Addressing Rigor and Reproducibility in Thermal, Heterogeneous Catalysis

John West, Johnson Matthey
Neil Schweitzer, Northwestern University
Rajamani Gounder, Purdue University
Robert Rioux, Penn State University
January 24, 2024
Resources

- **Website:** [chemcatbio.org](http://chemcatbio.org)
  - Tools and capabilities
  - Publications
  - Webinars
  - Interactive technology briefs

- **Tools:**
  - Catalyst Property Database
  - CatCost
  - Surface Phase Explorer

- **Newsletter:** The Accelerator
  - Subscribe

Biomass resources in the United States could be harnessed to produce up to 50 billion gallons of biofuel each year. That's enough to fuel all domestic and international air travel.

ChemCatBio helps decarbonize our economy by accelerating the development of catalytic technologies that convert biomass and waste resources into renewable fuels and chemicals.

**Mission**
Accelerate the catalyst and process development cycle for bioenergy applications

**Vision**
The rapid decarbonization of our economy

News
The U.S. Department of Energy just announced its Clean Fuels and Products Shot, which intersects with ChemCatBio's mission to develop catalytic technologies for renewable fuels and chemicals.

Syngas can be converted into energy-dense hydrocarbons in a single reactor. Explore the details in the latest interactive ChemCatBio technology brief.
Housekeeping

- Attendees will be in listen-only mode
- Audio connection options:
  - Computer audio
  - Dial in through your phone (best connection)
- Automated closed captions are available
- Use the Q&A panel to ask questions
- Technical difficulties? Contact Erik Ringle through the chat section, lower right of your screen
- Recording will be available at: https://www.chemcatbio.org/webinars.html

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First Speaker

John West
Johnson Matthey

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Johnson Matthey: strong credentials supporting our strategy

- **Strong brand**: 206 year history
- **Technology leadership**: #1 or 2 in chosen markets
- **2022/23 sales**: £4,201 million
- **12,600 employees worldwide**:

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¹Sales excluding precious metals ²As at 31st March 2023
Over 200 years of solving the world’s biggest challenges

1817 Precious metal assayer
1918 Powell-Deering method
1874 Standard kilogramme weight
1960 Electrocatals for NASA’s fuel cells
1974 The world’s first emissions control autocatalyst
1983 Platinum group metal circular economy
2002 Hydrogen fuel cell components
2002 Syngas and chemicals process design and licensing
2020 Hydrogen electrolyser components
2018 Our first commercial sustainable fuels plant license
Scenario:
• Target Rhodium loading: 0.3 wt%
• Catalyst loading 3 metric tonnes
  • ~12 drums of catalyst
• Value of Rhodium £8.5 million
Neil Schweitzer
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Science Has a Public Perception Problem

What drives mistrust in Science?
- Influence of political groups/lobbies
- Public misunderstanding of the scientific method
  - Media coverage of reproducibility issues
A Reproducibility CRISIS!!!

Why Most Published Research Findings Are False

Why Science Is Not Necessarily Self-Correcting

Science Fictions

How FRAUD, BIAS, NEGLIGENCE, and HYPE Undermine the Search for Truth

RIGOR MORTIS
How SLOPPY SCIENCE creates WORTHLESS CURES, CRUSHES HOPE, AND WASTES BILLIONS

Believe it or not: how much can we rely on published data on potential drug targets?

Science has been in a “replication crisis” for a decade. Have we learned anything?

Bad papers are still published. But some other things might be getting better.

Replication crisis

From Wikipedia, the free encyclopedia

The replication crisis (also called the replicability crisis and the reproducibility crisis) is an ongoing methodological crisis in which the results of many scientific studies are difficult or impossible to reproduce. Because the reproducibility of empirical results is an essential part of the scientific method, such failures undermine the credibility of theories building on them and potentially call into question substantial parts of scientific knowledge.

The replication crisis is frequently discussed in relation to psychology and medicine, where considerable efforts have been undertaken to reinvestigate classic results, to determine whether they are reliable, and if they turn out not to be, the reasons for the failure. Data strongly indicates that other natural and social sciences are affected as well.

The phrase replication crisis was coined in the early 2010s as part of a growing awareness of the problem. Considerations of causes and remedies have given rise to a new scientific discipline, metascience, which uses methods of empirical research to examine empirical research practice.

Considerations about reproducibility fall into two categories. Reproducibility in the narrow sense refers to re-examining and validating the analysis of a given set of data. Replication refers to repeating the experiment or study to obtain new, independent data with the goal of reaching the same or similar conclusions.
Scientists Tend to Agree...

- *Nature* survey of 1,576 scientists (106 which were chemists)

This is admittedly a small sample size of self-selected participants...

**BUT is consistent with the attitude of many researchers I have interacted with**

Why Is Reproducibility Important?

- It is important for a research community to have reasonable expectations for the *normal variance* of a particular measurement.
  - Interlaboratory studies are used to determine these values.
  - Standard practice for institutions like NIST and ASTM.

