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aCe
Catalysis Engineering

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CUSTOMIZED HIGH-PRODUCTIVITY CATALYST SCREENING

In 2018, Prof. Javier Pérez-Ramírez began work on a new experimental unit for more rapid and rigorous catalyst testing, for the advanced Catalysis engineering (aCe) group at ETH Zurich, Switzerland. This note describes the implementation and results of the associated collaborative project with Micromeritics Instrument Corp., a global leader in material characterization technologies.

The aCe group at ETH Zurich works at the forefront of heterogeneous catalysis, with a focus on applications for sustainable technology. Their work involves the precise synthesis of catalyst candidates, advanced characterization to establish structure-function relationships at length scales ranging from the molecular to the technical or bulk scale, and catalyst evaluation under industrially relevant process conditions. The group is headed by Prof. Javier Pérez-Ramírez a prize-winning chemical engineer noted for his work to design catalysts that tackle challenges of significant societal concern. Core research themes include the functionalization of natural gas, the valorization of carbon dioxide, and the conversion of biomass to chemical building blocks.

A recent success for the aCe group has been the synthesis of an indium oxide catalyst with palladium atoms inserted into its structure that is highly active for the direct conversion of carbon dioxide and hydrogen into methanol [1]. Methanol, an important fuel and bulk chemical is conventionally manufactured from syngas (a mixture of carbon monoxide and hydrogen), a feedstock derived from fossil fuels. The direct conversion of carbon dioxide, in contrast, utilizes a waste gas of environmental concern. The commercial potential of the catalyst has been recognized by Total, a global energy company, which is working collaboratively with Prof. Pérez-Ramírez on this technology [2]. The expansion of the CO_2 valorization program served as an important stimulus to invest in new equipment to increase the rate at which the group could generate detailed and accurate kinetic data.

This paper describes how the professor's plans for a new customized catalyst evaluation unit were realized, the decision-making process around how best to implement the project, critical features of the resulting solution, and its initial impact on the research of the group. The new Micromeritics® Multi Reactor 4 (MR-4) unit has successfully delivered a substantial increase in experimental productivity. The group can now test 20 – 24 catalysts or alternatively generate 60 – 120 high-quality kinetic data points for a single catalyst each week.

The catalyst development workflow

Research heterogeneous catalysts, as distinct from commercial, industrial analogues, consist of a single bulk or supported active phase in powder form [3]. Catalyst development begins with the synthesis of candidates for a target reaction which are subsequently screened using an array of analytical techniques. The aCe group uses a range of Micromeritics systems to elucidate reaction mechanisms and define characteristics that confer or limit performance via:

- Physisorption studies – which quantify surface area and porosity, characteristics that define catalyst dispersion, and the ease with which specific molecules can move towards and away from the catalytic site.
- Chemisorption studies – which quantify and characterize active catalyst sites on a catalyst and their reactivity towards specific molecules.
- Temperature programmed analyses – such as temperature programmed reduction, temperature programmed oxidation, and temperature programmed desorption which provide detailed insight into reaction and deactivation mechanisms.

Using these techniques researchers can focus attention on the most promising catalyst candidates and learn how to optimize the reaction environment at the molecular level. The group has significant expertise in the nanostructuring of catalysts to enhance reactivity which is directly underpinned by information from these techniques. However, determining catalyst performance for a specific reaction, stability assessment and the generation of robust kinetic data, call for extensive further evaluation.

The aCe group uses a Micromeritics Flow Reactor FR-100 (see figure 1) for catalyst evaluation under industrially representative conditions. The FR-100 is a fully automated modular laboratory reactor unit for investigating catalyst activity, yield, and selectivity. Testing requires just a few grams of catalyst and generates complete mass balance data for the reaction. Gaseous reactants flowing into the reactor are subject to precise mass flow control while liquid feeds are introduced at an accurately known flowrate by metering pump. The products and unreacted feed exit through a low volume separator to produce liquid and gas streams for compositional analysis, to enable closing of the mass balance. The aCe group has leveraged the Flow Reactor FR-100 extensively, but their unit has just a single reactor limiting the number of catalysts that can be screened. The aim of investing in a new unit was to quadruplicate the capabilities of the Flow Reactor FR-100 in a unit, thus offering much higher experimental throughput.

