EMSL

Science Made Possible

Catalyzing a Cleaner Energy Future

When asked about catalysts, most people probably remember a simple definition copied from the chalkboard in an early chemistry class: *a substance that accelerates or modifies a chemical reaction without itself being affected*. Or certain personalities may spring to mind; the term is routinely borrowed from chemistry to refer, in social and professional contexts, to a person or team whose energetic, efficient work quickly creates change in a given field. Or the first thought may be of the car in one's driveway and its catalytic converter, which chemically grabs some of the worst pollutants from exhaust and makes them harmless before they reach the tailpipe.

Experts at EMSL and PNNL—in collaboration with partners around the world—use cutting-edge tools to study catalysts and help industries tailor them for high-impact applications.

In a way, continuing work by scientists at the Environmental Molecular Sciences Laboratory (EMSL) and Pacific Northwest National Laboratory (PNNL) embodies all three of these notions. Because chemical transformations are at the heart of numerous types of energy production and use, and because catalysts are essential ingredients for these transformations, the two institutions have recognized the critical priority to dig beyond that simple definition for a deeper fundamental understanding of *how* catalysts aid reactions. As for the "human catalysts," EMSL provides transformational tools and expertise, while bringing together interdisciplinary "teams of teams" to tackle challenges in the field of catalysis. These teams include high-profile scientific users that come from across the globe and just across campus at PNNL's Institute for Integrated Catalysis (IIC). And of course, sustained, high-impact success has enabled many market-deployed applications—including the catalytic converters in driveways all over the world.

EMSL's chief scientist Don Baer said, "If you pick the right problem and form the right team, then you accelerate science." Like a good catalyst, this enables a better output: real solutions to energy and environmental challenges.

An Identity of Chemistry for Energy

PNNL's story of high-impact catalysis science doesn't begin in 2001, when the IIC was formed. Nor does it begin with the EMSL's 1997 ribbon-cutting as a new national scientific user facility. These are turning points in a larger narrative that can be traced back to the 1970s and the very formation of the U.S. Department of Energy (DOE). Chuck Peden, catalysis scientist and PNNL Laboratory Fellow, remembers exploring the Lab's catalysis landscape from his first days on the job in the early 1990s.

"When I arrived to help form EMSL, I was thrilled about the new user facility's potential impact on fundamental chemistry, and particularly catalysis," Peden said. "But I was struck by the strong history of *applied* catalysis research at PNNL. They had been doing outstanding work since the energy crisis of the 1970s. But it was applied work for their DOE clients, so it was virtually unknown in the broader research community. It really took me by surprise."

As Peden was becoming familiar with PNNL's identity, there were already plans in the works to capitalize on—and complement—the Lab's strengths by choosing EMSL's scientific focus.

Picking the Problem

In 1990, Don Baer organized a workshop that brought laboratory leaders together to discuss one question: exactly what is needed on the fundamental side of the molecular sciences to support applied solutions to energy and environmental challenges?

"We walked away from that meeting with a clear charter for one area of EMSL," Baer said. "To strive for a deeper fundamental understanding of the surface chemistry of oxides and minerals. Discoveries in this area are critically important for catalysis, energy materials, and environmental cleanup." With this direction confirmed for EMSL, the surface chemistry and catalysis expertise of scientists like Peden would prove to be a perfect fit.

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>
> – Don Baer, EMSL Interim Chief Scientist

Forming the Team

Through the late nineties, the broad array of tools and user projects within the fledgling EMSL led to solid productivity and new understanding in fundamental catalysis. But shortly after the turn of the century, it had become clear to Peden, Baer, and others that PNNL's long-held strengths in applied catalysis were interacting with EMSL to create something special.

"In a way, it was a perfect marriage," Peden recalls. "With EMSL bringing new capabilities and expertise on the fundamental side, and PNNL continuing its leadership in several applied areas, we realized we had the critical mass to form a catalysis effort that was, and is, unmatched anywhere else in the nation."

The IIC was born, originally housed in EMSL, and it began carrying out programmatic research as a new center of excellence in catalysis for the Department of Energy within PNNL. EMSL has remained focused on growing as a national scientific user facility and continuing to develop world-leading capabilities in interfacial science—capabilities that teams of researchers, including those from the IIC, are able to use for new catalysis discoveries.

