

Artist's concept illustration depicting pairs of rhodium and tungsten atoms finding each other and performing chemistry on a porous carrier, called a support.

"PAIR-SITE" CATALYSIS

A Cleaner, More Efficient Way to Speed Up Chemical Reactions

Catalysis is an enormous field comprising thousands of complex materials — *catalysts* — that speed up and direct chemical reactions and make it possible to produce everything from yogurt and laundry detergent, to paper and plastic, to gasoline and fertilizer. "The configurations and arrangements at the atomistic scale of the different components you put in catalysts dictate how reactive they'll be for the different kinds of chemistries they are required to perform," says **Phil Christopher**, professor of chemical engineering at UC Santa Barbara, an expert in catalysis, and a UCSB Mellichamp Chair in Sustainable Manufacturing. "The interactions between the catalyst and the chemicals being converted are an interesting and complex dance that can be challenging to understand."

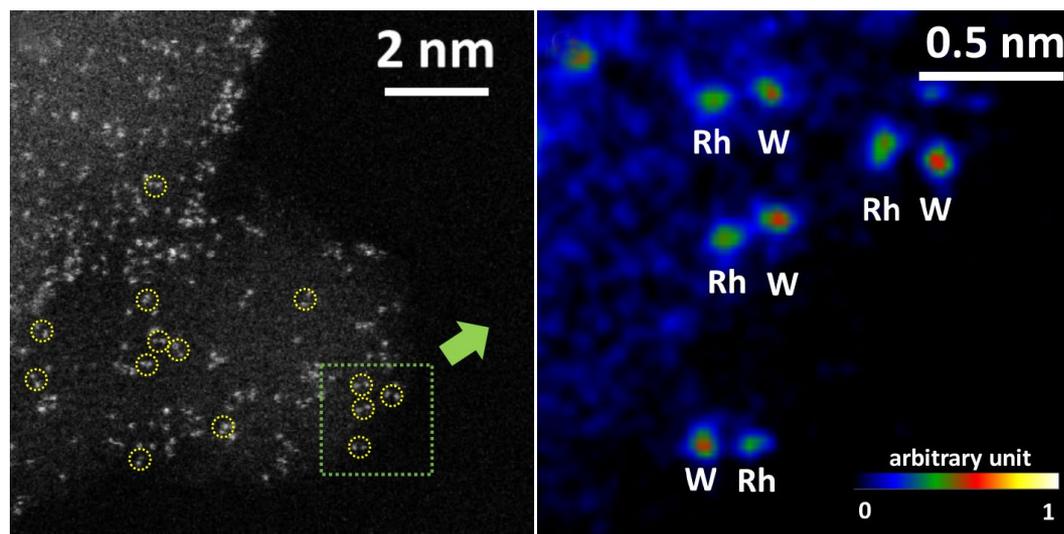
Many solid catalysts are porous materials that contain metal structures at nanometer length scales in their pores, where the reaction occurs as the material to be catalyzed encounters them. Often, the chemical reaction being catalyzed occurs as multiple chemical species interact on the catalyst. Accordingly, researchers spend a great deal of time pondering how those chemical species can find each other on the surfaces of nanometer-sized metal domains located inside porous materials and then react to form the products of interest.

One longtime goal in the field has been to make the metal domains increasingly smaller, thus increasing the efficiency of metal use in the catalytic process. "If you have a big chunk of expensive metal, most of that metal is in the middle, not at the surface, so, you use only a small fraction of the material to do catalysis," Christopher explains. "If you shrink the metal domains down to one atom, then every atom has the chance to do chemistry."

"Furthermore," he continues, "researchers often combine multiple metals in nanometer-sized domains to optimize catalyst performance. The ultimate limit of that would be to place two different metals next to each other in pairs of atoms that exist across a porous carrier, called a *support*. The hope would be that the pairs of atoms could work in cooperation to efficiently catalyze the reaction of interest."

About four years ago, Christopher began working to realize the goal of creating a catalyst of that kind. Now, he and his colleagues have synthesized such structures and identified rhodium and tungsten as elements that could work together to catalyze specific reactions. The research was funded through one of the U.S. Department of Energy's Energy Frontier Research Centers, named the Catalysis Center for Energy Innovation.

A paper about the work, co-authored by Christopher, a former



Electron microscopy images reveal pairs of individual rhodium (Rh) and tungsten (W) atoms, creating a novel interaction that accelerates catalytic action.

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NOT ONLY DID WE PUT THE ATOMS NEXT TO EACH OTHER, BUT WE DID IT IN A WAY THAT TAKES THEM BEYOND BEING JUST A STATIC PAIR SITTING THERE. THEY ARE WORKING COOPERATIVELY TO ENABLE EFFICIENT REACTIVITY.