High productivity catalyst evaluation unit Micromeritics Multi Catalyst Reactor 4, evaluation unit

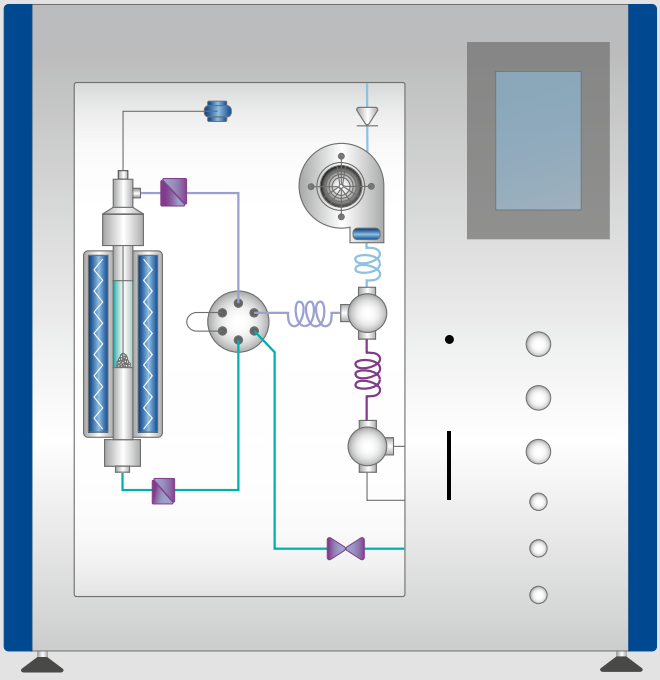

Figure 1: A schematic of the Micromeritics Flow Reactor FR-100 catalyst screening unit

Designing a unit for the generation of larger data sets, moving towards 'big data'?

It has become increasingly evident that artificial intelligence and machine learning techniques have the potential to accelerate and enhance heterogeneous catalyst research. These techniques rely on the availability of large data sets creating a clear requirement for higher experimental productivity. The ability to produce significant quantities of high-quality kinetic data is becoming more important and for Prof. Pérez-Ramírez the potential value of applying cutting edge, machine learning techniques to accelerate development of the indium oxide catalyst was a defining factor in the decision to invest in a new catalyst evaluation unit.

Key design criteria for the unit included:

- Four reactors, and the capability to simultaneously test multiple catalyst candidates.
- Integration with a single existing GC analyzer to minimize capital cost.
- Fully automated control and integrated software that could efficiently handle large quantities of data.

These criteria were discussed with a number of potential suppliers to identify a preferred partner for the project. Delivering effective analysis for all four reactors with just a single gas chromatograph (GC) was an issue for some, with few presenting a workable hardware design. Micromeritics was selected based on a robust solution to this issue and demonstrated capabilities with respect to control and software, evident in the FR-100. The scale of microreactor systems can make precise reactant metering, temperature control, and full automation problematic but these are all critical for efficient, accurate experimentation. Micromeritics' collaborative approach was also influential with the company offering expert knowledge of hardware and software design to complement the professor's understanding of the chemistry and experimental requirements.

Experimenting with the new unit

The project took approximately nine months from initial sign-off on the paperwork to finished installation. Two months were spent commissioning and optimizing the resulting unit, which is complex and substantial, with a footprint around 3m by 3m. The MR-4 is now fully operational, offering two modes of catalyst testing that provide simultaneous:

- Screening of four different catalyst samples, applying an identical sequence of two to three different reaction conditions to each, typically a set per day, or
- Testing of four different catalysts under distinct conditions over a longer time to produce multiple kinetic data sets.

A novel manifold design ensures that all four reactors are sampled rapidly and simultaneously, from very early on in a test. The resulting samples then effectively 'queue' at the single GC for analysis. This solution ensures that performance can be assessed at the same time on stream for all catalysts in the different reactors. Besides, any events that occur early in the reaction are captured reliably. In contrast, sequentially sampling each reactor and analyzing the sample would require approximately 15 minutes per reactor, meaning that an hour could elapse before sampling of the last reactor. This approach would risk missing, for example, a rapid deactivation, undermining experimental productivity.

The software for the unit features an advanced interface that mirrors those found in a modern plant control room. It is extremely robust and straightforward for everyone in the group to use. A defining feature is the software data handling capabilities, which allow manipulation of the vast amounts of data being generated, in real-time. This is in sharp contrast to designs that require the exporting of results to separate spreadsheeting and data handling packages. Instantaneous plots of, for example, selectivity as a function of time or flow rate allow for extremely efficient experimental monitoring and support decisive action where necessary, such as a change of conditions to investigate an observed trend. These capabilities directly impact the rate at which useful information is produced.

Using the new unit, the group can now screen 20 – 24 different catalyst candidates in a week. Alternatively, the unit can be used to efficiently generate kinetic data for individual catalysts by varying partial pressure, reactant feed mixture, and weight hourly space velocity (WHSV) (via total flow rate). All four reactors sit in a single oven, so temperature is not independently variable from reactor to reactor, though individual ovens for each reactor would be technically feasible. The decision to have a single oven was a design choice made to reduce cost and complexity and the effect of temperature is therefore investigated in sequential runs. Around 60 – 120 kinetic data points per catalyst (i.e. 60 – 120 mass balances associated with different running conditions) can be generated over the course of a week, a considerable experimental output.

