Low Energy Electron Microscopy (LEEM) Studies of Nanoscale Resolved Reaction Kinetics on Catalytic Surfaces

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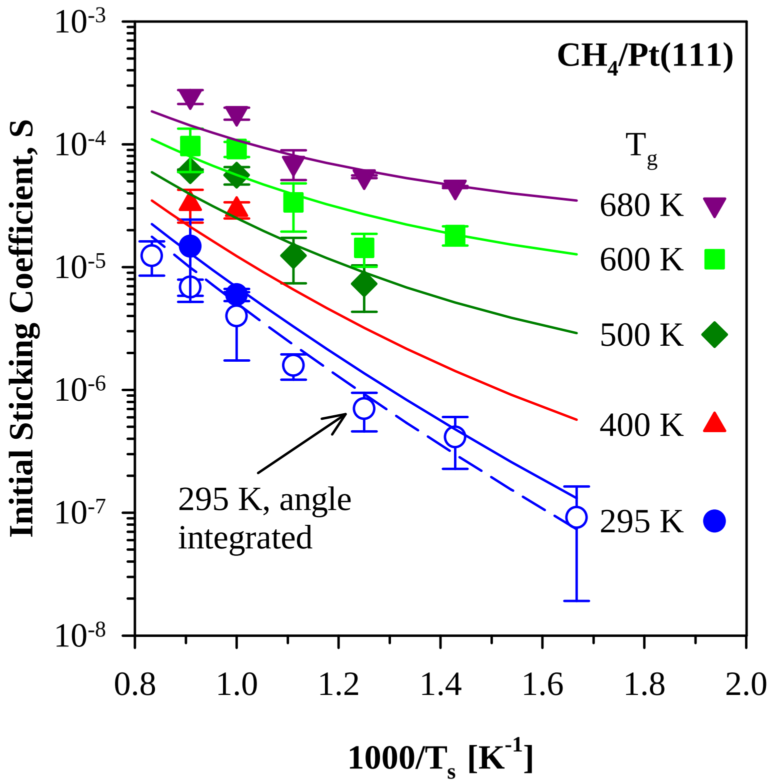
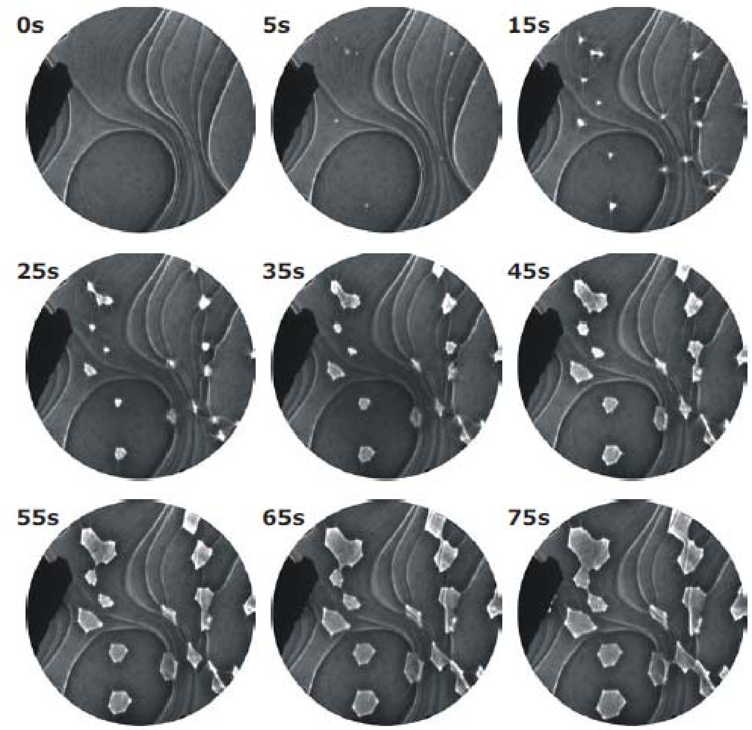
Surface Science of Reforming

The initial C-H bond cleavage of alkanes on metal catalysts is considered to be the rate determining step in the reforming of natural gas to produce H_2 & syngas.



Alkane dissociative sticking coefficients with $T_g \neq T_s$.



