NOTES FROM WORKING GROUP DISCUSSIONS, FRIDAY, JUNE 20, 2003

OBJECTIVE FOR WORKING GROUPS WAS TO ADDRESS THE FOLLOWING GRAND CHALLENGE:

Control composition and structure over length scales from 1 nm – 1 micron

What would we like to do?

What don't we know?

How do we eliminate "what we don't know"?

ASSEMBLY WORKING GROUP

What we would like to do (applications)

- Splitting water with light
- Control composition over multiple length scales; controlled synthesis and assembly of important functionalities
- Integrated nanosystems that embody catalysis
  - Environmental remib.
  - Sensing and diagnostics
  - Microrobotics
  - Fuel cells
  - Energy conversions
  - Health
- Multi-scale modeling
- Efficiency and selectivity in synthesis (examples: RT select. oxids hydroaminations)

Scientific Issues

- Metastability (control, prediction)
  - Analogy with biology
- Nanostructures that bind and kill (selectively)
- Viruses, bacteria

What we don't know (can't do) (need to learn)

- Understand forces operative on relevant length scales
- Control collective behavior and kinetic pathways of assembly
- Control, predict metastability (analogy in biology)
- Active site structures, dynamics
- Can't control composition
- Can't control shape and asymmetry (low symmetry)
- Can't control size of catalytic nanostructures
- Can't control surface properties of nanostructures
- Can't control surface heterogeneity
- Don't know structure-reactivity correlations
- Spatial, vectorial control of assemblies
  - Spatial vectorial coupling of catalytic functions (multi-step reactions) compartmentalization
- Dynamic control of accessibility to sites
- Allosteric control (cf. enzymes)

Transport on the nanoscale in confined environment
Control nanostructures for regulation (traffic control) of reactivity, selectivity (cf. MMO, CH_4 in, CH_3OH out)
Understanding "long-range" interactions between catalytic functions
Fabricate complex structures below 1 □ scale for microrobotics
Catalysis for driving nanosized moving parts

What are the themes behind what we need to learn?

Building block synthesis (molecular, particle, surface heterogeneity)
Supramolecular/nanoscale assembly
    Collective behavior/weak forces
    Extending tools top down and bottom up
    Selective trafficking, transport
    Self-assembly; heterostructure assembly
    Directed assembly
Enzyme-like recognition, regulation, allosteric control
Identification of active sites
Thermodynamic, kinetic, mechanistic, and phase-transformation investigations
Understanding chemical/catalytic size, shape and collective effects on a 1-1000 nm scale "Quantum catalysis"(?)
Catalytic production of nanostructures
Using biological systems to make nanostructures

What we need to learn (how to eliminate what we don't know)

What are broader themes behind what we need to learn?
In situ monitoring of size, shape
How to control growth (using surface chemistry)
New synthetic techniques to bridge top down (30 nm – 10 □), bottom up (0.1 – 100 nm)
How to control surface functionality
Identify noncovalent, weak long-range interactions for directed assembly
Learn kinetics and thermodynamics of phase transformations of nanostructures (build knowledge base)
In situ identification and characterization of active sites
Understanding effect of size, shape on selectivity, activity (identifying discontinuities) how reactivity changes on nanoscale
Learn how to synthesize heterostructures

CHARACTERIZATION WORKING GROUP
Catalyst Nanometrology
Synthesis → Structure → Reactivity

What we would like to do

- Observe multiple length scales simultaneously
  - WAXS/SAXS/USAXS
  - TEM-SEM (FE)
  - In situ
- Spectroscopy at several L.S.
  - Electronic structure
  - Vibrational spectroscopy
  - Nanoscale resolution
  - In situ
  - Single molecule spectroscopy
- Method development – Stretch existing methods
  - Pressure and temperature
  - Spatial resolution
  - Time resolution
  - *Examples:* In situ STEM → EELS, → Z-contrast
    - Nanoprobe spectroscopy
      - STM/AFM
      - High T/High P
    - Time resolved EXAFS
    - Vibrational spect. nanoscale
    - NMR/EMR → small scale, → T,P, → RXN systems
  - Adopt methods from biophysics
- Characterization NEEDS theory
  - Quantitative simulation of measurements
  - Couple theorists – experimentalist
    - NSF should recognize this more explicitly (appropriate level of interactions)
    - Long-term commitment to achieve success
- Reactivity at nanoscale
  - Nanoanalytics
    - Nanoreactors linked to synthesis, reaction rate
    - Breakthroughs in detection, e.g., MS, IR microscopy/solid argon
    - B.T. presentation[?]
  - Quantify surface energetics between nanoparticles and supports
    - AFM techniques
    - In situ force curves
  - Quantify interparticle forces at nanoscale in liquid phase
    - DLUO does not apply
- Examples
  - Nucleation and growth in heterogeneous supports
  - Nanostructure stability upon activation

In situ deactivation (RXN)
Evaluate synthesis of nanostructures in situ

COMPUTATION AND MODELING WORKING GROUP

Ultimate challenge of controlling structure to function to synthesis
Understanding fundamental physical principles operating at relevant time and length scales
Control of metastability

Synthesis to structure – Challenges
- Need to understand collective phenomena of multicomponent systems
- Solution phase chemistry
  - Nucleation, precipitation, growth, solubility
  - Dependence of reaction environment
- Controlling growth (kinetics and mode)
- Functionalization and patterning of nanoparticles
- Predicting composition, structure and shape

Needs
- Understanding reactions in solution at a molecular level
- Reactive potentials
- New methods to bridge multiple time scales (MC methods)
- Computation has unique ability to describe rate event
- Identification of relevant order parameters
- Develop databases (segregation energies, alloys); from this establish general principles
- Retrosynthetic approaches to inorganic chemistry LHASA
- Role of simulation in combinatorial/HTE methods
  - Design protocols to search phase space

Wish list to experimentalists
- Measure nucleation rates
- Well defined experiments (conditions)
- Temporal identification of solution intermediates and precipitates
- Computational/experimental identification of model systems
- Rates of elementary steps

Structure to function
- Challenges
  - Method accuracy
  - Model accuracy
  - Multiscale methods
  - Identify the active site along with its environment for metastable molecular and nanoscale assemblies
  - Elucidate the dynamics of the active site and its environment along with the resulting catalytic kinetics
  - Design and optimization of active site and its environment
  - Stability and deactivation
- Needs
  - Better DFT functionals
  - Multilevel electronic structure

- Monte Carlo and molecular and reaction dynamic methods
- Reliable sampling of phase space
- Connect theory to characterization

Modularization

- Coupling multiple processes to enable the synthesis of complex products to remove the need for separation
- In situ assembly
- Mechanisms for “communication”
  - Patterning surfaces, transport of intermediates
- Control nanoscale assemblies