Combinatorial Heterogeneous Catalysis

Identification of a new blue photoluminescent (PL) composite material, Gd₃Ga₄O₁₂/SiO₂

Role of catalysis in the economy

- Catalysts are used globally in the manufacture of over 7,000 products worth over $3 trillion per year
- Catalysts are used in 60% of chemicals production and 90% of processes
- Globally catalyst manufacturing is about an $8.5 billion per year industry
- Globally there are about 100 catalyst manufacturing companies


<table>
<thead>
<tr>
<th>Catalyst usage</th>
<th>Annual turnover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum Refining</td>
<td>$2.2 billion</td>
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<tr>
<td>Polymerization</td>
<td>$2.2 billion</td>
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<tr>
<td>Chemicals Production</td>
<td>$2.1 billion</td>
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<tr>
<td>Environmental Protection</td>
<td>$2.1 billion</td>
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</table>
Parameter space

Let us assume first that there are 50 useful, stable elements in the periodic table that are suitable candidates for heterogeneous catalysis:

\[ N(n_E/n_r) = n_E!/[n_r!(n_E-n_r)!] \]

- \( N \) = total number of combinations
- \( n_E \) = number of elements
- \( n_r \) = specific groups (binary, ternary etc.)

...gives 1225 binary, 19 600 ternary, 230 000 quaternary, and \( 10^{10} \) decanary combinations of these elements!

Combinatorial catalysis

Large diversities of solid-state materials libraries are prepared, processed, and tested for activity and selectivity in a high-throughput fashion.

- speeds up the pace of research
- the chances of discovery of totally new and unexpected catalytic materials are increased
- use of systematically acquired data and data-mining technologies
- discovery of trends and patterns of structure–activity relations from large databases
Rapid library synthesis

- Two primary categories:
  1. thin film deposition (on-chip)
  2. solution-based synthesis (microwells)

- Since the ultimate goal of catalysis research is to develop industrial catalysts, it is desirable that each step of the combinatorial effort lends itself to large-scale production

Thin-film deposition

- Library is annealed to induce interfilm diffusion and to form alloys
- Fabricated using semiconductor device manufacturing techniques
CO oxidation screening

- thin-film library with 120 ternary combinations of Rh-Pd-Pt
- prepared by sequentially depositing films of the individual elements onto a quartz substrate
- 1.5 mm diameter spots using masks
- deposition process was accomplished in 10 sequential steps, with 10 nm of material being deposited in each step

![Diagram](image)

Solution-based synthesis

Miniaturization and automation of coprecipitation and impregnation methods:

Micro-jet liquid-dispensation system

![Diagram](image)

Composition mapping

Array microreactor

![Diagram](image)
Anode electrocatalyst for methanol oxidation

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{Cl}_2 + 6\text{H}^+ \rightarrow 6\text{Cl}^- \]

Ternary Pt-Os-Rh array, prepared by manually pipetting metal salts and aqueous NaBH₄ onto Toray carbon paper:

Pt-Rh-Os ternary array in 6 M aqueous methanol (pH 6) quinine indicator.

Borohydride-reduced, inkjet-printed array of electrocatalysts on Toray carbon paper:


4% Pt/41% Ru/10% Os/5% Ir

High throughput screening

“\ When new active solids are developed empirically, by trial-and-error processes employed on a few selected samples, the whole procedure is highly speculative and leads to a very slow rate of discovery for the industry in question. “

• Implements ways to identify the best possible candidate
• Methods adapted from drug discovery tools
• Automated protocols for testing
The split & pool method

A massive parallel arrangement of micro-reaction chambers containing individual beads, each bead representing one catalyst as a member of a library of solid catalysts.

- Enables the generation of every possible combination in a search space
- Difficulty in recognition of a molecule in a mixture
- Useful tool for primary screening

The hierarchical approach

- Targeted to identify the best combinations of redox metals
- As the screening proceeds, the number of components in the catalytic system increases
- Higher degrees of interactions are sought in a stepwise manner

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<td></td>
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</table>

| M1    | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| M2    | 90.0| 78.6| 67.1| 55.7| 44.3| 32.9| 21.4| 10.0|
| Total | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
Design of experiments (DoE) methodology

- Simultaneous modification of variables (factors) and the avoidance of redundant experiments
- Quantifies the effect of each individual variable on the targeted properties
- Efficient for the fine optimization of both catalyst synthesis and process conditions

Evolutionary algorithms

- Mimic the evolutionary process of living species by using similar genetic operators—mating, crossover and mutation—to single out the individuals with the “genetic information” leading to optimum performance
- New population is generated through genetic operators
• The optimal population size and the total number of generations required to find the global optimum

![Graphs showing population growth over generations with different population sizes.](image)

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Reactor Design

• Ideally can be used to measure kinetics
• High modularity allows adaptation to different process conditions
• Chemical inertness, low dead volume and highly reproducible conditions in the channels
• all relevant process conditions must be controlled and monitored, i.e. *in situ* parallel measurement of pressure, temperature, flow, stirring, gas uptake and reaction product composition

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*Six-flow reactor setup adapted to fast kinetic studies.*
Use of model reactions

- Mechanisms are usually well-known or at least well-documented
- Use of simple reaction mixtures and the absence of industrial constraints make it easy to set up the appropriate reactions
- Example: o-xylene hydrogenation
  1. structure sensitive
  2. cis/trans selectivity can give an indication of the electronic density of the metal centers

![Diagram](image1.png)

The closer the points are together, the more similar the physiochemical properties of the catalyst.

Computational chemistry

- Used to predict catalyst activities
- Identify the most promising compounds among thousands of possibilities, or at least to weed out insufficiently active compounds
- Example: density functional theory (DFT) method to predict catalyst activity using the energy of dissociation of reactants on the metallic surface as the descriptor directing catalyst activity

![Diagram](image2.png)
Conclusions

The possibility of performing hundreds or thousands of experiments increases the chance of success...

...you might graduate a lot faster.