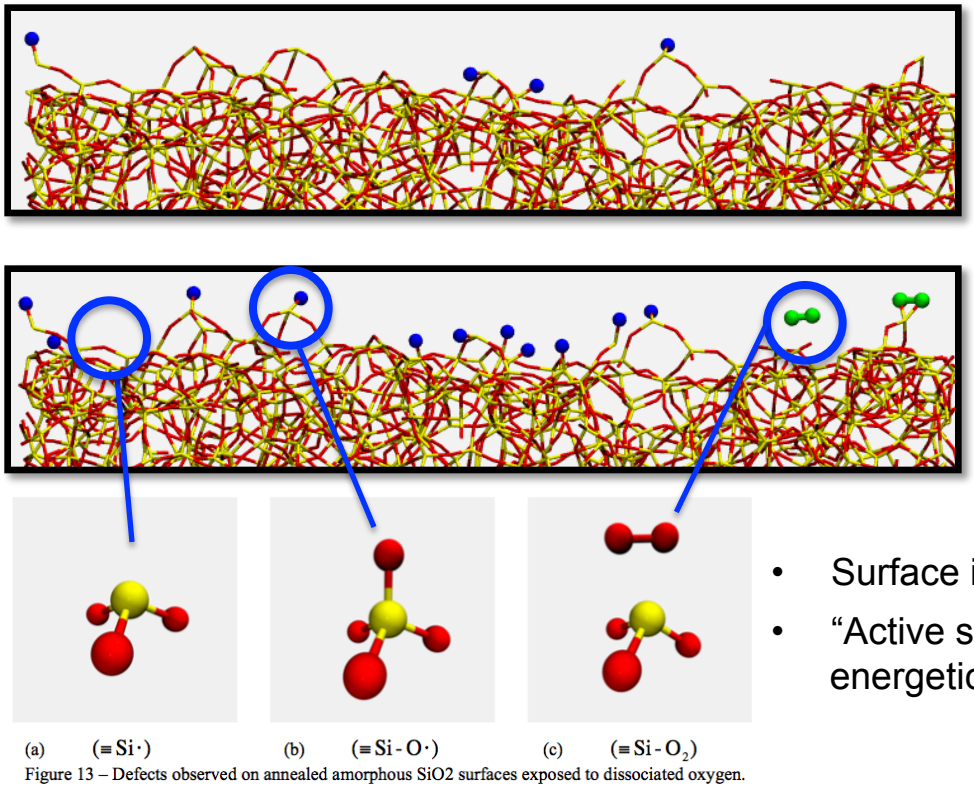


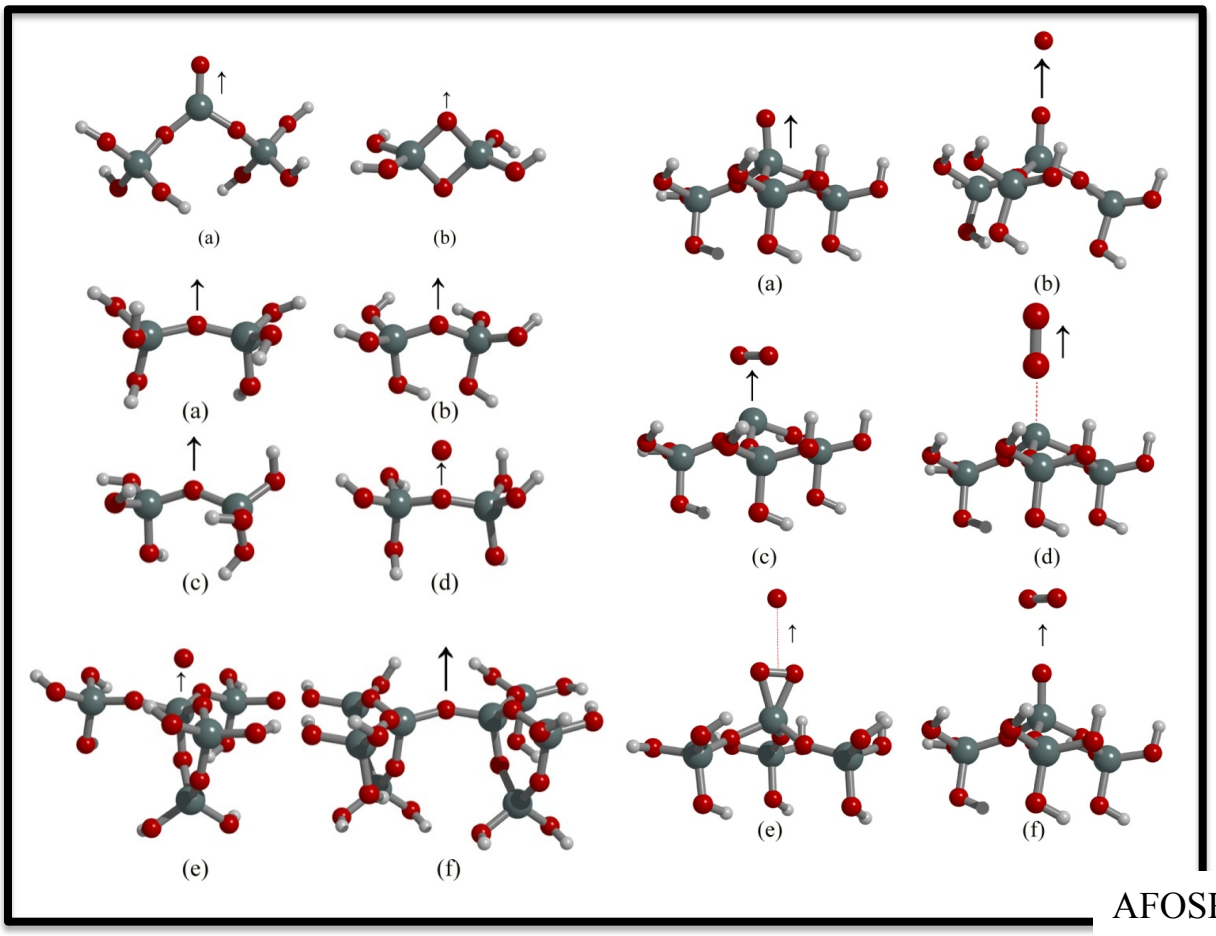
Figure 13 – Defects observed on annealed amorphous SiO2 surfaces exposed to dissociated oxygen.

