PERSPECTIVES: PHOTOCATALYSIS

Fuel from Photons

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The laws of thermodynamics are as rigid and unforgiving as a California electricity wholesaler: If you want energy, you're going to have to pay for it (shown as L′ in the figure). From a scientific perspective, this simply means that to get energy out of a system, at least that amount of energy will collectively have to be spent. By far the most abundant and, arguably, most environmentally friendly currency at our disposal for paying this cost is sunlight.

Enhanced online at www.sciencemag.org/cgi/content/full/293/5535/1599

It has been estimated that the amount of solar energy reaching Earth's surface every day is more than mankind could use in 30 years (*1*). Nature recognized the wisdom of tapping into this resource billions of years ago, when it came up with the photosynthetic apparatus for converting sunlight into usable chemical and/or mechanical energy. But the scientific community has yet to develop artificial methods for efficient solar energy conversion that can compete, economically or otherwise, with other sources of energy such as fossil fuels and nuclear fission. On page 1639 of this issue, Heyduk and Nocera (*2*) offer a tantalizing glimpse into the possible future of solar energy research—a rough blueprint of how chemists might go about taking a cue from nature in using solar energy to generate a resource that helps solve our energy needs.

The resource in question is molecular hydrogen, H_2. The notion of H_2 as a fuel source has already garnered the attention of the industrial community—witness General Motors' unveiling on 7 August 2001 of their stationary generator based on a hydrogen fuel cell—and plays a key role in the Bush Administration's policy concerning alternative fuels (*3*). Ignoring for the moment the practical problems associated with this particular fuel, a number of fundamental scientific questions arise when considering the production of H_2 on a meaningful scale.

First, one would like to start from a cheap, widely available source of hydrogen ions (H^+) that will eventually be reduced to form H_2. Second, the process should be catalytic so that the production of H_2 will at least have the potential to be cost-effective. And third, one would ideally like to have a substantial degree of control over the process to facilitate a microscopic understanding of the chemistry and provide macroscopic tunability of fuel production.

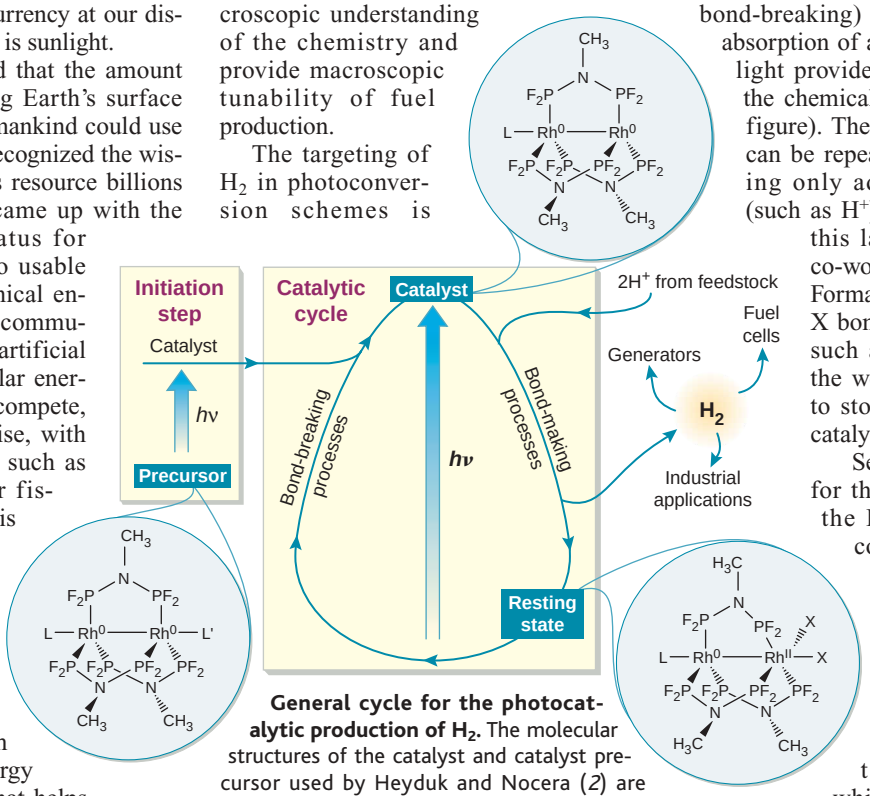
The targeting of H_2 in photoconversion schemes is about as old as the idea of solar energy conversion itself. It was obvious early on that acids provide an almost ideal source for the protons needed. Catalytic production of hydrogen—one of the most important considerations—was achieved more slowly but can now be done under a variety of conditions (*4*). The most successful approaches involve heterogeneous reactions, that is, reactions in which the reactant species are in different phases (such as solid and gas).

