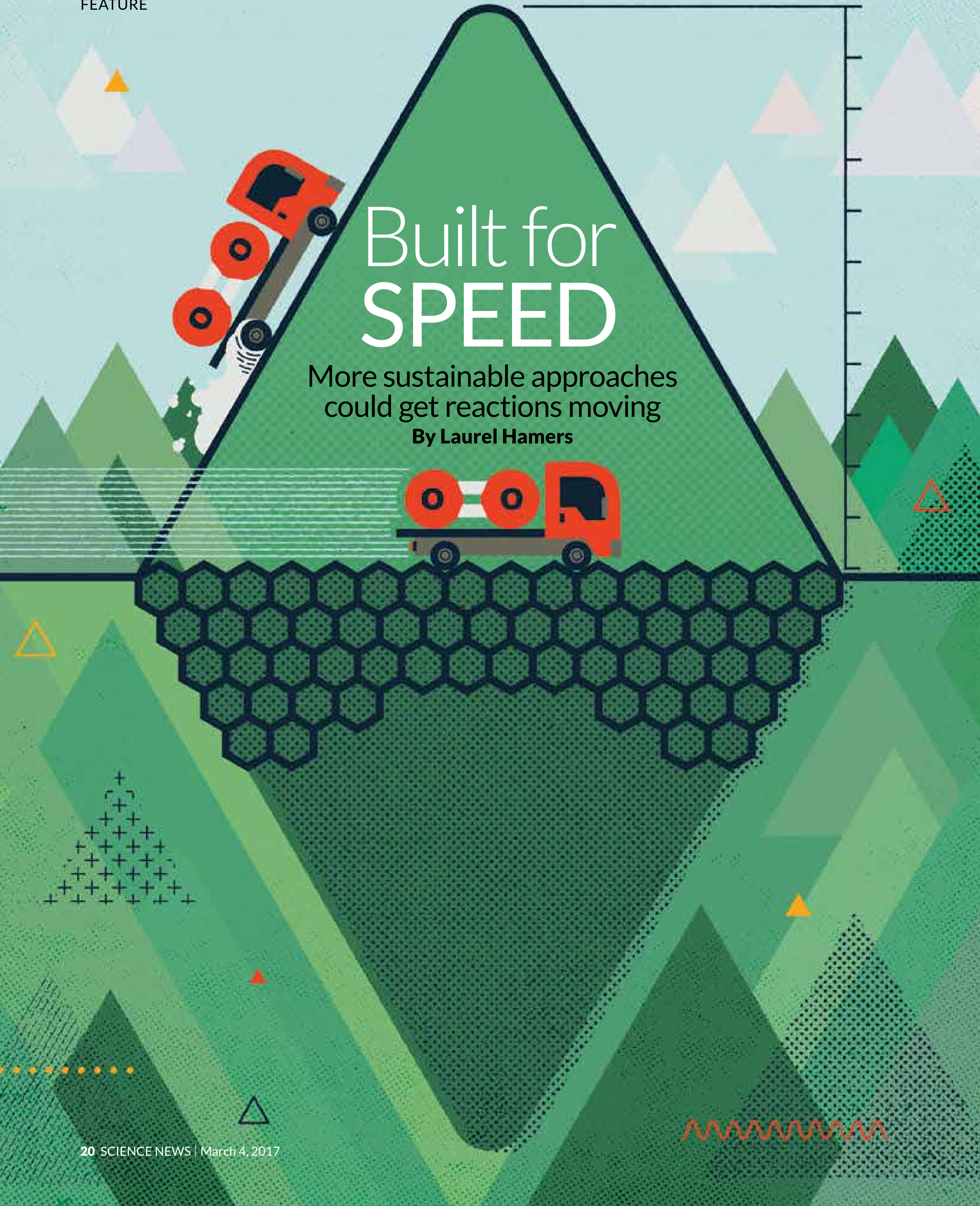


Built for SPEED

More sustainable approaches could get reactions moving

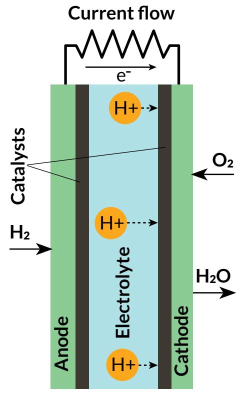
By Laurel Hamers

Platinum, one of the rarest and most expensive metals on Earth, may soon find itself out of a job. Known for its allure in engagement rings, platinum is also treasured for its ability to jump-start chemical reactions. It's an excellent catalyst, able to turn standoffish molecules into fast friends. But Earth's supply of the metal is limited, so scientists are trying to coax materials that aren't platinum — aren't even metals — into acting like they are.

For years, platinum has been offering behind-the-scenes hustle in catalytic converters, which remove harmful pollutants from auto exhaust. It's also one of a handful of rare metals that move along chemical reactions in many well-established industries. And now, clean energy technology opens a new and growing market for the metal. Energy-converting devices like fuel cells being developed to power some types of electric vehicles rely on platinum's catalytic properties to transform hydrogen into electricity. Even generating the hydrogen fuel itself depends on platinum.

Without a cheaper substitute for platinum, these clean energy technologies won't be able to compete against fossil fuels, says Liming Dai, a materials scientist at Case Western Reserve University in Cleveland.

To reduce the pressure on platinum, Dai and others are engineering new materials that have the same catalytic powers as platinum and other metals — without the high price tag. Some researchers are replacing expensive metals with cheaper, more abundant building blocks, like carbon. Others are turning to biology, using catalysts perfected by years of evolution as inspiration. And when platinum really is best for a job, researchers are retooling how it is used to get more bang for the buck.