Graphene growth on Pt(111) LEEM movies at 190 μm f.o.v.

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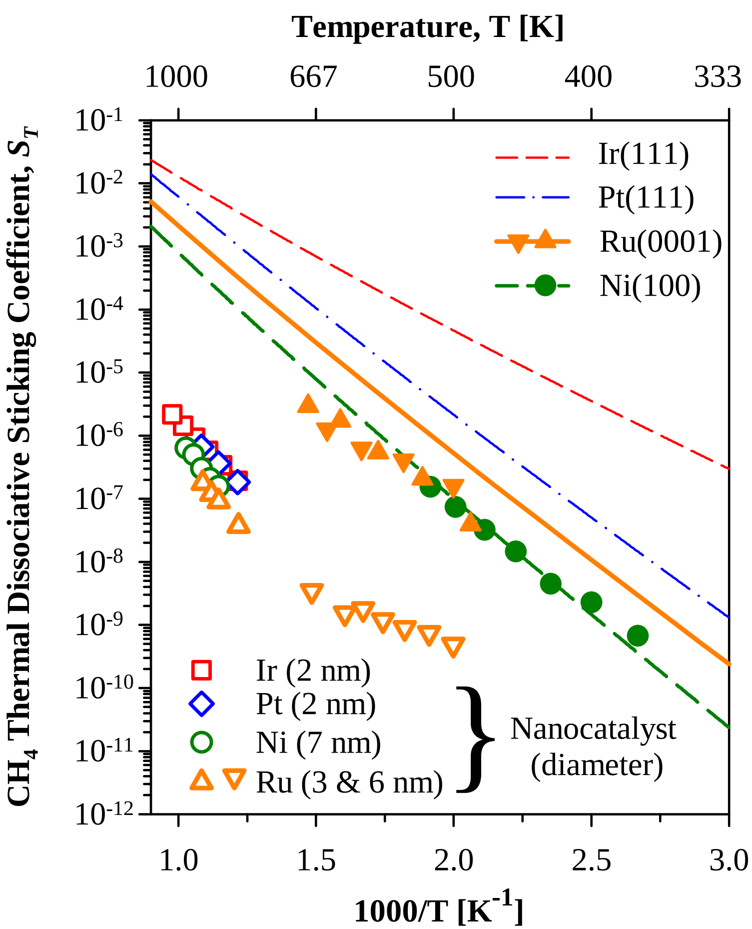
Prospects for Improvement



Dissociative sticking coefficients for CH_4,

S(flat metals) >> S(nanocatalysts)

- A surprising result since stepped surfaces, as found on high curvature nanocatalysts, are typically thought to be more active than flat surfaces.
- Perhaps, C build-up limits the number of active sites available on the nanocatalysts since only ~10^{-3} of the nanocatalyst sites seem active. Is graphene responsible?
- Opportunity for improving/understanding CH_4 reforming catalysts?

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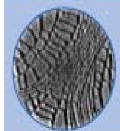
Abbott & Harrison, *J. Catal.* **254**, 27-38 (2008)

Low Energy Electron Microscopy

PEEM

Photoelectron emission microscopy. Electrons are excited with a UV light source. The contrast is based on work function differences on the sample. The photoelectron angular distribution is visible in the intermediate image plane.

MEM

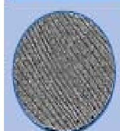


Mirror electron microscopy. The electron energy is reduced to where the electrons return in the retarding field, before they hit the sample surface. The contrast mechanism is based on local changes in the retarding field on the sample surface, such as steps and grains.

Dark field imaging

Usage of one LEED spot in the intermediate plane for imaging. All areas on the surface that contribute to the existence of this spot appear bright in the image, all other areas appear dark.

Phase contrast

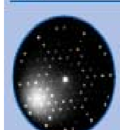


Usage of the wave nature of the incident electron beam to generate a vertical diffraction contrast, e.g. to make steps visible on the surface.

Reflectivity contrast

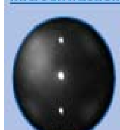
Different areas on the surface might show a difference in electron reflectivity, depending on the surface material and structure. The reflectivity coefficient depends on the incident electron energy. The most famous example is the difference between the (7x7) reconstruction and the (1x1) structure on the Si(111) surface at ~850°C. At an electron energy of about 10 eV the (7x7) areas appear much brighter than the remaining surface.