This heterogeneous approach has the obvious advantage that it actually works, at least on a relatively small scale, but heterogeneous reactions are notoriously difficult to characterize. In addition, solid-state catalysts tend to be ill-defined and often contain substantial amounts of expensive metals such as Pt. These factors make the heterogeneous route less than desirable. The ideal scenario, from a chemist's point of view, is the use of a molecular catalyst as part of a homogeneous reaction scheme—a tough problem that has yet to be solved.

Heyduk and Nocera now report important progress toward this goal (*2*). The path they take was initially demarcated by Gray and co-workers in the late 1970s, based on the chemistry of a class of dimeric rhodium complexes (*5*). A molecular system for producing H_2 will involve several bond-making and bond-breaking steps. The trick is to design a system in which the processes requiring input of energy (such as bond-breaking) are compensated by the absorption of a photon. In other words, light provides the means for driving the chemical reaction uphill (see the figure). The process is catalytic if it can be repeated many times, requiring only addition of a feedstock (such as H^+) to the reaction. It is in this last stage that Gray and co-workers ran into a problem: Formation of a very stable Rh-X bond (where X is a halogen such as Cl) essentially killed the would-be catalyst and led to stoichiometric (rather than catalytic) production of H_2.

Seizing upon the potential for this class of molecules if the Rh-X termination step could be overcome, Heyduk and Nocera make clever use of the valence states in the dirhodium core of their molecular catalyst. The valency of a metal is simply its formal oxidation state, a means by which chemists keep track of electrons. The reaction $2H^+ \rightarrow H_2$ requires two electrons; a molecular catalyst for the production of H_2 should therefore ideally be able to engage in two-electron processes. But nature has largely cornered the market on multielectron chemistry, and most photochemists live in a one-electron world.

The unique feature of the Heyduk-Nocera catalyst is that it can achieve a two-electron mixed valency; that is, the Rh centers in the molecule can differ by two units of charge. This unusual condition is made possible by the molecular design and is maintained throughout the critical stages of the reaction cycle.



General cycle for the photocatalytic production of H_2. The molecular structures of the catalyst and catalyst precursor used by Heyduk and Nocera (*2*) are shown.

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In their system, the chemistry is initiated after photoexcitation of the catalyst precursor (see the figure). This liberates CO from the coordination sphere of one of the Rh centers, providing the necessary vacancy for the proton source (present as a hydrohalic acid, HX) to bind to the catalyst and leading to the formation of half an equivalent of H_2 in what is likely a thermal process. At this stage, the photochemical cycle begins, with photon absorption producing another vacancy and yielding another 0.5 equivalents of H_2. The absorption of the next photon activates the Rh-X moiety to reform the same species as is produced after the initial loss of CO [see Scheme 2 in (*2*)]. This completes the catalytic cycle.

Heyduk and Nocera provide evidence for catalysis by documenting the production of more than 100 μmol of H_2 from a solution containing less than 1 μmol of the catalyst precursor. The two-electron mixed valency likely plays an important role in facilitating catalytic turnover by helping to maintain the integrity of the catalyst after the Rh-X elimination step. This is the truly novel feature of their system.

To be fair, their success is tempered by certain problems not unlike those faced by Gray and co-workers. As the authors themselves point out, a complete catalytic system would have to be able to handle the other half of the reaction, the halogen (X) from the hydrohalic acid. In the present case, a trap removes X from the cycle, eventually leading to the buildup of an unwanted side product. In addition, the conversion efficiency is very low and the catalyst degrades too readily for long-term practicality.