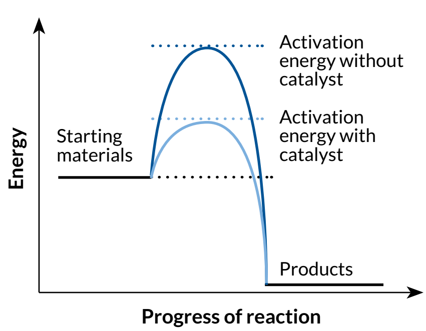


Adding zip In a fuel cell, catalysts help hydrogen and oxygen atoms reshuffle, forming water. In the process shown, hydrogen ions move through an electrolyte while hydrogen's electrons generate current. Hydrogen and oxygen meet at the cathode.

Moving right along

Catalysts are the unsung heroes of the chemical reactions that make human society tick. These molecular matchmakers are used in manufacturing plastics and pharmaceuticals, petroleum and coal processing and now clean energy technology. Catalysts are even inside our bodies, in the form of enzymes that break food into nutrients and help cells make energy.

A lesser effort Catalysts lower the amount of energy needed to make a chemical reaction run. The starting materials and ending products are the same, but the catalyst offers an easier route to get between the two.



During any chemical reaction, molecules break chemical bonds between their atomic building blocks and then make new bonds with different atoms — like swapping partners at a square dance. Sometimes, those partnerships are easy to break: A molecule has certain properties that let it lure away atoms from another molecule. But in stable partnerships, the molecules are content as they are. Left together for a very long period of time, a few might eventually switch partners. But there's no mass frenzy of bond breaking and rebuilding.

Catalysts make this breaking and rebuilding happen more efficiently by lowering the activation energy — the threshold amount of energy needed to make a chemical reaction go. Starting and ending products stay the same; the catalyst just changes the path, building a paved highway to bypass a bumpy dirt road. With an easier route, molecules that might take years to react can do so in seconds instead. A catalyst doesn't get used up in the reaction, though. Like a wingman, it incentivizes other molecules to react, and then it bows out.

