Profile of Cynthia Friend

Farooq Ahmed, *Science Writer*

In 2015, the United Nations released Sustainable Development Goals aimed at improving the environment and supporting vulnerable populations around the globe (1). Among the goals are those intended to reduce energy consumption and invest in clean energy, to encourage innovation in industry and develop efficient production methods, and to promote gender equality. Over the course of her career, Cynthia Friend, the Theodore Williams Richards professor of chemistry and professor of materials science at Harvard University, has engaged in efforts that directly address these goals and several others. The first female full professor of chemistry at Harvard, Friend studies the surface chemistry of heterogeneous catalysts. Her research could help increase the efficiency of many industrial processes while decreasing the production of wasteful and harmful byproducts. With nearly one-quarter of worldwide energy use attributed to the synthesis of chemicals and fuel, her work may have a lasting impact on humans' ability to conserve the planet's natural resources. In her Inaugural Article (2), Friend, who was elected to the National Academy of Sciences in 2019, describes the development of a highly selective catalyst that uses palladium and silver to promote hydrogenation, a key industrial reaction that typically occurs at extremely high temperatures.

Cynthia Friend. Image credit: Robert J. Madix (photographer).

Golf Lessons

The daughter of World War II veterans, Friend was born and raised in southern Nebraska. Her parents supported her curiosity, and her father, while working on the family's cars and home, taught her basic electrical and mechanical engineering. Friend says this early training "turned out to be really important as I started my career in the physical sciences." She credits the space race of the midtwentieth century, as well as her high school's flexible scheduling, which allowed her to pursue an independent study project, with sustaining her interest in science.

Friend developed an early interest in golf, playing on a cow pasture together with her family—an experience that gave her some of her fondest memories. "Walking around, hitting golf balls, and seeing the cattle out there—it was fantastic," she says. These days, Friend sometimes competes in golf tournaments. She says golf gives her an outlet from scientific research, boosts her confidence, and has taught her how to respond to failure.

After completing high school, Friend left for the West Coast, encouraged by a family friend, and studied chemistry at the University of California, Davis. Later, she attended the University of California, Berkeley, where her undergraduate advisor, physical chemist Peter Rock, had completed his doctorate. At the time, University of California, Berkeley "was a powerhouse in physical chemistry. It was absolutely my first choice," she says.

Parallel Chemistry

At Berkeley, Friend was one of just four women in a class of around 100 chemistry graduate students. She studied with inorganic chemist Earl Muetterties, who greatly influenced her trajectory as a chemist.

This is a Profile of a member of the National Academy of Sciences to accompany the member's Inaugural Article, 10.1073/pnas.2010413117.
First published September 11, 2020.

"He was able to draw parallels between chemistry on the surfaces of metals and in organometallic compounds. That was very pivotal in my thinking, because one of the aspects of my work that's a bit different from others is that I think in terms of localized bonding and coordination chemistry—and then I map that onto solids," she explains. Coordination complexes contain metal atom centers bound to ligands that are often organic molecules, and Friend's graduate research explored the coordination chemistry of nickel surfaces, among others (3).

Friend says her graduate advisor, Muetterties, helped her connect experimental work to theoretical chemistry. "At that time, it wasn't possible to do powerful electronic structure calculations like you can now. But you could get qualitative information about bonding." This led to a productive collaboration on hydrodesulfurization of cyclic sulfides with theoretical chemist Roald Hoffmann, who won the Nobel Prize in chemistry in 1981 (4). Friend's work helped establish a model of how molecular structure affects the reaction mechanisms of different catalysts, focusing on commercially widespread molybdenum catalysts (5).

Changing Field

After graduating from Berkeley in 1981, Friend completed a brief postdoctoral fellowship at Stanford University before joining Harvard as an assistant professor of chemistry.

When she started at Harvard, Friend was one of two female chemists in the department. In 1989, Friend became Harvard's first female full professor of chemistry as well as the first assistant professor in chemistry to receive a promotion in two decades. Friend points out that small administrative changes can have large impacts on the career development and retention of junior faculty. It is partly why she feels strongly that professors should serve in administrative roles. "Leadership really matters," she says.