LEED

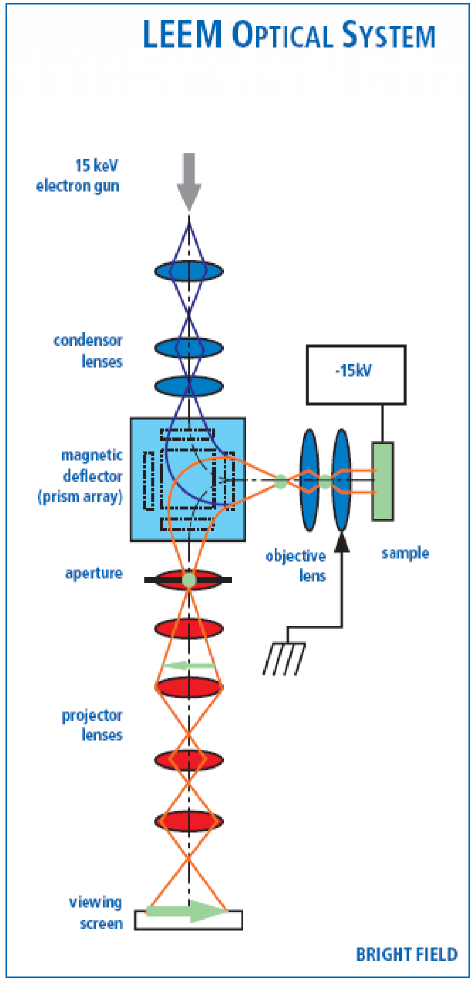


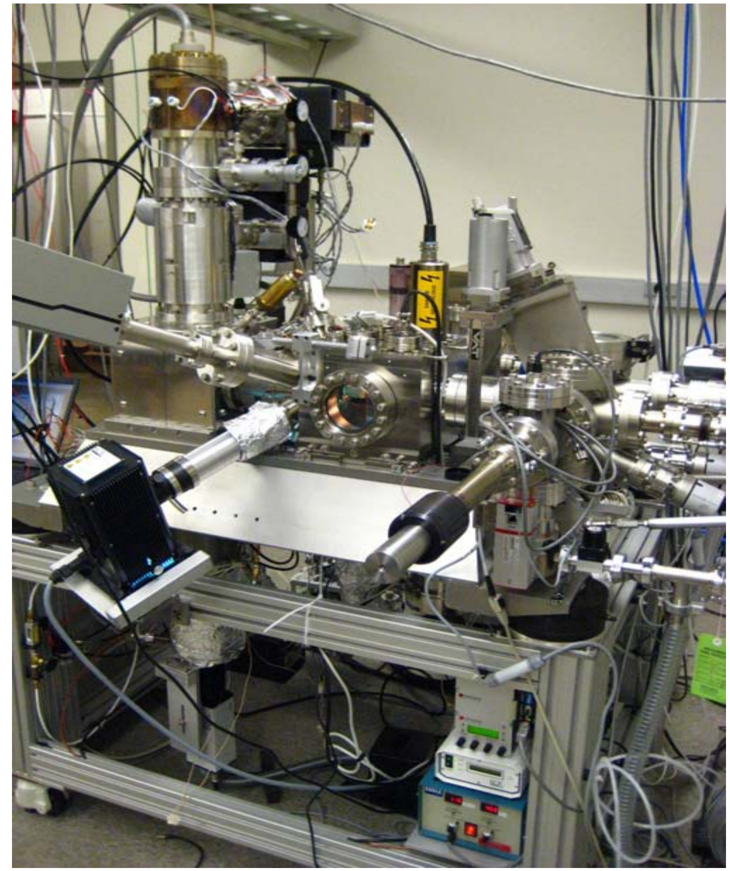
Since a diffraction pattern is formed in the backfocal plane of the objective lens, it is possible to image this pattern on the screen (LEED).

Microdiffraction



By restricting the electron beam to a very small area on the surface (<< 1 µm), it is possible to determine the LEED pattern of small areas on the surface, like the LEED pattern of single islands or terraces in order to determine their crystal structure and orientation.