A hydrogen fuel cell, for example, works by reacting hydrogen gas (H_2) with oxygen gas (O_2) to make water (H_2O) and electricity. The fuel cell needs to break apart the atoms of the hydrogen and oxygen molecules and reshuffle them into new molecules. Without some assistance, the reshuffling happens very slowly. Platinum propels those reactions along.

Platinum works well in fuel cell reactions because it interacts just the right amount with both hydrogen and oxygen. That is, the platinum surface attracts the gas molecules, pulling them close together to speed along the reaction. But then it lets its handiwork float free. Chemists call that "turnover" — how efficiently a catalyst can draw in molecules, help them react, then send them back out into the world.

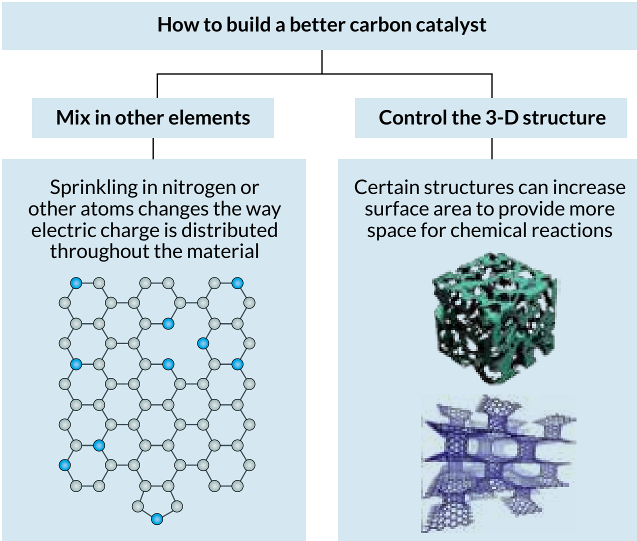
Platinum isn't the only superstar catalyst. Other metals with similar chemical properties also get the job done — palladium, ruthenium and iridium, for example. But those elements are also expensive and hard to get. They are so good at what they do that it's hard to find a substitute. But promising new options are in the works.

Carbon is key

Carbon is a particularly attractive alternative to precious metals like platinum because it's cheap, abundant and can be assembled into many different structures.

Carbon atoms can arrange themselves into flat sheets of orderly hexagonal rings, like chicken wire. Rolling these chicken wire sheets — known as graphene — into hollow tubes makes carbon nanotubes, which are stronger than steel for their weight. But carbon-only structures don't make great catalysts.

"Really pure graphene isn't catalytically active," says



Carbon and then some By itself, carbon is not a great catalyst. But mixing in other elements (left) and changing its three-dimensional structure (right) give it new powers. Scientists can vary these parameters to design carbon catalysts suited to different situations.

Huixin He, a chemist at Rutgers University in Newark, N.J. But replacing some of the carbon atoms in the framework with nitrogen, phosphorus or other atoms changes the way electric charge is distributed throughout the material. And that can make carbon behave more like a metal. For example, nitrogen atoms sprinkled like chocolate chips into the carbon structure draw negatively charged electrons away from the carbon atoms. The carbon atoms are left with a more positive charge, making them more attractive to the reaction that needs a nudge.

That movement of electrical charge is a prerequisite for a material to act as a catalyst, says Dai, who has pioneered the development of carbon-based, metal-free catalysts. His lab group demonstrated in 2009 in *Science* that clumps of nitrogen-containing carbon nanotubes aligned vertically — like a fistful of uncooked spaghetti — could stand in for platinum to help break apart oxygen inside fuel cells.

To perfect the technology, which he has patented, Dai has been swapping in different atoms in different combinations and experimenting with various carbon structures. Should the catalyst be a flat sheet of graphene or a forest of rolled up nanotubes, or some hybrid of both? Should it contain just nitrogen and carbon, or a smorgasbord of other elements, too? The answer depends on the specific application.

In 2015 in *Science Advances,* Dai demonstrated that nitrogen-studded nanotubes worked in acid-containing fuel cells, one of the most promising designs for electric vehicles.