Friend arrived in Cambridge, MA at the dawn of the personal computer era. She recalled receiving an early IBM computer with floppy drives and no hard drive. Access to computers made data collection easier, even if chemists had to write their own programs back then, and experimental tools like photoelectron spectroscopy began to reveal deeper molecular structural detail. Machine learning algorithms and X-ray scattering techniques have since taken over, and Friend says the combination of sophisticated electronic structure calculations with improved experimental methods has been a boon for physical chemistry and materials science. Spectroscopic advances, in particular, allowed Friend and colleagues to describe general mechanisms for a range of complex surface interactions, including alkyl oxidation and alcohol chemistry on metal surfaces (6).

This progress also helped Friend and collaborators develop and examine novel materials, such as titanium sulfide nanocrystals, which they deposited on a surface of gold (7). Because of its high electrical conductivity, titanium sulfide has been used as a solid electrolyte in rechargeable batteries, including solid-state lithium–ion batteries for electric vehicles.

In addition to molybdenum, the precious metals gold and silver have emerged as important elements in industrial catalysts. The key, Friend says, is that they are intrinsically unreactive across a range of temperatures and pressures. "You can control the density of their active sites and, thus, their selectivity." Her work on methanol oxidation conducted on nanoporous gold surfaces demonstrated that the reaction can occur at low temperatures and ambient conditions. The work has implications for the sustainable synthesis of esters used in fragrances, flavorings, and insulation (8).

Additionally, one of the reactions she began studying while at Harvard was the removal of sulfur from organic compounds. Desulfurization is critical to many industries, including in petrochemical processes and environmental remediation, because sulfur can inactivate catalysts and can be toxic to the environment.

Sustainable Catalysts

To advance the study of catalysts, Friend helped found the Center for Integrated Mesoscale Architectures for Sustainable Catalysis in 2014 and serves as its director. Funded by the US Department of Energy, the center, she says, "brings together people with expertise at Harvard and six partner institutions from across the US to transform how catalysts are designed."

Inspiration for the center was rooted in the long collaboration with her husband, chemical engineer Robert J. Madix, who was on the faculty at Stanford University until he joined Harvard in 2005. "We commuted between the two institutions for 17 years," she says. In addition to experimental chemists, the center draws on expertise from multiple disciplines, including chemical engineers, theoreticians, nanotechnologists, physicists, and computer scientists.

Collaboration has been important to Friend, especially as her work has delved into the mechanisms of heterogeneous catalysis. Complex materials that interact with reactants in different phases, heterogeneous catalysts often restructure under reaction conditions. "We can take our fundamental understanding of a reaction mechanism and, based on that, we can actually predict catalytic behavior and fundamental chemical steps," she explains.

In a recent review article, Friend and coworkers (9) described the many ways metallic gold catalyzes the oxygenation of alcohols and amides, with an emphasis on gas-phase and liquid-phase systems. The resultant products of these reactions have uses in the food industry, cosmetics, textiles, and pharmaceutical synthesis. Friend points out that almost 16% of medicinal chemistry reactions are acylations, used to produce amines and esters, making it the most common reaction in that field.

Although her research may have implications for industrial chemistry, she says, "Our dream would be to take our ideas and make a smaller-scale process from them—not something on a huge commodity scale." Her laboratory is also working on fundamental photochemistry, which may aid in clean fuel efforts, as well as an application that would aid in the destruction of chemical weapons at room temperature.

In her Inaugural Article (2), Friend reports using the metal palladium to drive the hydrogenation of silver, which can then be used for selective catalysis. Although widely used as a catalyst, silver deactivates after prolonged carbon exposure. By controlling the hydrogenation of silver with palladium, Friend has devised a way to extend the use of both metals and increase the efficiency of the reaction, which could lead to a decreased need to mine palladium and silver, among other benefits.

"Because it is not an energetically favorable mechanism, we had to create a dense phase of hydrogen on palladium to drive the migration to silver," she says. The palladium−silver interface length controls the rate of hydrogen atom migration.

This kind of surface chemistry, Friend points out, is of tremendous importance to catalysis. "The energy efficiency of catalytic processes hinges on achieving high selectivity and activity," she says. "With an increased urgency about sustainability, research on catalyst mechanics will help determine our carbon footprint and play a role in energy efficiency and also energy security."

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