However, the importance of this work does not lie in the specifics of the catalyst's performance, but rather in the new opportunities it offers. Heyduk and Nocera have taken fundamental ideas of photochemistry and harnessed them to achieve a long sought-after but elusive goal, the molecular-based photocatalytic production of a usable fuel. What the scientific community does along this exciting new path remains to be seen.

References and Notes

1. Information obtained from the Web site at the National Renewal Energy Laboratory, Golden, CO (www.nrel.gov).
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PERSPECTIVES: SURFACE SCIENCE

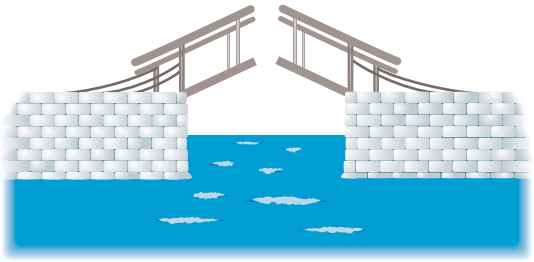
Bridging Gaps and Opening Windows

Nils I. Jaeger

On page 1635 of this issue, Sachs *et al*. (*1*) demonstrate how advanced surface science tools allow a catalyzed chemical reaction to be monitored in situ on the atomic scale while spatiotemporal patterns such as reaction fronts crossing the surface of a catalyst are observed under the same conditions on the micrometer scale. A gap between length scales several orders of magnitude apart is thus bridged. Systems of increasing complexity may be studied by adapting this approach.

The paper is a milestone in the ongoing efforts to observe, analyze, and simulate spatiotemporal patterns that evolve on surfaces in nonlinear chemical reaction systems far from equilibrium. Such patterns play a crucial role in catalytic processes but are difficult to understand in detail because of their complexity.

Because of technical constraints, catalytic phenomena on surfaces were long studied with model reactions on single-crystal surfaces of metals under ultrahigh vacuum conditions. However, application of the acquired knowledge in the rational design of catalysts and the control of catalyst performance under realistic conditions was hampered by the fact that up to 80% of chemical production depends on catalysis at ambient or elevated pressure. Furthermore, "real" catalysts are highly complex systems such as dispersed metals on oxidic supports.



Lowering the bridge. New techniques allow the characterization of spatiotemporal reaction patterns across a range of pressures and length scales, thus bridging the previous gap between operating conditions of real catalysts and model systems accessible to direct observation.

These problems are gradually being overcome as techniques are developed that can operate from ultrahigh vacuum to millibar pressures on complex materials. For example, infrared-visible sum frequency generation (SFG) surface vibrational spectroscopy is capable of operating at elevated pressures. In this method, vibrations in reactant molecules adsorbed on the surface of a catalyst are excited by absorbing energy from overlapping pulses of visible and of tunable infrared light. The generated signal provides almost exclusive information on the state of adsorbed molecules and hence their reactivity across a wide range of pressures (*2*, *3*). The power of the method was recently demonstrated by Dellwig *et al*. (*4*), who studied the dynamics of carbon monoxide adsorbed on palladium clusters deposited on an alumina support at pressures of up to 200 mbar. Structural information was obtained in parallel under ultrahigh vacuum conditions from scanning tunneling microscopy at atomic resolution (*4*).

However, such studies do not provide information on dynamic changes in the structure of the nanometer-sized metal particles, which often play an important role in the activity of real catalysts. In situ structural information on the operating catalyst is therefore needed. Efforts to build the bridge on the high-pressure side of the gap are in progress, for example, with the use of in situ x-ray absorption spectroscopy on the working catalyst (*5*). In situ high-resolution electron microscopy under millibar pressures may be available in the near future.

A detailed understanding of surface reactions and the mechanisms leading to spatiotemporal structures has emerged from such studies (*1*, *4*), opening a window toward rational catalyst design. Ingenious strategies are emerging, such as the microchemical engineering of catalytic reactions (*6*). With microlithograpic techniques, the size and geometry of catalytically active surfaces can be tuned to optimize the interaction of

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