A Lean Machine Made Possible

As they soon discovered, if you've formed the right team, sometimes a problem picks you.

A specific example came just after the IIC was formed, when the large engine manufacturer Cummins Inc., along with its catalyst provider Johnson Matthey Catalysts, approached Peden and his colleagues with a problem. To improve fuel efficiency by more than 25 percent over standard gasoline engines, Cummins was developing a "lean-burn" diesel engine for use in passenger vehicles such as the Dodge Ram pickup truck. "Lean" refers to using more air and less fuel during combustion in the engine (higher air-to-fuel ratios). While providing incredible gains in fuel savings, unfortunately the lean-burn engine could not meet strict emissions standards because of the poor performance of its catalytic converter. So, with the dual impacts of cleaner air and greater fuel efficiency hanging in the balance, new and significantly improved catalyst technologies were a necessity.

EMSL's 900-MHz NMR spectrometer is one of the most powerful NMR tools in the world, allowing scientists to explore unprecedented molecular-level details of catalysts.

One of the main jobs of an autocatalyst is to remove nitrogen oxides referred to as "NO_X" (NO and NO_2) from engine exhaust. Holding a jar of typical NO_X, one would guess from pure appearance that the red, smog-like gas is quite harmful to humans—and in this case, looks are not deceiving. However, NO_X has a harmless cousin that makes up 80 percent of the air we breathe: nitrogen gas, or N_2. Effective catalysts simply convert the NO_X to N_2. From many years of research and development, effective catalysts to carry out this conversion in the exhaust of today's gasoline-powered vehicles have been improved to the point where NO_X emissions are no longer a major problem. These catalysts are the main components of the catalytic converters on the vehicles we use every day. Unfortunately, these catalytic converters are ineffective for removing NO_X from the more fuel-efficient lean-burn engine-powered vehicles.

As part of their efforts to develop and commercialize clean lean-burn diesel engines, Cummins and Johnson Matthey engineers were studying a recently invented material that was the foundation for a new catalyst technology, known as the Lean-NO_X Trap (LNT), which could operate effectively for NO_X removal from the exhaust of these fuel-efficient engines. But they faced serious problems with the durability of these catalysts. The answers to *why* they failed too early would require unique fundamental studies of the materials involved, which are typically beyond the scope of companies whose expertise lies in product engineering.

This is where DOE national scientific user facilities and national laboratories play an important role. In 2003, Cummins and PNNL began a collaborative, multi-year Cooperative Research and Development

Agreement (CRADA) to explore these problems using techniques and capabilities available at EMSL, which is funded by DOE's Office of Biological and Environmental Research. With initial funding from both DOE's office of Basic Energy Sciences and its Vehicle Technologies Program, PNNL scientist Ja Hun Kwak led an international team of researchers, including Peden, in studies that would greatly aid the development of Lean NO_X Trap catalysts.

Spectroscopic Surprises

The team integrated several EMSL capabilities, including various microscopy, diffraction, and spectroscopy instruments, as well as three generations of EMSL supercomputers. They examined the underlying material properties of Johnson Matthey's catalyst, which was composed of platinum (Pt) metal and barium oxide (BaO) dispersed on an aluminum oxide (alumina) support. Because many autocatalysts involve precious metals like Pt, small particles of the metal are spread out across a support material to maximize the surface area available to the reactants while minimizing costs. However, the research team found that the growth of these small Pt particles was one of the direct results of typical operation of this catalyst technology, a process that was clearly detrimental to its performance. To remedy this problem, it was important to fundamentally understand the chemical and physical interactions between the catalytic Pt and BaO materials and the alumina support. Unfortunately, such interactions are incredibly difficult to characterize.

Of all the tools and techniques the team used, ultrahigh-field, solid-state nuclear magnetic resonance (NMR) spectroscopy—specifically with EMSL's 900-MHz NMR spectrometer—led to the most surprising and important results. NMR, which is sort of like an MRI procedure for atoms and molecules, is a very valuable tool for understanding catalysts, but it has generally failed to live up to its potential for studying catalytic materials such as alumina—until now. The 900-MHz instrument, which is one of the largest NMR magnets in the world, allowed the team to generate the highest-resolution spectra ever obtained for an alumina support, and the first quantitative, atomic-scale observation of how it interacts with a catalytic material such as Pt.