- Validate predicted amorphous SiO_2 structure with experiment (stable reconstructions and defect structures observed)
- Simulate exposure to dissociated oxygen at high temperature, observe *in-situ* surface structure and chemical defects
- Surface is largely non-catalytic (stable reconstructions)
- "Active sites" are defects where recombination is energetically favorable (focus on these)

The ≡Si· and ≡Si-O· defects have been observed experimentally on vacuum fractured and irradiated silica surfaces, and by MD simulations of silica surfaces with different interatomic potentials

A New ReaxFF$_{SiO-GSI}$ for Gas Surface Interactions

- Original ReaxFF$_{SiO}$ was trained to DFT data for bulk silica, not specific defects, and not for gas-surface interactions
- Don Truhlar's group (Department of Chemistry, Minnesota) performed quantum chemistry calculations for all relevant surface reconstructions, defects, and oxygen-surface interactions

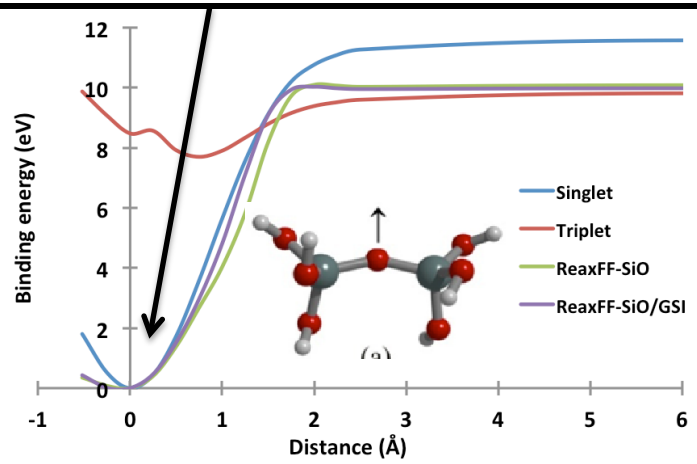


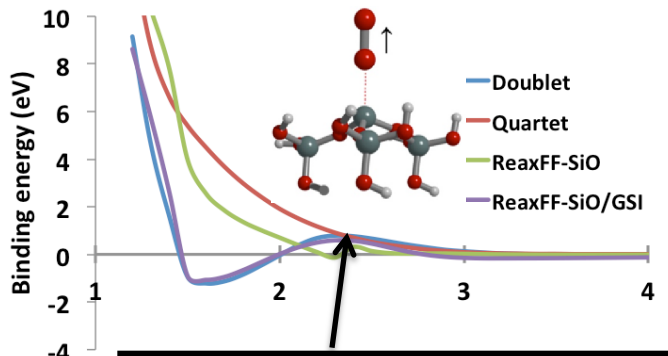
- Minnesota M06-L and M06-2X functionals
- Explicity correlated CCSD(T)-F12 method
- Various cluster sizes
- Potential energy curves computed for Singlet/Triplet and Doublet/Quartet spin states

A New ReaxFF$_{SiO\text{-}GSI}$ for Gas Surface Interactions

- An extensive Density Functional Theory (DFT) study was performed for dominant mechanisms (i.e. specific defects and reaction pathways)
- A new potential (ReaxFF$_{SiO\text{-}\boldsymbol{GSI}}$) was fit to DFT data

strong O binding on reconstructed surface





energy barrier for O_2 desorption

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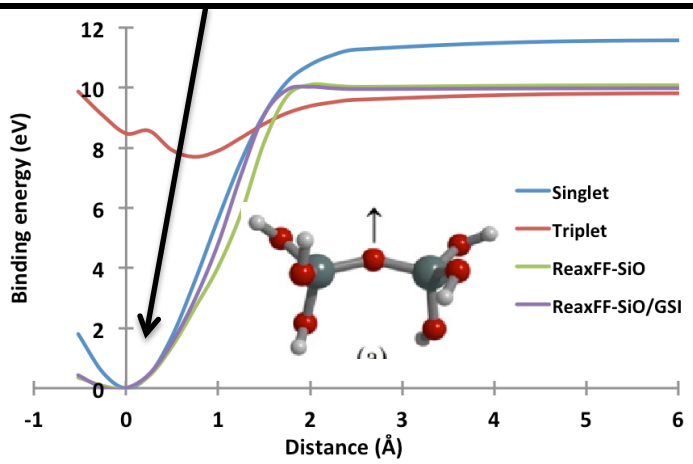

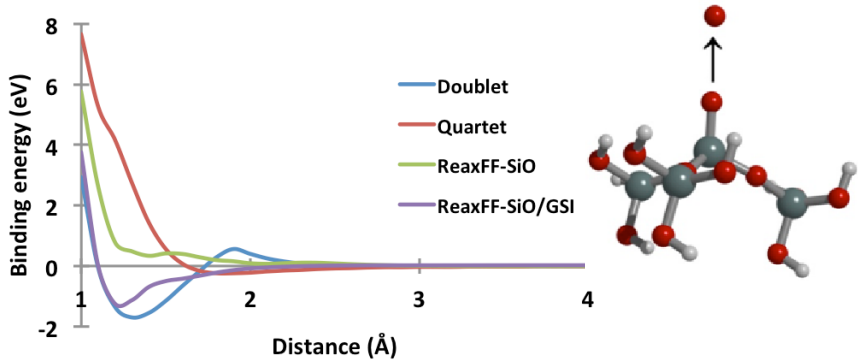

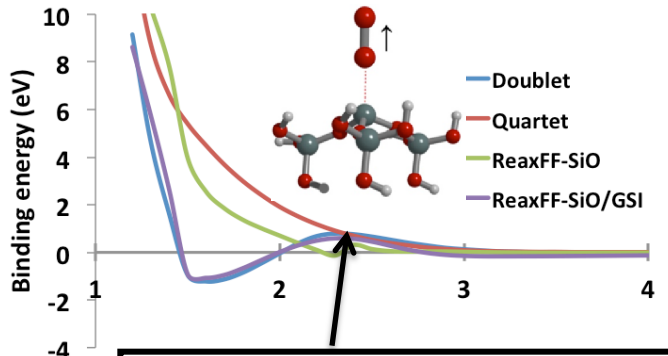

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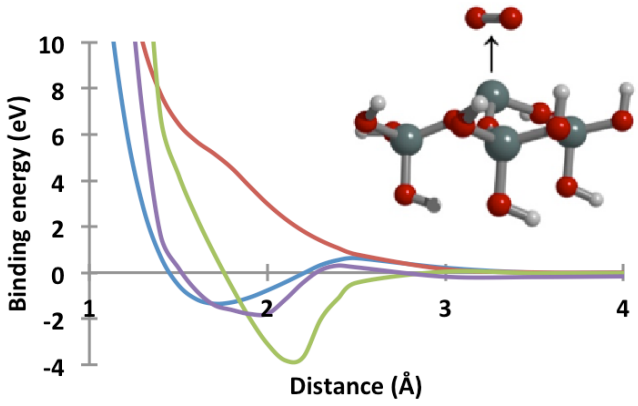
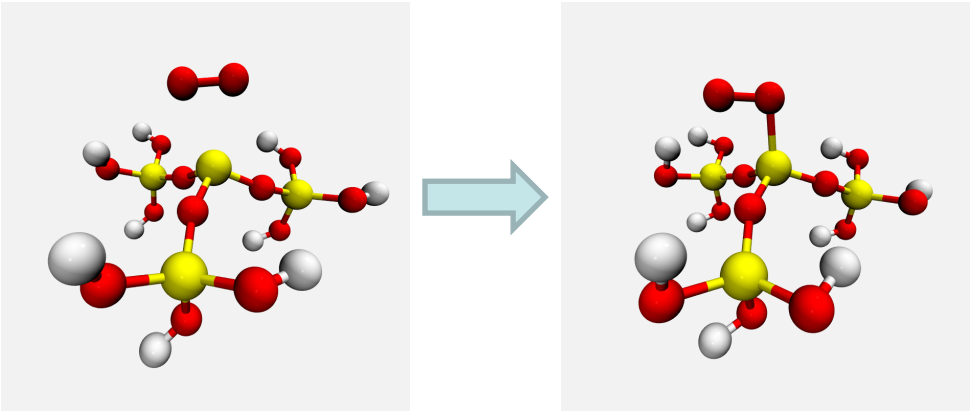


A New ReaxFF$_{SiO\text{-}GSI}$ for Gas Surface Interactions

- Result: A single FF that accurately models bulk SiO_2 polymorphs, surface reconstructions, and ***all*** catalytic defects; validated with experiment. Also, specific oxygen-silica interactions, reaction pathways, consistent with DFT.



