The Combinatorial Platform

Goal: Application of High Throughput Materials Discovery to Find Compositions of Matter that Maximizes Specific Material Properties

Paul L. Richter
Fuel Cell Acquisition Group, Inc.
Union, NJ

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Traditional Surface Chemistry Describes Heterogeneous Catalysts

- **Surface Chemical Bond: Adsorption of Reactants**

  Heterogeneous catalysis relies on the opening of new, fast reaction channels involving the adsorption and conversion of reactants on the surface of the catalyst. Consequently, the key to the success of catalytic processes lies in the details of the interactions between the surface and the adsorbed molecules—the adsorbates. The unique tilted CO adsorption arrangement observed on a few metal surfaces has been modeled with isolated molecules.

Traditional Surface Chemistry Describes Heterogeneous Catalysts

- **Surface Energetics: Adsorption of Reactants and Desorption of Products**

  The viability of a catalytic process depends on the strength (energy) of the adsorbate-surface bonds. Initial studies on the kinetics (rates) of simple adsorbtion and desorption steps at a molecular level addressed this problem by assuming that activation energies depend on the coverage, that is, the surface concentration, of the adsorbates. More accurate kinetic experiments have indicated that reaction rates also depend on the local special arrangement of the adsorbates on the surface. The clustering of adsorbed oxygen atoms can significantly enhance the rate of the oxidation of CO on Pt(111). Catalysis requires the balance of adsorption, reaction, and desorption. Both catalyst strongly adsorbing and catalyst weakly adsorbing equals no reaction.

Traditional Surface Chemistry Describes Heterogeneous Catalysts

- **Catalytic Site: Surface Diffusion of Reactants, Reaction, and Diffusion of Products**

  The strong dependence of reaction rates on the structure of the catalyst.

- **Selectivity**

  A good catalyst should be able to promote the formation of the desired products preferentially.

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- **Materials Dispersion: Nanoparticle Shape and Size Influence Catalytic Chemistry**

  Nanoscale has a role in catalysis. Catalysts are an existing nanotechnology. Most practical catalysts consist of small particles finely dispersed on high surface-area porous solids. The performance of electrocatalysts depends in part on the activity of support surfaces. Good particle size effect for oxygen reduction rate is 3 nm. Oxygen reduction by platinum is based on *d*-band vacancy. Nanoparticles can be created by e-beam lithography, photolithography, and deposition.

- **and Other Unique Features**

  The identification of adsorbates can be accomplished by their unique spectroscopic features.

High Throughput Experimentation (HTE) Program

- **automated catalyst synthesis**
- **fast and reliable assays for catalytic activity**
- **data algorithms and data management system**
- **automated equipment**

Hanak of RCA Laboratories stated the feasibility objective as “synthesizing, analyzing, testing, and evaluating large parts of multicomponent systems in single steps.” Hanak also showed how a multicomponent single target could be used to deposit a spread of compositions on a single substrate.

Combinatorial Laboratory Organization

- Computational Material Science/Database/Data Mining/Design of Experiments/Statistics Team
- Analytical Development Team
- Combinatorial Library Synthesis Team
- Engineering and Microreactor Design Team

Combinatorial Material Science Tasks

- ## Task I. Computational Material Science

Fast workstations with multiple 64-bit CPUs and state-of the-art software are available. These computations allows one scientist to run multiple chemical reactions 24 hours a day, 7 days a week. By performing “experiments” on a computer, computational scientists can eliminate non-productive reaction possibilities and narrow the scope of probable laboratory successes. Density functional theory (DFT) calculations have reached an accuracy and speed to narrow our search for materials with specific properties.

- ## Task II. Design of Experiments

Library preparation, component characterization, property identification, and structure/property relationships yield an enormous amount of data. We are providing an intelligent database to handle the amount of data generated in a transparent and efficient manner. We are providing capabilities for data retrieval and evaluation, but also in the design of higher order library generations.

We need to have descriptors of solids to design a computer-based library. Probably a heterogeneous catalyst cannot be completely described at all. It is not only the chemical composition, but also the number and identity of phases present, the single crystal planes expressed on the surface of the catalyst, the surface composition which can deviate from the bulk composition and many more, which eventually determines the catalytic performance. Additionally, even exactly knowing the properties of a perfect heterogeneous catalyst would not mean to have a way how to synthesize it. We will place in a relational database several properties of the solids, such as synthesis parameters and chemical composition. With this set of descriptors a new library can now be theoretically designed and experimentally tested.

Combinatorial Material Science Tasks

- ## Task III. Combinatorial Library Synthesis

Physical vapor deposition has long been used to prepare stoichiometric ranges of compounds or to explore phase diagrams using the so-called composition spread approach. In this method a large range of stoichiometries of binary, ternary, or quaternary systems is made on a single substrate in a single deposition run. In such an approach, the substrate is generally covered by a continuous film rather than individual isolated pixels of material, as is common in materials science.

Gradient arrays are tools in combinatorial material science for the discovery of new leads. Intimate mixing of the elements as sputtered, because any heating step to cause interdiffusion of thick layers would crystallize the amorphous phases. We expect monolayer and nanoparticle coverage. Sputter deposition technique is easily and inexpensively built, a similar sputter program will enable our research program in combinatorial materials synthesis to prosper without large scale funding.

- ## Task IV. Traditional Material Analysis

Chemical, morphological and crystallographic properties of the newly prepared electrocatalysts will be characterized using various techniques.

Combinatorial Material Science Tasks

- **Task V. Microreactor Screening**

  Primary screening of catalysts by real time parallel analysis systems include infrared thermography, colorimetrical applications, and FPA infrared spectroscopy.

  Secondary screening of complete MEAs by 25-spot array Smotkin device. The Smotkin device can easily be scaled up to evaluate 96 MEAs at one time. Cell performance will be illustrated by *V-I* curves. Standard testing conditions will yield fair comparisons.

  Future screening devices may include semiconductor Lab-on-a-Chip. Positive current from electrochemical anode reaction or reverse cathode reaction will be recorded through 1,000 to 15,000 individual microelectrodes.

- **Task VI. Evaluate, Report and Loop**