"In this study, the ability to use the ultrahigh-field magnet completely overcame previous difficulties with using NMR for alumina-supported catalysts," Peden says. "We could not have done these experiments without access to EMSL's 900. The capability allowed us to start asking much deeper scientific questions, and it led to unprecedented results that we certainly didn't expect."

These results challenged some very fundamental notions of how catalysts function, calling into question the standard 'chalkboard' descriptions of their preparation and operation. Peden explained why.

"Part of what makes a catalyst a catalyst is that it is supposedly unchanged by the chemical reaction it is involved with. But as it turns out, at least in this case, the catalyst changes greatly. As the catalyst's barium oxide additive was storing and converting NO_X, the catalyst was growing and shrinking on macroscopic scales, morphing from nanoparticle sizes to orders-of-magnitude bigger."

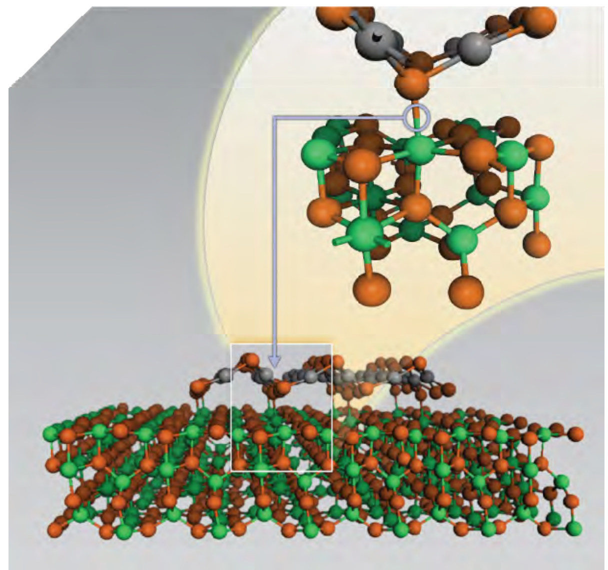
Armed with this information, the researchers then applied the same multiple experimental characterizations—and integration with supercomputer models—to study the catalyst's shortfalls: it was suffering from both sulfur poisoning and degradation at high temperatures, problems that were preventing Cummins and Johnson Matthey from being able to commercialize the technology. In particular, the BaO additive wasn't only hungry for NO_X, but for sulfur dioxide (SO_2) as well, which was also found in the lean exhaust. In fact, the BaO preferred to fill up on SO_2, leaving little or no room for NO_X. To remove the sulfur, the catalyst must be treated at high temperatures. But the research team also showed that this causes many types of damage including growth in the size of Pt particles.

By decoupling these two failures and showing how and why they happen at a molecular level, the researchers provided their industry partners with new, essential design parameters for the materials and operation of the LNT catalyst technology. Later designs were able to largely circumvent these issues, and the 2007 Heavy-Duty Dodge Ram became the first commercial implementation of the LNT technology in the United States.

Cummins Vice President and Chief Technical Officer, Dr. John C. Wall, recognized the wealth of new understanding that wouldn't have been possible without IIC, EMSL, and the National Synchrotron Light Source at Brookhaven National Laboratory—another DOE user facility the team used to conduct experiments.

"In addition [to new understanding of sulfur poisoning and thermal damage], I would like to acknowledge that the CRADA provided us with access to the other discoveries made at PNNL in the area of NO_X storage component morphological mobility, which proved key to interpreting many features of these uniquely complex catalytic systems."

While supporting Cummins's lean engines during a key crossroads in the technology's development, these discoveries quickly extended benefits beyond the corporations directly involved. The surprising catalyst morphology findings, which were published in *Science*, have been cited numerous times, showing added value for the broader catalysis and emissions-control community. Today, similar LNT catalysts are used in other vehicles, including new models of the diesel Volkswagen Jetta, thereby making possible the introduction of these clean and very fuel-efficient vehicles to the U.S. market.