The 3rd dominant defect is altered with new FF. There is experimental evidence for this defect on mechanically fractured silica [1].

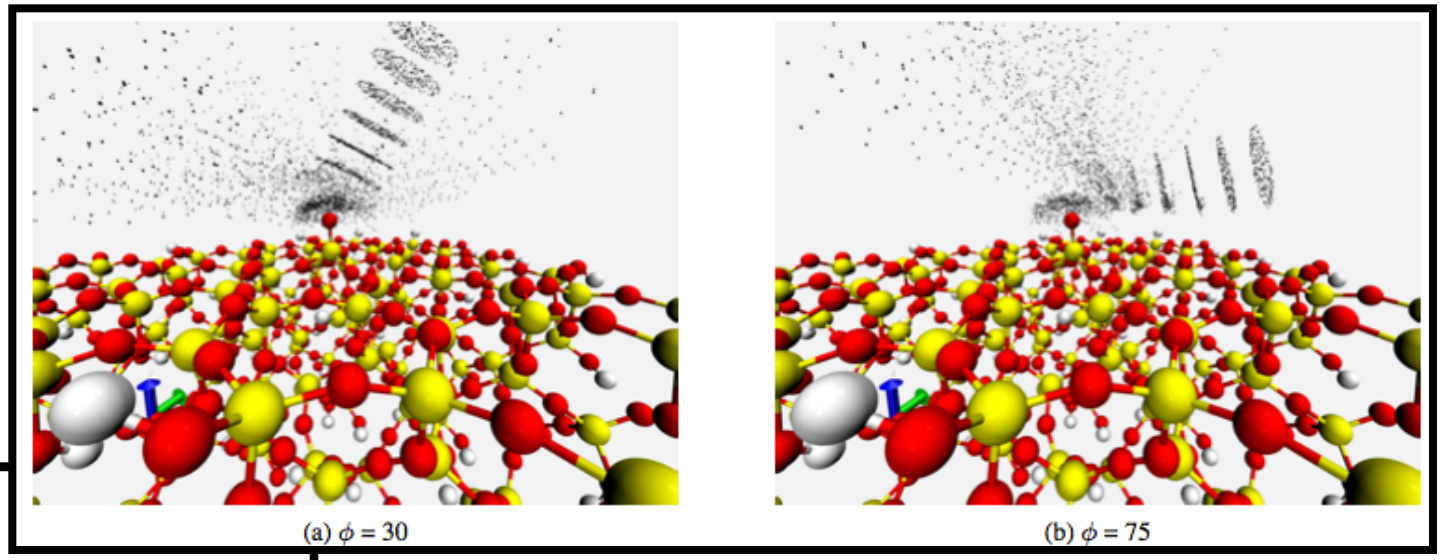
- Surface structure and defects at high temperature, well modeled by ReaxFF$_{SiO\text{-}GSI}$ (fit to lowest potential energy surface)
- Precise, quantitative analysis of oxygen (O/O_2) interactions with reconstructed surface and defects, is quite challenging:
  - which PES should be used for trajectories? Singlet, Triplet, Doublet, Quartet?
  - how precisely must ReaxFF fit the DFT data?

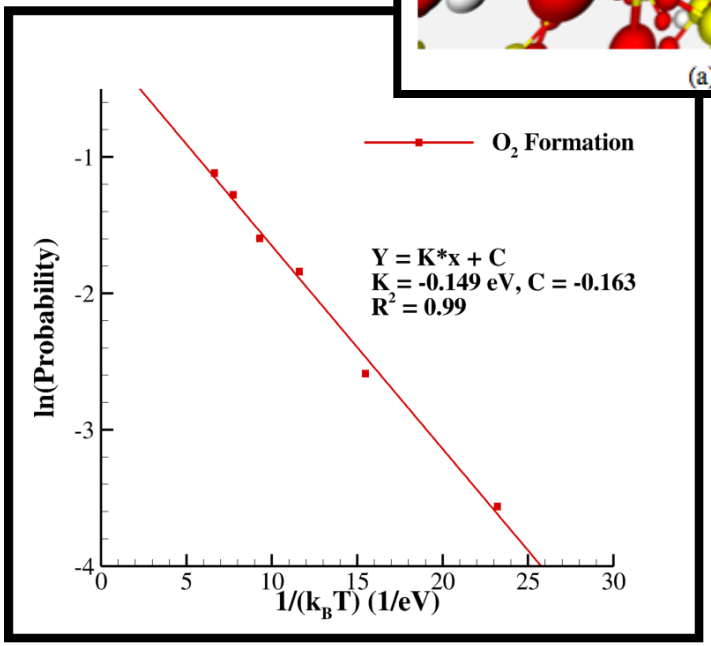
[1] A. P. Legrand, *The Properties of Silica Surfaces*, 1998

Gas-Surface Trajectory Analysis

- A large number of trajectory calculations were performed to determine activation energies and steric factors for each reaction mechanism

Ex. Trajectories well-fit by:
E_{a2} = 0.15 eV
A_2 = 0.850





Probability of hitting a site

Probability site is occupied by reactant

Probability of reacting

Flux to surface

$$r_2 = F_{kin} a_{site} [S] \Theta_o A_2 e^{-E_{a2}/k_B T} \quad (s^{-1}m^{-2})$$