Other researchers are playing their own riffs on the carbon concept. To produce graphene's orderly structure requires just the right temperature and specific reaction conditions. Amorphous carbon materials — in which the atoms are randomly clumped together — can be easier to make, Rutgers' He says.

In one experiment, He's team started with liquid phytic acid, a substance made of carbon, oxygen and phosphorus. Microwaving the liquid for less than a minute transformed it into a sooty black powder that she describes as a sticky sort of sand.

"Phytic acid strongly absorbs microwave energy and changes it to heat so fast," she says. The heat rearranges the atoms into a jumbled carbon structure studded with phosphorus atoms. Like the nitrogen atoms in Dai's nanotubes, the phosphorus atoms changed the movement of electric charge through the material and made it catalytically active, He and colleagues reported last year in *ACS Nano*.

The sooty phytic acid–based catalyst could help move along a different form of clean energy: It sped up a reaction that turns a big, hard-to-use molecule found in cellulose — a tough, woody component of plants — into something that can react with other molecules. That product could then be used to make fuel or other chemicals. He is still tweaking the catalyst to make it work better.

He's catalyst particles get mixed into the chemical reaction (and later need to be strained out). These more jumbled carbon structures with nitrogen or phosphorus sprinkled in can work in fuel cells, too — and, she says, they're easier to make than graphene.

Enzyme-inspired energy

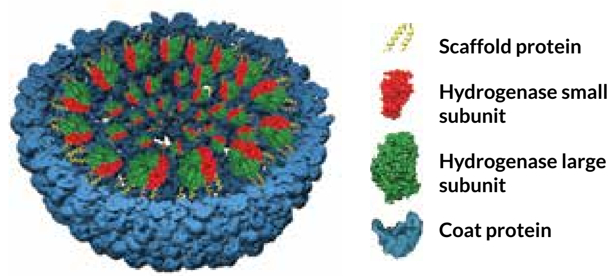
Rather than design new materials from the bottom up, some scientists are repurposing catalysts already used in nature: enzymes. Inside living things, enzymes are involved in everything from copying genetic material to breaking down food and nutrients.

Enzymes have a few advantages as catalysts, says M.G. Finn, a chemist at Georgia Tech. They tend to be very specific for a particular reaction, so they won't waste much energy propelling undesired side reactions. And because they can evolve, enzymes can be tailored to meet different needs.

On their own, enzymes can be too fragile to use in industrial manufacturing, says Trevor Douglas, a chemist at Indiana University in Bloomington. For a solution, his team looked to viruses, which already package enzymes and other proteins inside protective cases.

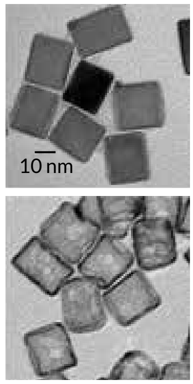
"We can use these compartments to stabilize the enzymes, to protect them from things that might chew them up in the

Taking from nature Scientists have engineered bacteria to pump out biological catalysts called hydrogenase enzymes (red and green) packaged inside protective casings (blue). The packaging could help the fragile enzymes work as catalysts in an industrial setting.



FROM TOP: X. LIU, L. DAI/*NATURE REVIEWS MATERIALS* 2016; P.C. JORDAN *ET AL*/*NATURE CHEMISTRY* 2016 environment," Douglas says. The researchers are engineering bacteria to churn out virus-inspired capsules that can be used as catalysts in a variety of applications.

His team mostly uses enzymes called hydrogenases, but other enzymes can work, too. The researchers put the genetic instructions for making the enzymes and for building a protective coating into *Escherichia coli* bacteria. The bacteria go into production mode, pumping out particles with the hydrogenase enzymes protected inside, Douglas and colleagues reported last year in *Nature*. The protective coating keeps chunky enzymes contained, but lets the molecules they assist get in and out.



Etching out the insides of solid metal cubes (top) leaves nanocage catalysts (bottom) that use less platinum.