Dosing alkenes & O_2 allowed study of graphene growth and oxidation.

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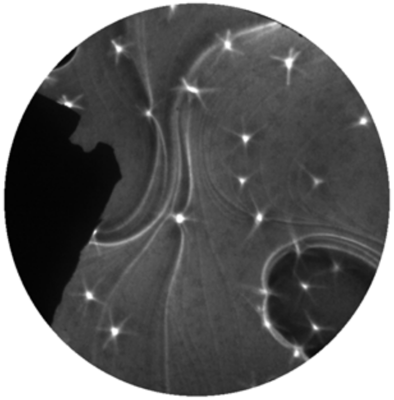
Graphene Growth on Pt(111)



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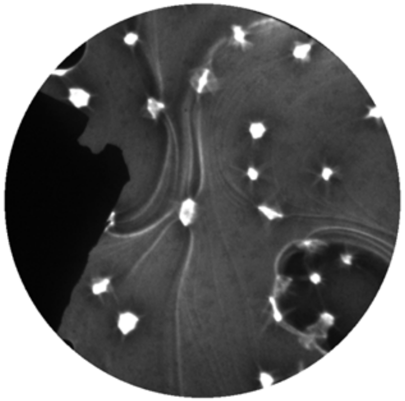
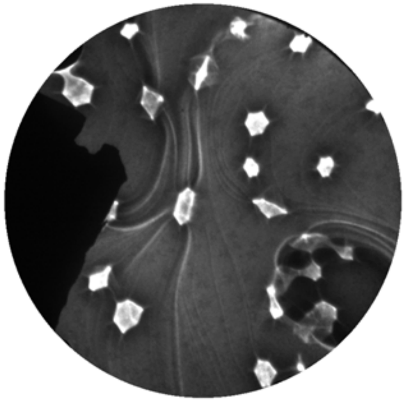


80 sec



125 sec

Nucleation of graphene on Pt(111) by ethylene CVD under $P(C_2H_4)$ = 5×10^{-8} mbar and T_s = 1050 K (field of view is 190 μm.).

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Graphene Oxidation on Pt(111)

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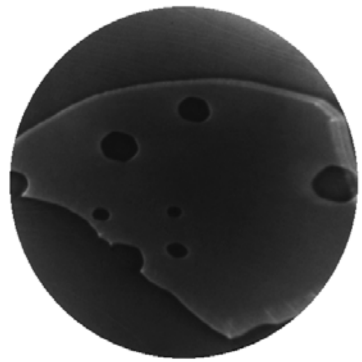

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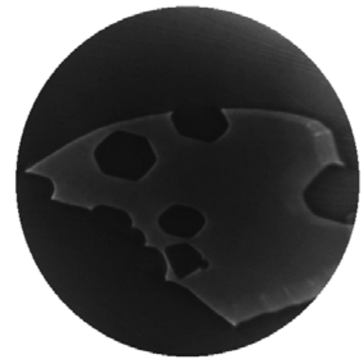

50 sec

Oxidation of graphene on Pt(111) under $P(O_2) = 1 \times 10^{-8}$ mbar and $T_s = 990$ K (field of view is 10 μm.).