Concentration of surface sites

Macroscopic Rate Model for CFD

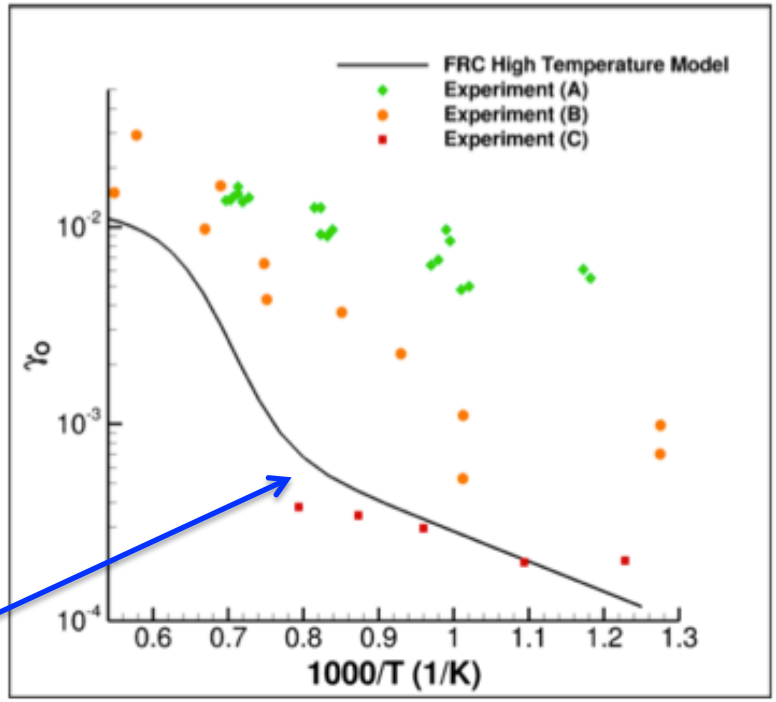
A CFD rate model for oxygen-silica catalysis consistent with physical chemistry:

$$
\begin{aligned}
O + E_s &\rightleftharpoons O_s && (1)\\
O + O_s &\rightleftharpoons O_2 + E_s && (2)\\
O + O_s &\rightleftharpoons O_{2s} && (3)\\
O + O_{2s} &\rightleftharpoons O_2 + O_s && (4)\\
O_2 + E_s &\rightleftharpoons O_{2s} && (5)
\end{aligned}
$$

x	(A_x^f)	(E_f^F) (eV)	(A_x^r)	(E_r^F) (eV)
1	1.0	0.0	10^{13} - 10^{15}	4.19
2	0.169	0.401	0.0 - 1.0	1.33
3	0.850	0.149	10^{13} - 10^{15}	3.96
4	0.172	0.303	0.0 -1.0	1.61
5	1.0	0.0	10^{13} - 10^{15}	2.88

Rate	Rate Equation	Rate constant (k_i)	units
r_1^f	$k_1^f[O][E_s]$	$(\bar{c}_O/4) \times (2\pi r_c^2) \times (A_1^f e^{-E_1^f/(K_B T)})$	m^3/s
r_1^r	$k_1^r[O_s]$	$A_1^r e^{-E_1^r/(K_B T)}$	$1/s$
r_2^f	$k_2^f[O][O_s]$	$(\bar{c}_O/4) \times (2\pi r_c^2) \times (A_2^f e^{-E_2^f/(K_B T)})$	m^3/s
r_2^r	$k_2^r[O_2][E_s]$	$(\bar{c}_{O_2}/4) \times (2\pi r_c^2) \times (A_2^r e^{-E_2^r/(K_B T)})$	m^3/s
r_3^f	$k_3^f[O][O_s]$	$(\bar{c}_O/4) \times (2\pi r_c^2) \times (A_3^f e^{-E_3^f/(K_B T)})$	m^3/s
r_3^r	$k_3^r[O_{2s}]$	$A_3^r e^{-E_3^r/(K_B T)}$	$1/s$
r_4^f	$k_4^f[O][O_{2s}]$	$(\bar{c}_O/4) \times (2\pi r_c^2) \times (A_4^f e^{-E_4^f/(K_B T)})$	m^3/s
r_4^r	$k_4^r[O_2][O_s]$	$(\bar{c}_{O_2}/4) \times (2\pi r_c^2) \times (A_4^r e^{-E_4^f/(K_B T)})$	m^3/s
r_5^f	$k_5^f[O_2][E_s]$	$(\bar{c}_{O_2}/4) \times (2\pi r_c^2) \times (A_5^f e^{-E_5^f/(K_B T)})$	m^3/s
r_5^r	$k_5^r[O_{2s}]$	$A_r^5 e^{-E_5^r/(K_B T)}$	$1/s$

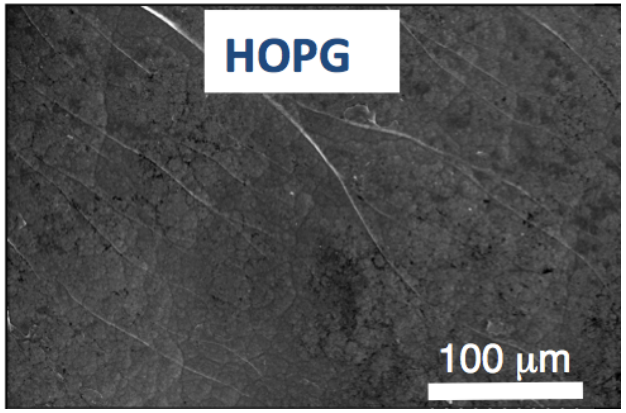
Table 4: Rate Constants and functional forms



Slope is very sensitive to energy barriers, ongoing (non-MURI) work to address this.

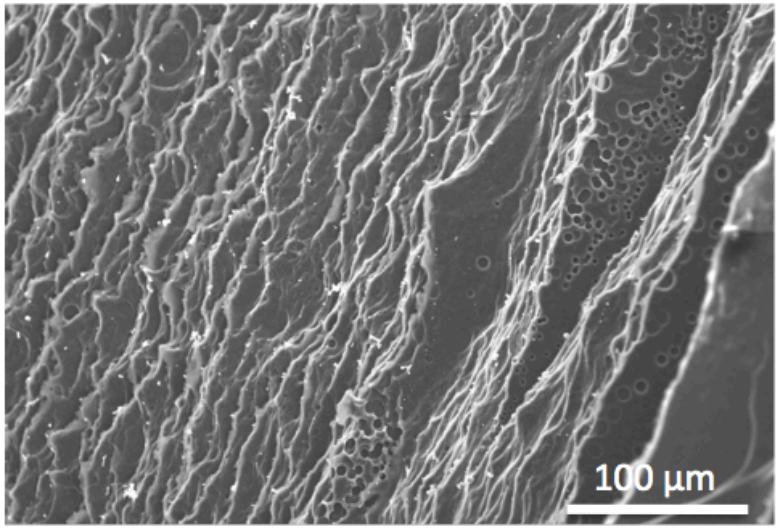
Carbon Oxidation Results

Highly Oriented Pyrolitic Graphite (HOPG) (Images from Corral *et al.*):

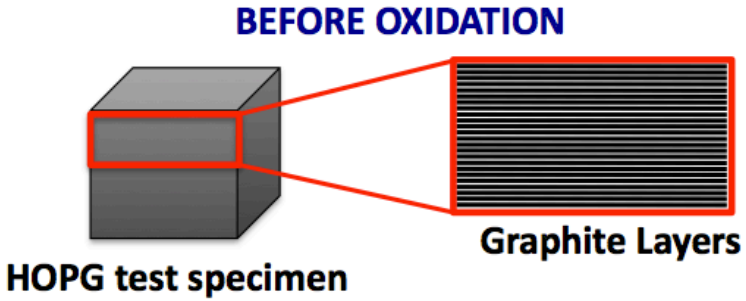


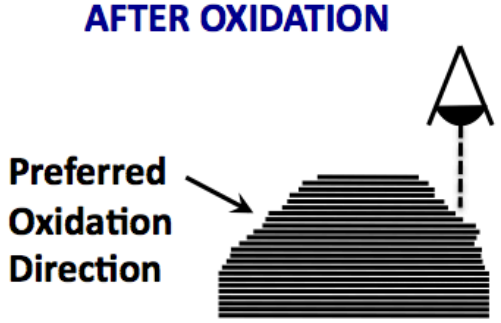
HOPG is a well-characterized, carbon-based material, ideal for bridging computational chemistry to macroscopic oxidation experiments.