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Examining the literature, we have not been able to determine why ±0.4% was chosen as the standard requirement.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
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</thead>
<tbody>
<tr>
<td>DL-tryptophan</td>
<td>64.66</td>
<td>5.91</td>
<td>13.62</td>
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</table>

There have been relatively few studies in reproducibility in catalysis, particularly comparing catalyst rates
- Ample reviews reporting data, but there are few analysis of the data

What is a reasonable variance for reported catalyst rates? An order of magnitude?
- Maybe it depends on the materials and the chemistry?

Fundamental questions about the reproducibility of catalyst measurements exist before we even consider the competency of the experminter or the rigor of the experiment!
Why isn't R+R a priority in science?

- A framework for the research ecosystem:

  - Conduct impactful science
  - Advance their career
  - Disseminate high-quality studies
  - Maximize revenue

Citation and publication-based metrics incentivize quantity and haste

Planning a Workshop

• What we know:
  1. Researchers have little confidence of data reported in the literature
  2. Catalysis is a complex science
     • *Irreproducibility* could stem from any stage of a study: synthesis, storage, characterization, or testing
     • There are lots of unknowns concerning the inherent reproducibility of measurements made in our field
  3. The current research ecosystem incentivizes publishing a lot and publishing quickly!

• How can we make an impact? (with little to no control over publishers or funders)
  - Our approach was to target two specific groups:
    1. Reviewers – the first line of defense for R+R in scientific literature
    2. New researchers in our field – who need to learn a lot of information in a little amount of time
Next Speaker

Robert Rioux
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Addressing Rigor and Reproducibility in Heterogeneous, Thermal Catalysis Workshop

Phase 1: Winter-Summer '22
- Introductory Sessions

Phase 2: July 21-22, 2022
- In-person Session
- Developing Training Modules/Classes
- Establishing a Database
- A network of Benchmarking Labs
- Others ???

Phase 3: Summer-Fall '22
- Fall '22 and Beyond
- Generate Media?
- Submit Funding Proposals?
- Others?

Financial support provided by the National Science Foundation, CBET Division, Catalysis Program under Grant No. 2152559 and the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC0022918.
## Phase I. Setting the Stage. Introducing the Problem. Learning From Other Fields.

- How widespread is the problem?
- What does it mean for data to be reproducible?
- What are possible systemic, institutional, or individual causes?
- How do researchers think about these problems in other fields?
- Can this problem be “solved,” and what would even be considered progress?

<table>
<thead>
<tr>
<th>The Ongoing Battle for More Credible Science: Identifying Interdisciplinary Lessons</th>
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<tr>
<td>Jennifer Tackett, Northwestern University and Editor-in-Chief of Clinical Psychological Science</td>
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<th>Lessons Learned From Systematic Studies of Experimental Replication in Adsorption Science</th>
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<td>David Sholl, Georgia Institute of Technology, Oak Ridge National Lab, and Editor-in-Chief of AIChE Journal</td>
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<th>The Importance of Standard Operation Procedures For Catalysis Research Accelerated By Artificial Intelligence</th>
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<td>Annette Trunschke, Fritz Haber Institute of the Max Planck Society</td>
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<th>The Data Sea Scrolls</th>
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<td>John Kitchin, Carnegie Mellon University</td>
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<th>A Unique Journal for the Publication of Reproducible Methods for the Synthesis of Organic Compounds</th>
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<td>Rick Danheiser, Massachusetts Institute of Technology and Editor-in-Chief of Organic Syntheses</td>
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<th>Panel Discussion with Journal Editors</th>
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<td>Moderator: Bruce Gates, UC Davis</td>
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<tr>
<td>Panel: Susannah Scott (ACS Catalysis), Johannes Lercher (Journal of Catalysis), Davide Esposito (Nature Catalysis), Junwang Tang (Chinese Journal of Catalysis)</td>
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The immediate outcome of this workshop will be an open access report with:

**Technical Content**
- Best practices for reporting data using common methodologies
- Recommendations for the use of benchmark materials

**For New Researchers:**
- Information currently only available in:
  - Hard-to-search/access literature articles
  - Specialized, expensive textbooks
  - The oral histories of some academic trees

**For Reviewers:**
- Serve as a reference for referring authors to best practice resources
- Help establish consistent guidelines for manuscript/proposal acceptance across different journals and funding agencies.

### Day 1 - Standardized Method Reporting
- **Bulk Synthesis (oxides, zeolites, MOFs, etc.)**
- **Deposition Synthesis (SEA)**
- **Catalyst Testing (Flow, Batch)**
- **Bulk Characterization (XRD, TPx, Physisorption)**
- **Site Characterization (probe molecules, titrations)**
- **Advanced Characterization (XAS, microscopy)**

### Day 2 - Guidelines for Benchmark Materials
- **Supported Metal Nanoparticles**
- **Single Atom Metals**
- **Metal Oxides**
- **Zeolites**
- **Metal Organic Frameworks**
- **Bifunctional Materials**
Phase II. Workshop Report

This report is divided among sections that align with the focused topics of breakout group discussions during the in-person workshop.