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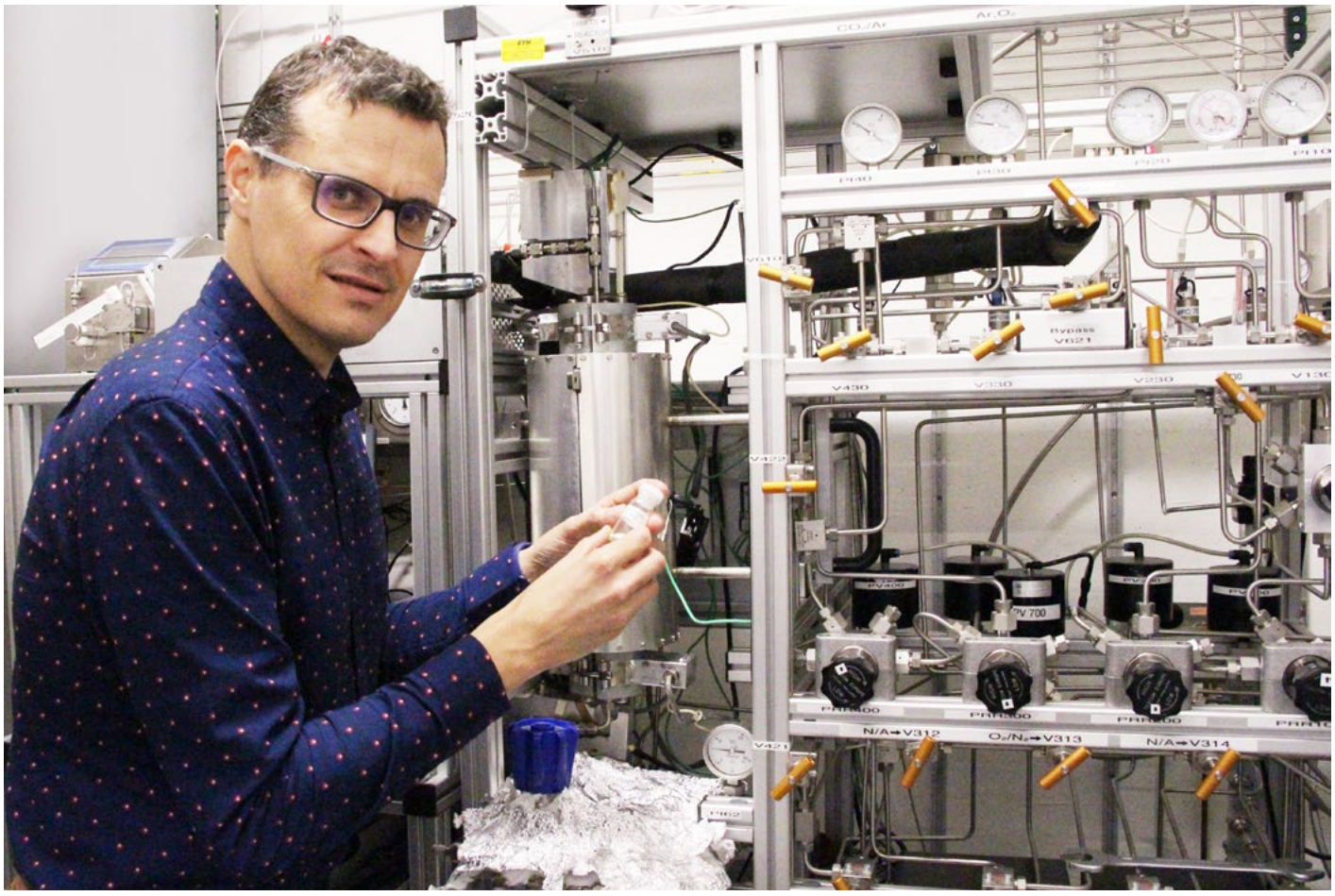
Last words

"Micromeritics has proven to be a truly professional, expert partner for this project and we're extremely pleased with the results," concludes Prof. Pérez Ramírez. "The company is really open to working collaboratively and brings excellent engineering skills to the table. We're delighted about the new unit and it is already making an impact on our rate of progress. Going forward it will play a major role in our work with academic and industrial partners and our ability to capitalize on machine learning techniques to advance the science of heterogeneous catalysis."



Prof. Dr. Javier Pérez-Ramírez in the high-pressure laboratory holding the catalyst developed for methanol synthesis via CO_2 hydrogenation

References:

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About Micromeritics Instrument Corporation

Micromeritics Instrument Corporation is a global provider of solutions for material characterization with best-in-class instrumentation and application expertise in five core areas: density; surface area and porosity; particle size and shape; powder flow and bulk characterization; and catalyst characterization and process development.

The company is headquartered in Norcross, Georgia, USA and has more than 400 employees worldwide. With a fully integrated operation that extends from a world class scientific knowledge base through to in-house manufacture, Micromeritics delivers an extensive range of high-performance products for oil processing, petrochemicals and catalysts, to food and pharmaceuticals, and works at the forefront of characterization technology for next generation materials such as graphene, metal-organic-frameworks, nanocatalysts, and zeolites.

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