Side of HOPG test specimen after oxidation



HOPG is composed of stacked graphitic layers that can only burn from the edge since their planar surface is protected by the layers above





Molecular Beam Experiments (O → HOPG)

- HOPG is a well-characterized material and Molecular Beam experiments have a well characterized environment
- $ReaxFF_{CHO}$ is available and validated for hydrocarbon chemistry [1]
- Revisit existing experiments (Minton) and DFT calculations (Paci et al.) for hyperthermal (5eV) O impacts on HOPG [2]

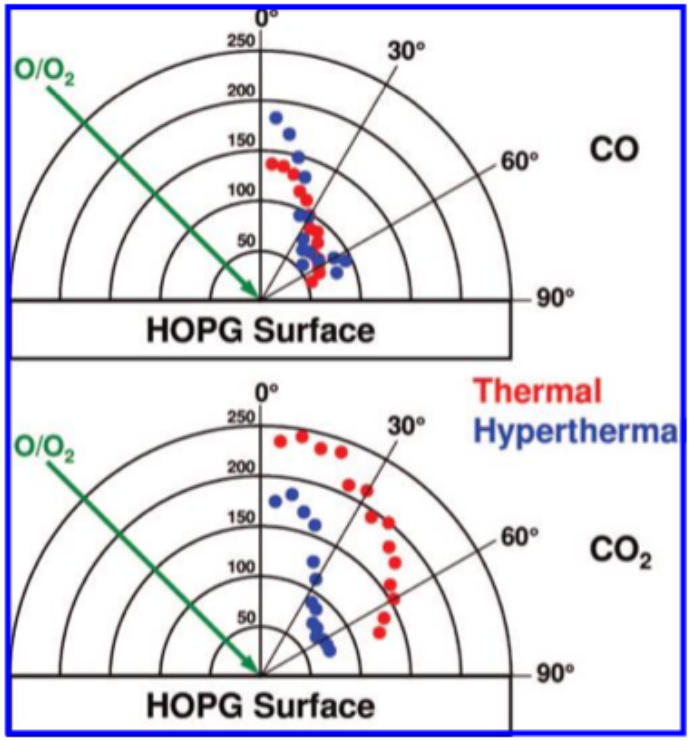
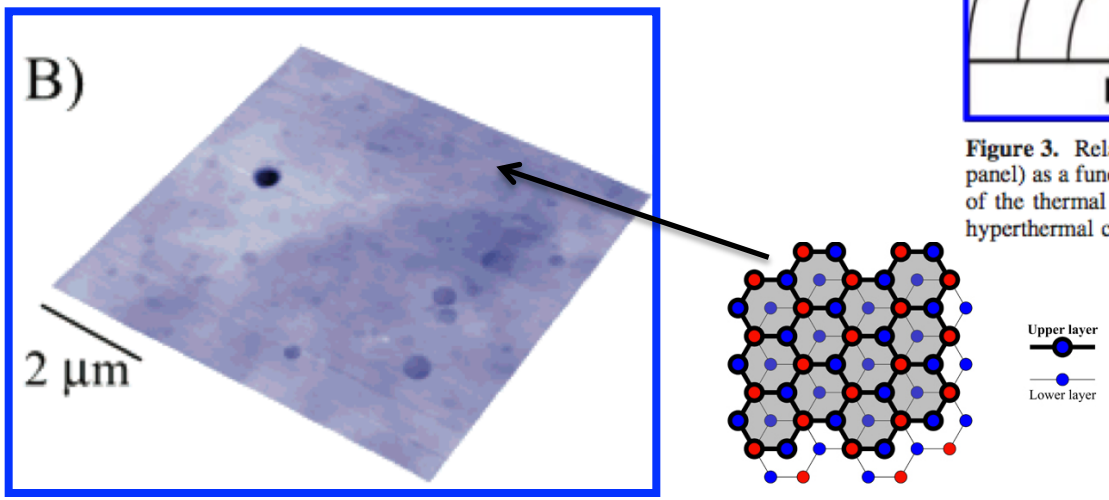


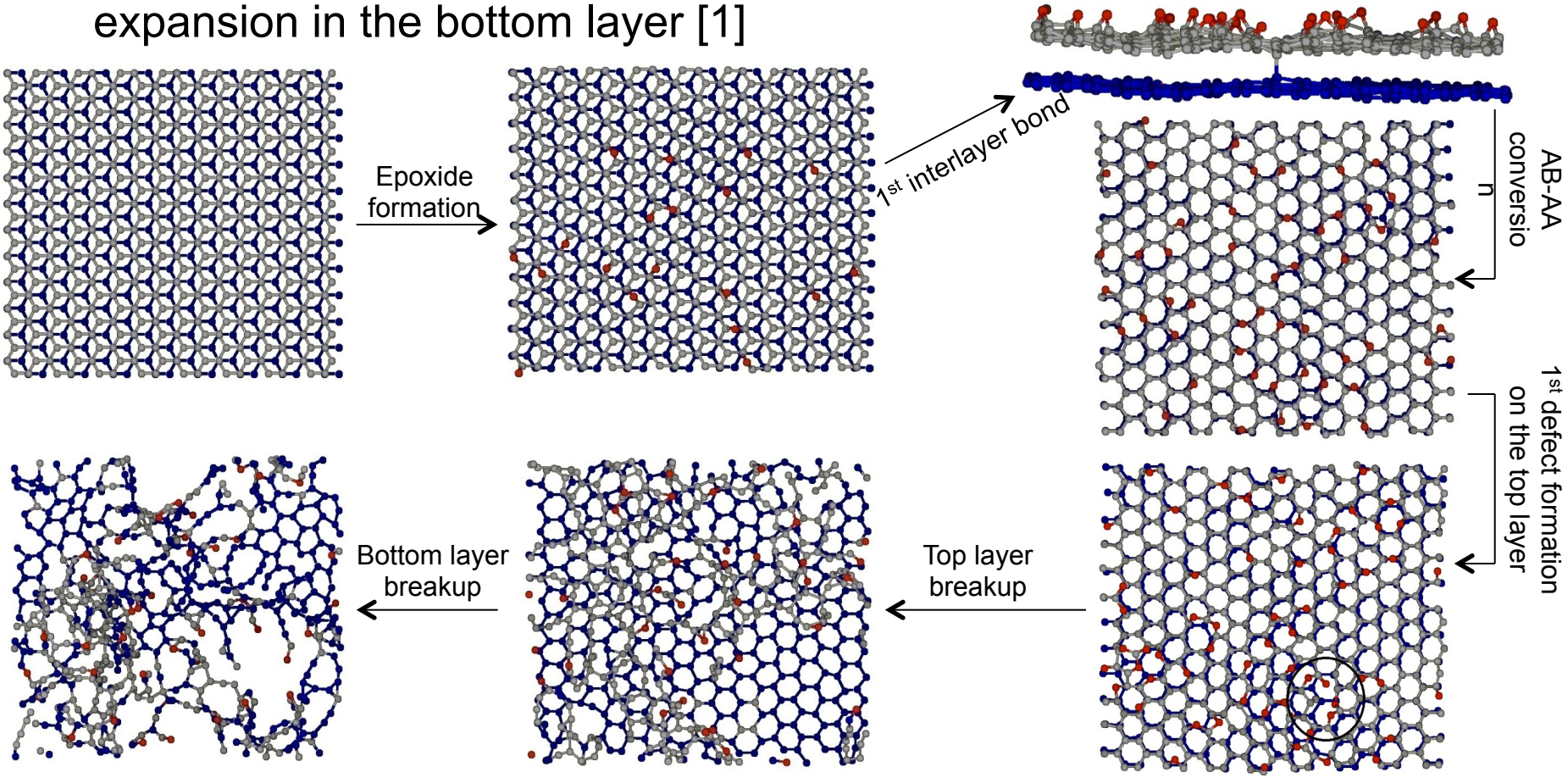
Figure 3. Relative flux of scattered CO (top panel) and CO_2 (bottom panel) as a function of θ_f, with $\theta_i = 45°$. Red circles represent the flux of the thermal components and blue circles represent the flux of the hyperthermal components.