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"What we've done is co-opt the biological processes," Douglas says. "All we have to do is grow the bacteria and turn on these genes." Bacteria, he points out, tend to grow quite easily. It's a sustainable system, and one that's easily tailored to different reactions by swapping out one enzyme for another.

The enzyme-containing particles can speed along generation of the hydrogen fuel, he has found. But there are still technical challenges: These catalysts last only a couple of days, and figuring out how to replace them inside a consumer device is hard.

Other scientists are using existing enzymes as templates for catalysts of their own design. The same family of hydrogenase enzymes that Douglas is packaging into capsules can be a launching point for lab-built catalysts that are even more efficient than their natural counterparts.

One of these hydrogenases has an iron core plus an amine — a nitrogen-containing string of atoms — hanging off. Just as the nitrogen worked into Dai's carbon nanotubes affected the way electrons were distributed throughout the material, the amine changes the way the rest of the molecule acts as a catalyst.

Morris Bullock, a researcher at Pacific Northwest National Laboratory in Richland, Wash., is trying to figure out exactly how that interaction plays out. He and colleagues are building catalysts with cheap and abundant metals like iron and nickel at their core, paired with different types of amines. By systematically varying the metal core and the structure and position of the amine, they're testing which combinations work best.

These amine-containing catalysts aren't ready for prime time yet — Bullock's team is focused on understanding how the catalysts work rather than on perfecting them for industry. But the findings provide a springboard for other scientists to push these catalysts toward commercialization.

Sticking with the metals

These new types of catalysts are promising — many of them can speed up reactions almost as well as a traditional platinum catalyst. But even researchers working on platinum alternatives agree that making sustainable and low-cost catalysts isn't always as simple as removing the expensive and rare metals.

"The calculation of sustainability is not completely straightforward," Finn says. Though he works with enzymes in his lab, he says, "a platinum-based catalyst that lasts for years is probably going to be more sustainable than an enzyme that degrades." It might end up being cheaper in the long run, too. That's why researchers working on these alternative catalysts are pushing to make their products more stable and longer-lasting.

It's also why many scientists haven't given up on metal. "I don't think you can say, 'Let's do without metals,' " says James Clark, a chemist at the University of York in England. "Certain metals have a certain functionality that's going to be very hard to replace." But, he adds, there are ways to use metals more efficiently, such as using nanoparticle-sized pieces that have a higher surface area than a flat sheet, or strategically combining small amounts of a rare metal with cheaper, more abundant nickel or iron. Changing the structure of the material on a nanoscale level also can make a difference.

"If you think about a catalyst, it's really the atoms on the surface that participate in the reaction. Those in the bulk may just provide mechanical support or are just wasted," says Younan Xia, a chemist at Georgia Tech. Xia is working on minimizing that waste.

One promising approach is to shape platinum into what Xia dubs "nanocages" — instead of a solid cube of metal, just the edges remain, like a frame.

In one experiment, Xia started with cubes of a different rare metal, palladium. He coated the palladium cubes with a thin layer of platinum just a few atoms thick — a pretty straightforward process. Then, a chemical etched away the palladium inside, leaving a hollow platinum skeleton. Because the palladium is removed from the final product, it can be used again and again. And the nanocage structure leaves less unused metal buried inside than a large flat sheet or a solid cube, Xia reported in 2015 in *Science*.

Since then, Xia's team has been developing more complex shapes for the nanocages. An icosahedron, a ball with 20 triangular faces, worked especially well. The slight disorder to the structure — the atoms don't crystallize quite perfectly — helped make it four times as active as a commercial platinum catalyst. He has made similar cages out of other rare metals like rhodium that could work as catalysts for other reactions.

It'll take more work before any of these new catalysts fully dethrone platinum and other precious metals. But once they do, that'll leave more precious metals to use in places where they can truly shine. ■

Explore more

- Xien Liu and Liming Dai. "Carbon-based metal-free catalysts." *Nature Reviews Materials*. September 13, 2016.