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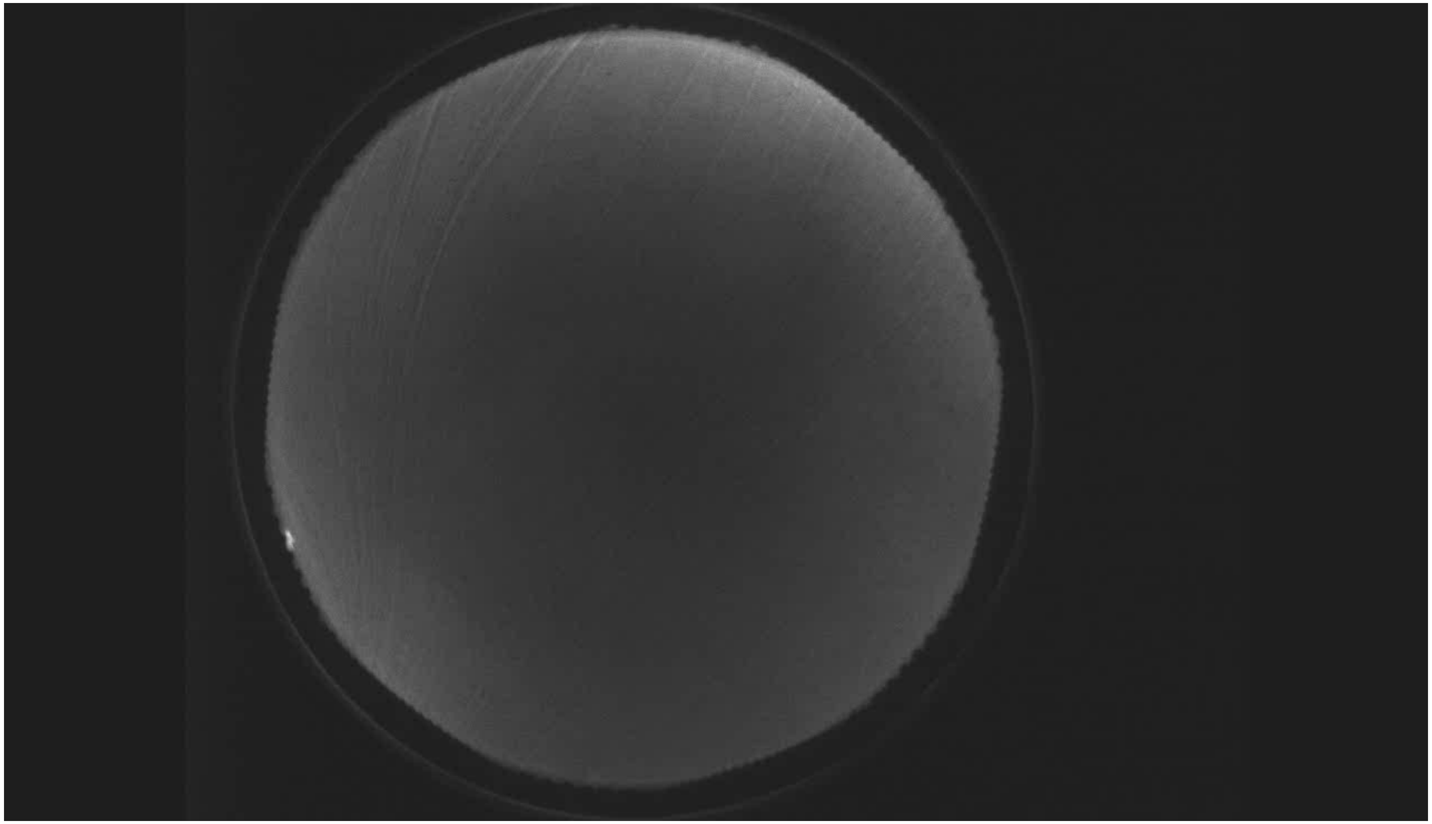
Graphene Growth/Oxidation on Pt(111)



10 μm f.o.v. at T_s = 1024 K, P = 10^{-7} Torr C_2H_4, then O_2.