[1] van Duin, A.C.T., Dasgupta, S., Lorant, F., Goddard, W.A., *J. Phys. Chem. A*, **2001**, 105, 9396
[2] Paci, J.T., Upadhyaya, H.P., Zhang J., Schatz G.C., Minton, T.K., *J. Phys. Chem. A*, **2009**, 113, 4677

ReaxFF Simulation Results vs. DFT

- Breakup of a 2-layer graphene stack in AB arrangement proceeds via epoxide formation on the top layer, AB to AA conversion, defect formation/expansion in top layer, and finally defect formation/ expansion in the bottom layer [1]



[1] Srinivasan, S. G. and van Duin, A. C. T., **2011**. Journal of Physical Chemistry A **115**, 13269-13280.

ReaxFF Simulation Results vs. DFT

- Our results in terms of the number of reactive events compared well with DFT results of Paci et al[1].

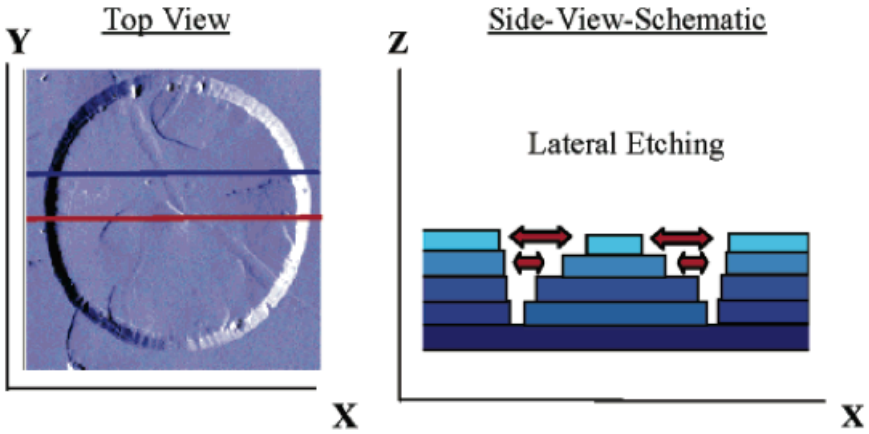
Reaction	Model I			Model II			Model III			Model IV		
	DFT		ReaxFF	DFT		ReaxFF	DFT		ReaxFF	DFT		ReaxFF
	O^1	O^3		O^1	O^3		O^1	O^3		O^1	O^3	
Ring Opening	36	32	16	9	17	26	9	16	13	0	0	0
Epoxide Formation	76	75	94	77	70	88	33	29	57	7	17	19
Epoxide Migration	37	21	3	34	46	0	11	20	17	21	17	25
Carbonyl Formation	3	2	2	1	0	3	0	0	15	0	0	14
O_2 Formation	1	0	2	17	17	2	55	53	20	79	76	72
CO_2 Formation	0	0	0	1	3	2	2	1	6	0	0	6
CO Formation	0	-	0	1	-	0	6	-	1	0	-	0
Dioxirane Formation	0	0	0	2	0	0	1	1	0	0	0	0
Inelastic O	0	0	0	1	7	2	1	13	11	0	4	0
Sheet Damage	0	0	1	0	0	0	0	0	4	3	2	14

O^1 – Oxygen atom trajectories run on lowest energy singlet PES
O^3 – Oxygen atom trajectories run on lowest energy triplet PES

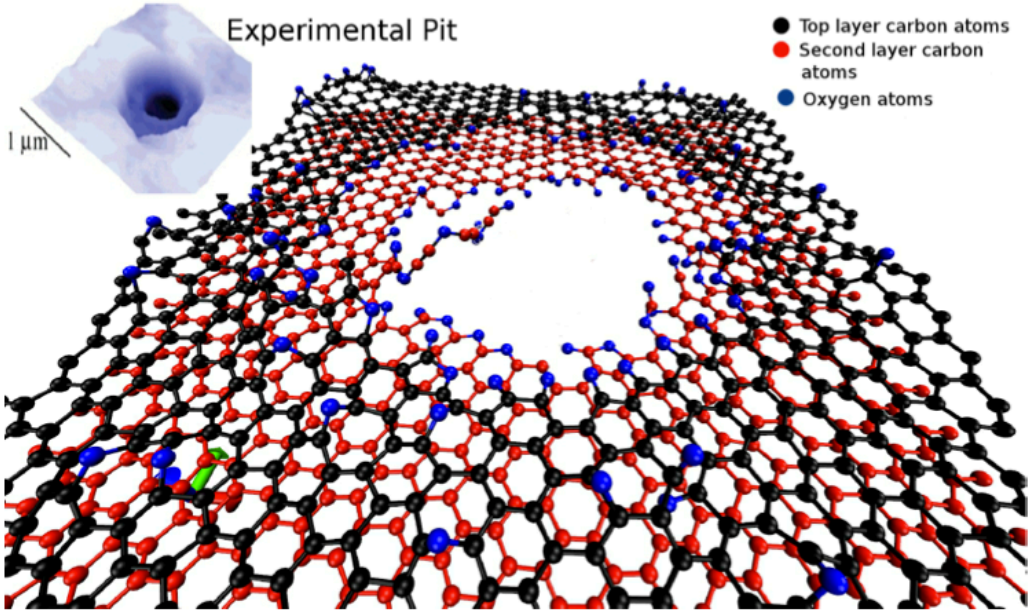
[1] Paci, J.T., Upadhyaya, H.P., Zhang J., Schatz G.C., Minton, T.K., *J. Phys. Chem. A*, **2009**, 113, 4677