The molecular-level interactions between catalysts and their support materials are of utmost importance when exploring ways to improve performance. In the autocatalyst the team studied in collaboration with Cummins, rafts of catalytic platinum oxide float above a sea of aluminum oxide, anchored by bonds between platinum and aluminum.

Real Teams + Real Experiments = Real Solutions

The LNT effort constitutes just one of many high-profile examples, but EMSL and IIC are leading a broader paradigm shift in the way scientists approach catalysis research. Even the best techniques, like ultrahigh-field NMR, have drawbacks. First, if they are not integrated with other instruments, methods, and supercomputing in the context of cross-disciplinary teams, the scientific and societal impact will be limited. Second, due to current limitations of the instruments, many of today's catalysis experiments are conducted under unrealistic conditions, rather than in the complex environment of real-world catalyst applications.

To address the former, EMSL is sharpening much of its focus to a handful of today's most pressing scientific challenges—like catalysis for energy-related materials—and bringing "teams of teams" from across disciplines to converge on new solutions. This includes enriching the successful partnership with PNNL's Institute for Integrated Catalysis to bridge the gap between fundamental and applied catalysis, as well as to bring together the highest-impact teams of researchers. Recently, Baer and Peden led a workshop at EMSL that included more than a dozen of the nation's top experimental and computational catalysis scientists. Once again, the discussion focused on "problem picking"—information that EMSL and IIC can use to guide the subsequent task of "team forming." While more traditional, single-principal-investigator research will certainly continue in EMSL, the user facility is both embracing and creating change. There is a growing consensus among scientific leaders that, in the future, innovation will be accelerated by increasing the formation of multi-disciplinary and often multi-institutional research teams.

To support better experimental science in real-world conditions, EMSL specializes in developing one-of-kind capabilities. By designing novel research tools and customizing off-the-shelf instruments to meet specific research needs, EMSL is helping fields like catalysis make a transition that is analogous to the move from photography to motion pictures: why piece together a story from before-and-after images when you can truly observe phenomena as they unfold?

But doing more realistic science comes with unique challenges. For example, the typical NMR experiment to characterize solid surfaces (like catalysts/supports) requires that samples spin incredibly fast. But treating the sample with realistic vehicle exhaust during the experiment presents a mechanical problem: the gas lines will twist and kink as the samples spin. While the problem is simple to identify, its solution has eluded scientists for decades, holding back an important area of real-world catalysis research. In 2009, IIC scientist Jian Zhi Hu earned a patent for a new DMAT (discrete magic-angle turning) probe, which basically captures NMR spectra while merely turning a sample back and forth quickly rather than spinning it, allowing pressurized gas lines to remain intact. Development of this solution included a collaborative scientific publication by EMSL NMR experts Jesse Sears and David Hoyt, PNNL engineer Yong Wang, and IIC's Hu, Peden, and Kwak. Today, this home-grown capability is available to EMSL's global user community in catalysis and many other fields. EMSL has also invested in a new state-of-the-art transmission electron microscope that can provide atomic-resolution images of catalysts as they operate under realistic conditions of temperature and pressure.

Mimicking real conditions changes catalysis research, but what about when the conditions themselves change? One yet-to-be-solved problem in autocatalysis involves fluctuating conditions: when an engine is cold, it releases more pollutants than normal because its catalyst is optimized for warmer engine exhaust. Similarly, it would be highly advantageous for other fuel-efficient engine technologies, such as lean-burn *gasoline* engines, to operate at temperatures above which the current LNT technology is effective. So, on a molecular level, what will it take to broaden the range of temperatures at which vehicle catalysts are effective? Looking ahead, this is one difficult question IIC scientists are tackling in separate research partnerships with Cummins, the Ford Motor Company, and General Motors.

Catalyzing a cleaner energy future does not simply mean purchasing a giant NMR magnet or pursuing certain collaborations in industry. In the case of EMSL and IIC, it means providing continued leadership that picks problems and forms teams in response to critical energy, environmental, and economic challenges. Building upon decades of success, these teams may just uncover chemistry's best answers to a future full of questions.

Funding

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