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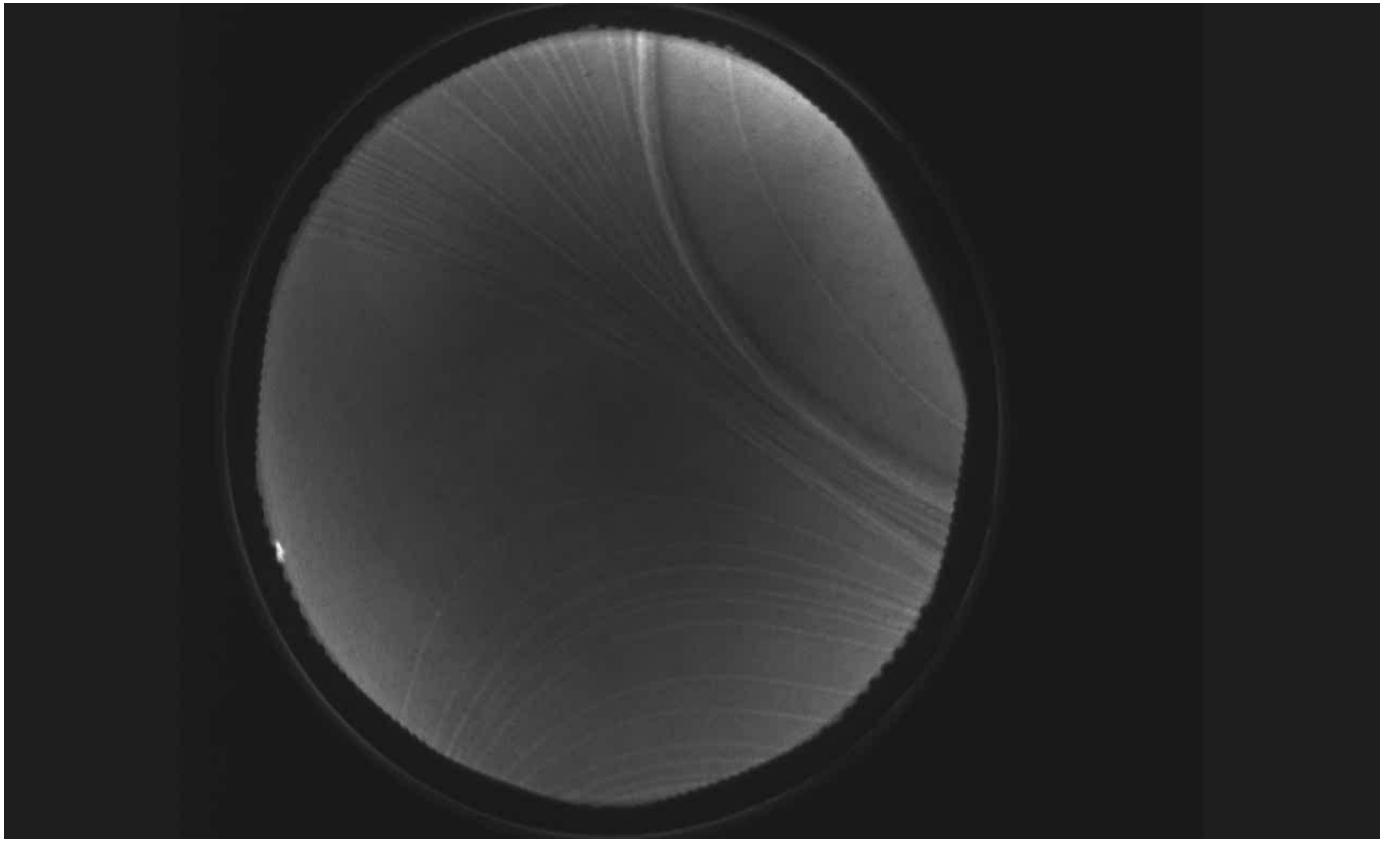
Graphene Growth/Oxidation on Pt(111)



10 μm f.o.v. at T_s = 1018 K, higher step density regions.