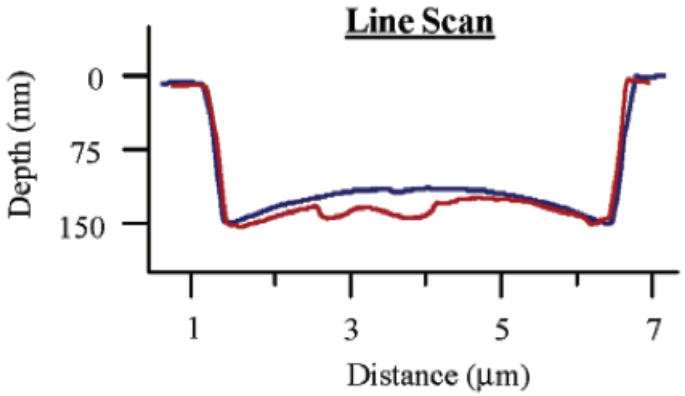
ReaxFF Simulation vs. Experiment

Experimental results for Highly Oriented Pyrolitic Graphite (HOPG) oxidized by molecular beam (Minton *et al.*):



Molecular dynamics simulation results matching molecular beam conditions.





Same behavior: Oxidation proceeds rapidly on graphene edges.
Forms shallow, but wide etch-pits.

ReaxFF Simulation vs. Experiment

- Interested in steady-state oxidation behavior (beam operates for minutes)
- 1000 sequential collisions [26 CO, 98 CO_2, 198 O_2 recombinations]
  - CO_2/CO: (~4 sim. vs. ~2 experiment)
  - O_2 recombination large in both experiment and simulation

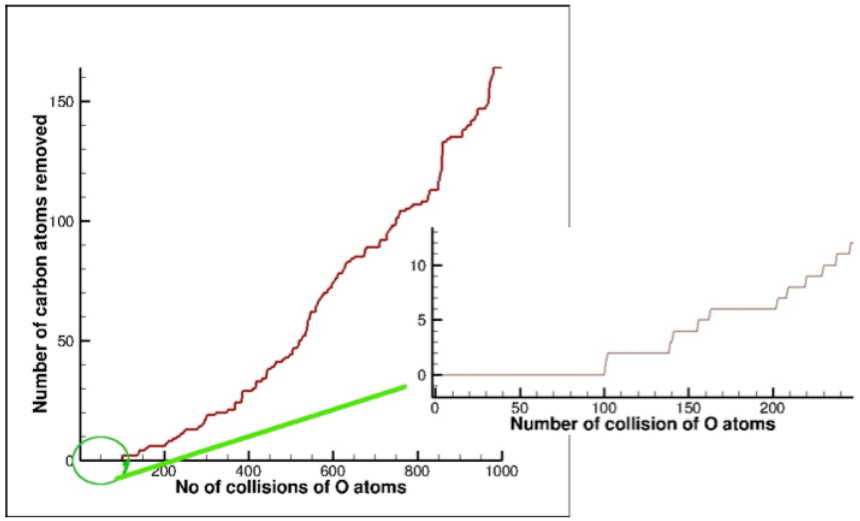


Figure 8. Figure shows the oxidation as a function of number of collisions at 600K.

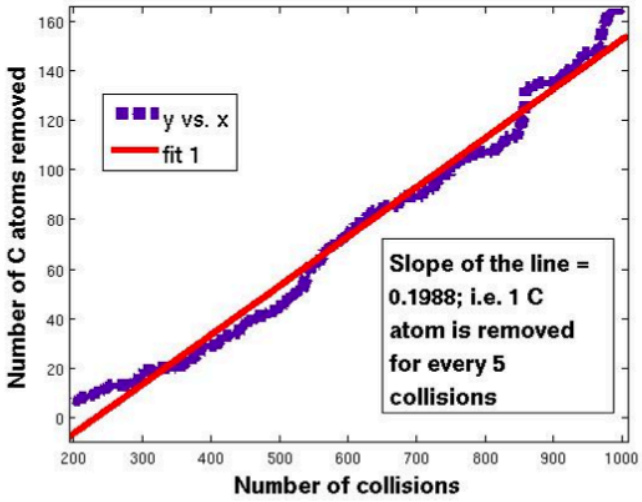
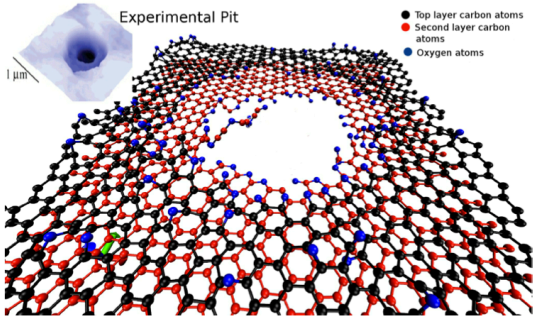


Figure 9. Figure showing a linear fit of the number of carbon atoms removed.



Excellent qualitative agreement with experiment, despite disparate spatial and temporal scales.

Future Oxidation Research

- New molecular beam experiments (with matching simulations) at various beam energies and high surface temperature (HOPG)
- Test a range of materials (in multiple facilities: MB, TGA furnace, LENS-XX)
  - HOPG, graphite, fiber-preform, carbon-carbon, polycrystalline graphite

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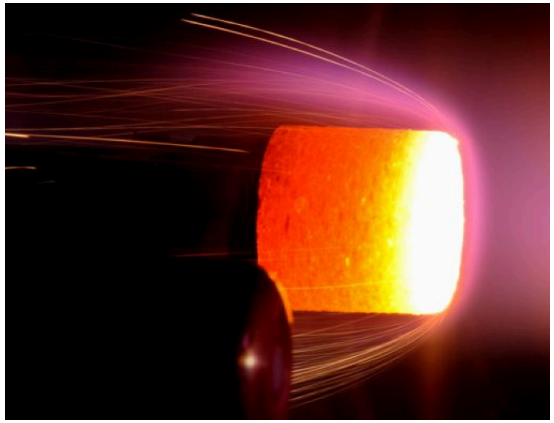
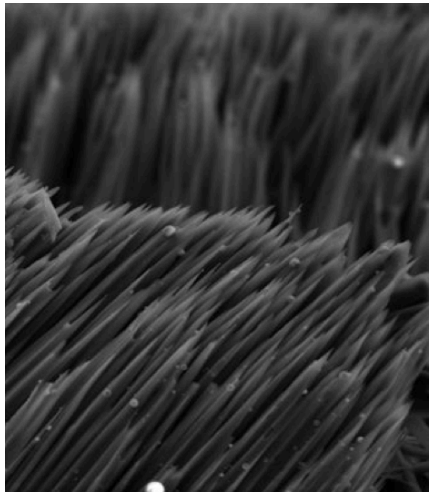