☞☞

— PHIL CHRISTOPHER

postdoctoral researcher in his lab **Insoo Ro**, now-graduated PhD student **Ji Qi**, current PhD student **Gregory Zakem**, and undergraduate student **Austin Morales**, along with colleagues from the University of Delaware, Columbia University, and UC Irvine, was published in the September 7 issue of *NATURE*. Christopher says that it describes "an observation of pairs of atoms that catalyze the conversion of three different chemical species in a cooperative process to form a single, desired product."

"Through our analyses," he adds, "we hypothesized that one reactant prefers to bind to rhodium, while another binds to tungsten, and that the third binds at the interface between rhodium and tungsten. The atoms then transfer reactants among each other, while dynamically moving closer to and farther

Phil Christopher (left) meets in his lab with (from left) PhD student Gregory Zakem, who is an author on the paper, PhD student Rosadriana Zelaya, and postdoctoral researcher Jaeha Lee.



from each other, ultimately enabling formation of the desired product. In catalysts that don't contain pairs of rhodium and tungsten atoms, it was observed that only two of the reactants can combine, forming undesired products rather than the desired product."

So far, the researchers have used their "pair-site" catalysts for only one specific but important and widely performed industrial reaction: hydroformylation, in which hydrogen, carbon monoxide, and an alkene (in this case ethylene) react to form the aldehyde propanal, aldehydes being building blocks for a wide range of commodity chemicals. "Oil or natural gas that you pull out of the ground contains hydrogens and carbons — hydrocarbons — and to make many consumer goods from them, you have to start by adding oxygen onto hydrocarbons," Christopher says. "Hydroformylation is one of the first processes used in industry to do that."

Making catalytic surfaces on which this chemistry can occur efficiently is extremely difficult, so current process chemistry instead employs liquid-phase catalysis. It requires liquid-soluble catalysts, which must be separated from products after catalysis.

Doing catalysis on surfaces could simplify the process. "The gas-phase reactants come into a reactor, convert to the product at the solid-catalyst surface, and come out the other side of the reactor," Christopher explains. "Unlike in liquid-phase catalysis, the catalyst is stationary, eliminating the need for post-catalysis separation."

Further, the on-surface method would, by definition, almost certainly be more environmentally friendly, because, Christopher notes, "removing sometimes-challenging separation steps means that less energy needs to be spent to produce products, so the process may cause fewer emissions."

However, he notes, "Even though our catalysts work more efficiently than most other catalytic surfaces, they are currently much less effective than liquid-phase catalysts, so there is still a long way to go before industry would potentially adopt these new materials."

Christopher believes that the paper was published in *NATURE* for a couple of reasons. First, he says, "It's hard to make a material where pairs of different metal atoms are stabilized next to each other across a support. We figured out how to do that and demonstrated that the material exhibited interesting behavior for a challenging reaction."

Second, he adds, "The rhodium and the tungsten work together in a very interesting way. They form a bond for a little while, they break apart, and they pass one of the reactants between them. So, not only did we put the atoms next to each other, but we did it in a way that takes them beyond being just a static pair sitting there; they are working cooperatively to enable efficient reactivity."

Christopher explains how his group makes the material: "A highly porous supporting material called *alumina* is suspended in water containing a source of tungsten, which is then dried and treated at high temperature. The alumina, containing dispersed tungsten, is then suspended in water that contains a source of rhodium at a basic pH of 10. This pH was found to enable the deposition of rhodium next to tungsten. We're still a little murky on how exactly rhodium and tungsten pairs form, but we have some ideas."

Preparing their experimental catalytic setup involved "loading about one gram of the catalyst into a tubular quartz reactor, elevating the temperature to approximately one hundred degrees Celsius [212 degrees Fahrenheit], and flowing the reactant mixture over the catalyst. This

amount of catalyst contains more than a quintillion [10^{18}] pairs of rhodium and tungsten atoms that were doing chemistry."

Colleagues at the University of Delaware performed simulations based on quantum chemistry that provided details about the mechanism of the reaction, and electron microscopy done at UC Irvine allowed the team "to see the pairs of atoms across the porous alumina support with adequate resolution to be able to say, 'That's tungsten, and that's rhodium in a pair.'"

"This combination of analyses provided detailed insights," Christopher continues. "Not only could we make a material where we thought we had these pairs, but we could also observe them and then understand how they're working together to do this chemistry much more efficiently than could, say, either one of them separately or other versions of this that we tried before."

Of course, new findings raise new questions, and, as Christopher says, "One question I get often is whether we have seen experimentally the dynamic behavior of the atoms moving to drive this chemistry. The answer is: not currently. The reactions happen on ultra-fast time scales, too quickly to be seen with a microscope. The best we can say is that the theory made numerous predictions that are consistent with experimental observations, so, if you believe that the coincidence is convincing, here is the mechanism that we think is at work."

This research has also led Christopher's group to consider whether there might be other recipes, pairs of other atoms, that might work as well or better than the current combination, or whether these materials could drive other important reactions, and also whether it would be "so challenging each time we try to make a new pair that it's prohibitive. We're thinking about it."