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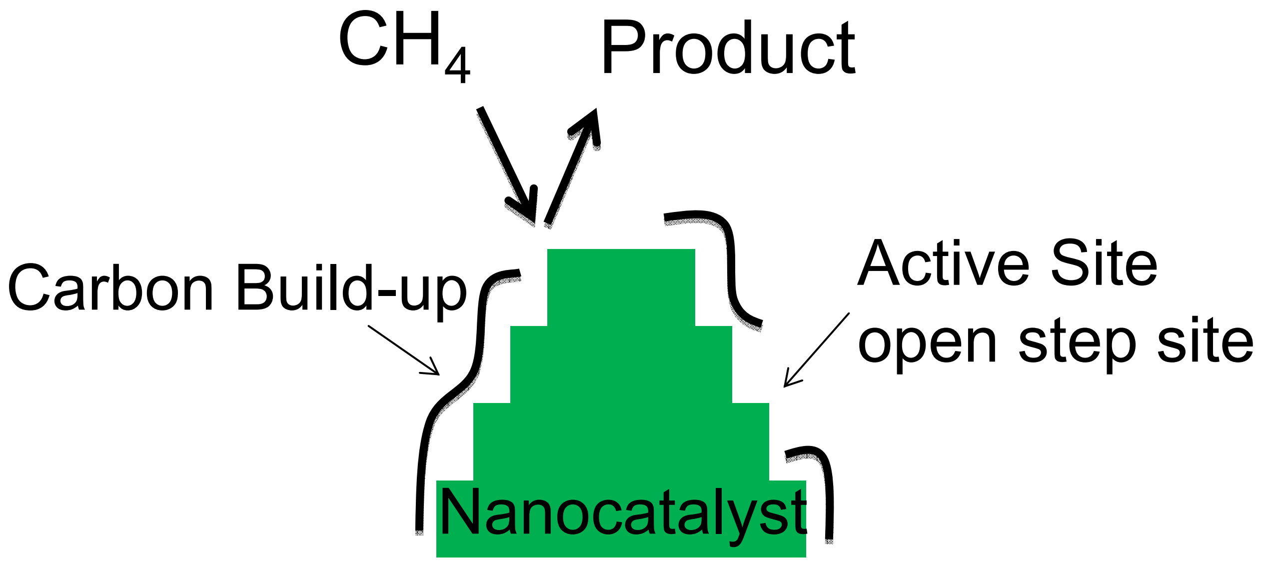
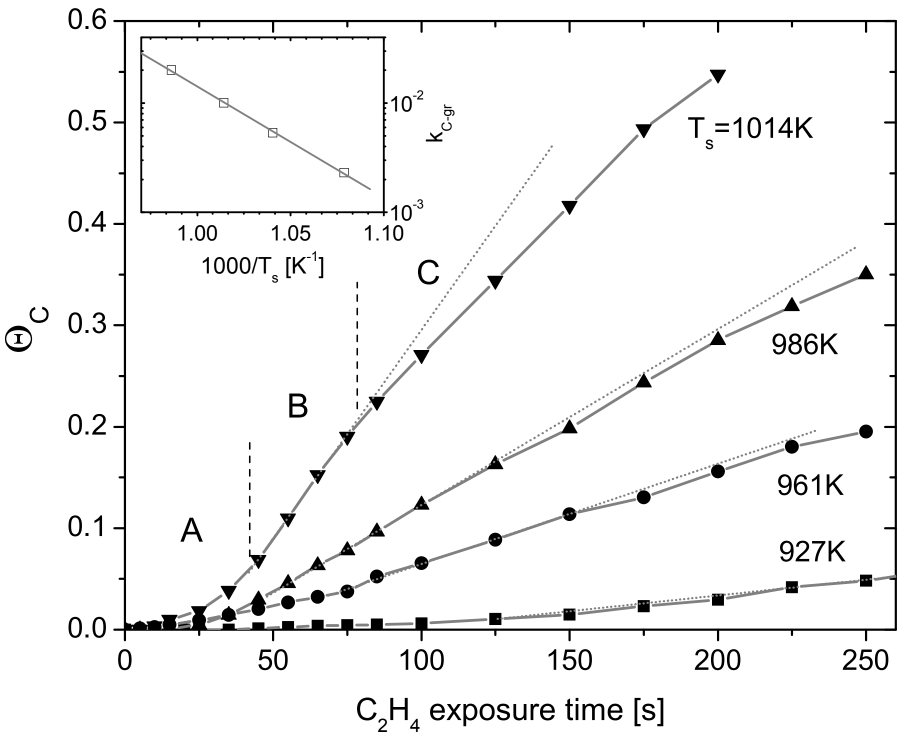
Schematic Operation of a Reforming Nanocatalyst



It may well be hard to wrap graphene around a half sphere.

Graphene Growth/Oxidation Kinetics



- Growth "E_a"= 194 kJ/mol
- Oxidation E_a = 243 kJ/mol

- Only 1 monolayer of graphene can be grown on Pt(111).

- Strong interactions with surface steps and defects.

Outcomes / Future plans

- LEEM equipped to examine catalysis & chemical vapor deposition.
- several papers submitted or in manuscript form, presentations at AVS & SE Catalysis Society meetings.
- NIST proposal submitted to study EUV mirror surfaces went unfunded.
- Plan to submit ACS PRF proposal to characterize nanoscale morphological effects in graphene growth by olefin & larger alkane CVD.