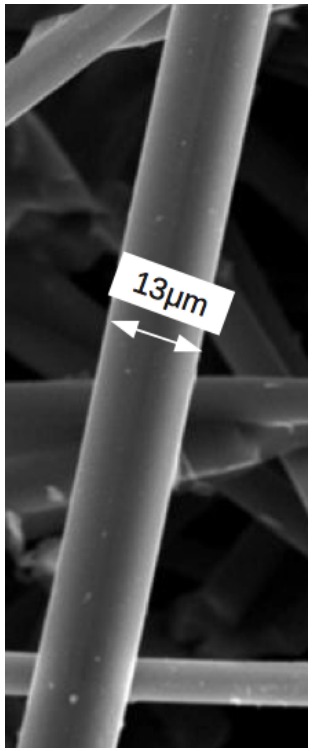
Fiber-preform ICP test at VKI



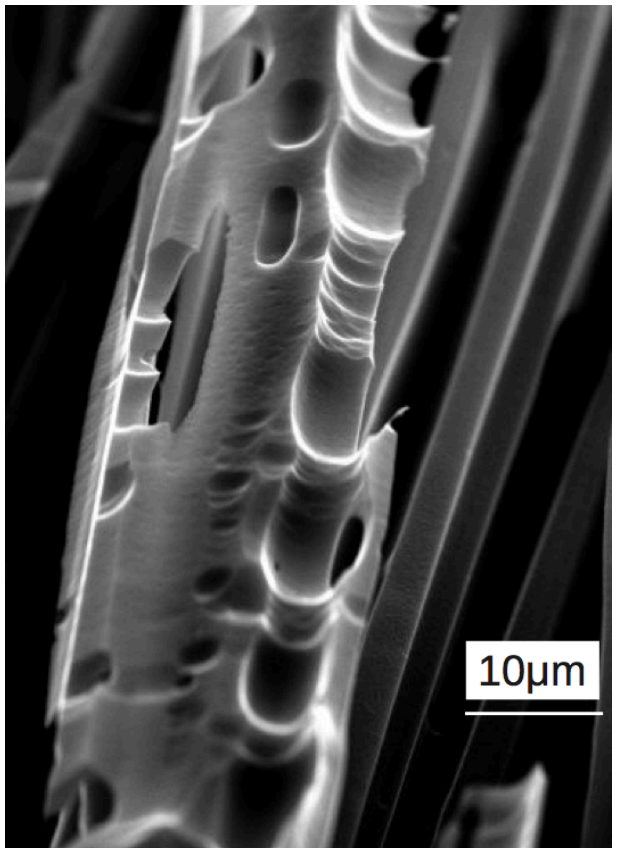
Fiber bundles after test

Images from the von Karman Insititue (VKI) for Fluid Dynamics, Belgium

Before



After



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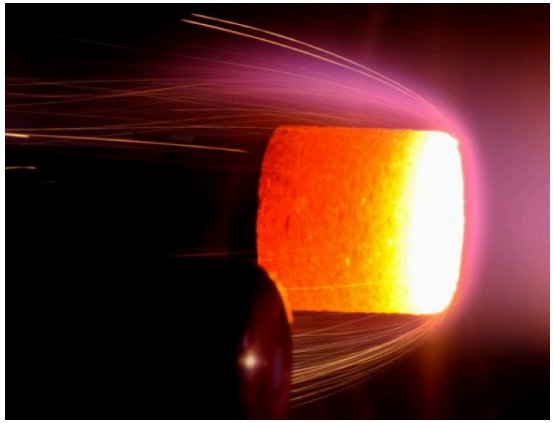

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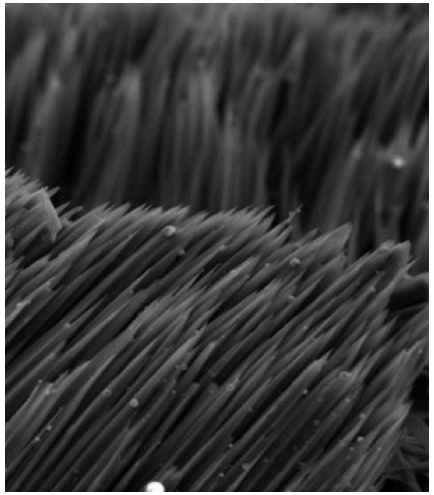

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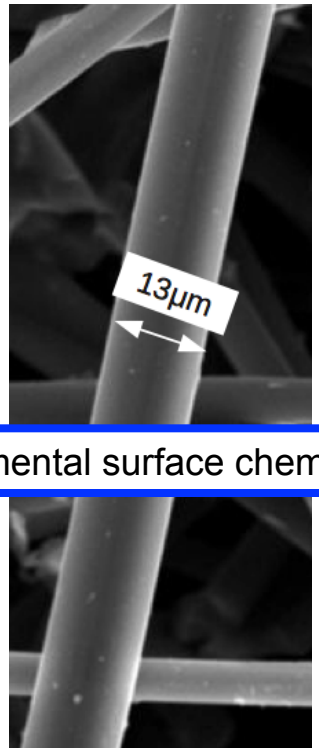
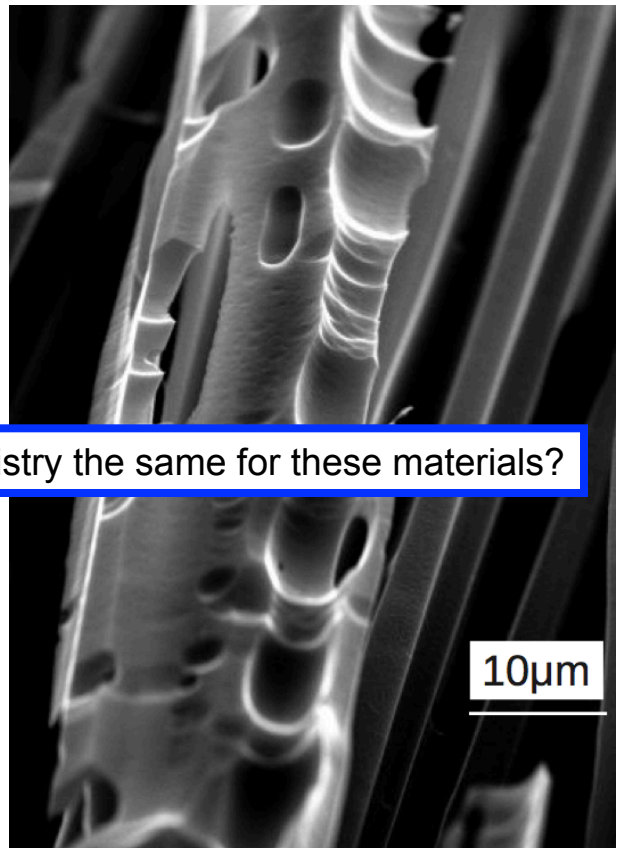


After



Is fundamental surface chemistry the same for these materials?

Atomistic – Continuum Modeling of Gas-Surface Interactions (Catalysis and Oxidation)

Prof. Donald Truhlar and Dr. Anant Kulkarni
Chemistry, University of Minnesota

Prof. Thomas Schwartzentruber, Paul Norman, Savio Poovathingal
Aerospace Engineering & Mechanics, University of Minnesota

Prof. Adri van Duin and Sriram Srinivasan
Mechanical and Nuclear Engineering, Penn State University

Fundamental Processes in High-Temperature Gas-Surface Interactions
[AFOSR FY2010 MURI #13]