- **As an example:**
  - Section 5 focuses on best practices for reactivity testing. The following report template for “Recommendations for Catalyst Testing” includes
  - Common Applications
  - Known Limitations
  - Specific Recommendations for Reporting Data in Literature
  - References for Best Practices

https://www.catalysisrr.org/
https://doi.org/10.5281/zenodo.8029159
Catalyst testing typically serves to achieve multiple objectives, which include:

- **Catalyst Performance**: Time-on-stream characteristics of \textit{rates, selectivities and yield}; regenerability.

- **Structure-Function Relationships**: Quantitative comparisons between \textit{material descriptors and observed catalytic} properties.

- **Determination of Mechanisms and Intrinsic Kinetics**: Identification of the reactive intermediates and intervening elementary steps responsible for consuming reagents and forming products.

**Technical recommendations to improve rigor and reproducibility**:

- Laboratory reactor selection and design
- Isothermal and isobaric operation
- Concentration gradients in reactors
- Contacting pattern in flow reactors
- Steady state operation
- Reproducibility and controls
- Pellet scale phenomena relevant for catalyst testing

**Recommendations for reporting results of catalyst testing**:

- Report normalized rates of reaction and not conversion or temperature required to attain a specific conversion
- Procedures and calculations in reporting of catalyst testing
Future Activities

- Future workshops on topics related to rigor and reproducibility
  
  • Thermal, heterogeneous catalysis (v2.0)
    - Planning to be held in coordination with a major (inter)national meeting
    - Updates to current workshop report
      - Preparing sections on materials, methods, etc. not covered in v1.0
  
  • Electrocatalysis
    - Co-organized by Eric Stuve and Liney Arnadottir
    - Steering committee: Jingguang Chen, Suljo Linic, Ezra Clark, Nirala Singh, Kelsey Stoerzinger, Buddie Mullins, and Gregory Jerkiewicz.
    - To be held July 9–11, 2024 at the University of Washington
  
  • Homogeneous Catalysis
    - Organized by Rory Waterman
  
  • Machine Learning in Catalysis
    - Organized by Hongliang Xin, John Kitchin, Nuria López, Neil Schweitzer
Future Activities

- Shorter articles and guides to be published on focused topics
Future Activities

- Other activities and initiatives for the community to consider
  • Catalysis-focused Interlaboratory studies (ILS)
  • Mechanisms to make benchmark materials broadly accessible
  • Producing training videos and learning modules

- Broader issues in community adoption and incentivization
  • Data storage, formatting, accessibility
  • Journal publications
  • Research proposals

NREL – Photovoltaic Cell Device Performance
Future Activities

- Catalysis-focused interlaboratory studies (ILS)
  - Establish standard properties of benchmark materials
  - Identify sources of measurement of instrumentation error
  - Identify sources of variation (e.g., sample storage, pretreatment)

- The community would benefit from ILS
  - Reaction rate measurements among labs (little precedent of such activities)
  - Case studies for different material classes and chemistries
    - e.g., Bio-feedstock processing often involves bi-functional (metal/acid) materials
    - Develop a benchmark sample (a physical mixture) and rate measurement
  - Methods (e.g., TEM, XAS)

- Funding and accessibility models to prevent "gatekeeping"

61 different research labs were given isotherm data for 18 different MOF’s and asked to calculate the BET surface area.

Fairen-Jimenez, D. et. al., "How Reproducible are Surface Areas Calculated from the BET Equation?" Advanced Materials, 2022, 34 (27), e2201502. DOI: 10.1002/adma.202201502.

Authors developed a computational algorithm – BET surface identification (BETSI) – to aid researchers.
Future Activities

- **Mechanisms to make benchmark materials broadly accessible**
  - Need routes for the sustainable and reproducible synthesis of (suitable) benchmark materials
    - One reason for the end of the Euro-Pt effort
  - Challenging to produce by a single source
    - A core facility might need to be established and funded to provide this service without passing the cost to the user
  - Alternatively, individual laboratories could use best practices and recipes
    - Organic development of a crowd-sourced database of synthesis, characterization and reaction data
    - Provide opportunities for training new researchers
Future Activities

- **Producing training videos and learning modules**
  - Videos on synthesis, characterization, testing
    - "Tips and tricks" to improve reproducibility
  - Publications on best practices and techniques
    - "Beginner's Guides"
  - Workshops and short courses
  - Target new researchers (e.g., students) to the field
  - Accessible to diverse researchers to enable bringing in other scientific expertise to catalysis

*youtube.com*
*(intro to chemistry lab techniques)*
This work was performed in collaboration with the Chemical Catalysis for Bioenergy Consortium (ChemCatBio, CCB), a member of the Energy Materials Network (EMN) chemcatbio.org

All information presented on past events have been archived on CatalysisRR.org. The greater vision of the effort, useful R&R resources and community R&R outreach are available too!
Acknowledgments

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