light conditions, but also those grown in the harsher, more-realistic environment of the field. This is a remarkable example of the use of fundamental knowledge of light harvesting and photoprotection to design plant varieties that have much-improved productivity in the field. Moreover, Kromdijk and colleagues' work is proof that the main processes of photosynthesis, such as light harvesting, are essential for plant development, growth and productivity.

This development paves the way for future work aimed at engineering new, highly productive crop varieties that can successfully grow in a wide variety of environments and climatic zones. In broadening the types of land that can be used to grow productive and stress-resilient crops, we can begin to prepare to meet the food demands of the growing worldwide population. ■

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CHEMISTRY

The long and winding road to catalysis

In chemical catalysis, spillover is the process in which hydrogen atoms are made from hydrogen molecules at one site and then added to other atoms or molecules at another. A study reveals details of this effect. SEE LETTER P.68

FRANCISCO ZAERA

Many chemical reactions are not intrinsically viable, but can be promoted with the assistance of solid catalysts. For example, processes involving hydrogen — which are ubiquitous in the chemical industry — require hydrogen molecules (H_2) first to be broken into atoms at a catalytic site. The subsequent addition of these hydrogen atoms to other atoms or molecules, as occurs in hydrogenation reactions, sometimes involves their migration to a different type of catalytic site. On page 68, Karim *et al.*[1] report a clever set of experiments that provides a direct demonstration of this mechanism, known as the spillover effect, in action.

Although the hydrogen–hydrogen bond in H_2 is strong and therefore unlikely to break under normal reaction conditions, it can be easily broken (dissociated) on the surfaces of transition metals such as platinum[2]. But those metals are sometimes ineffective at facilitating hydrogenations, for which a different type of catalyst might be required. It has long been known that H_2 dissociation and hydrogenation reactions can be carried out separately from each other — that is, the catalysts needed for each step can be at different locations in a given solid, or even on different solids, and still promote the overall conversion. This behaviour has been explained in terms of a spillover effect, by which hydrogen atoms formed on platinum nanoparticles migrate through a long, circuitous path along the surface of a catalyst support (typically, an oxide) until they reach the second catalyst[3] (Fig. 1).

There have been several attempts to prove the existence of the spillover effect over the years, but all have provided only indirect evidence for it[4]. For instance, a platinum tip of a scanning tunnelling microscope (STM) has been used in experiments to dissociate H_2 and facilitate the hydrogenation of carbonaceous species deposited on the surface being imaged[5]. Infrared absorption spectra from catalysts made of gold nanoparticles dispersed on a titanium dioxide support indicated that sites at the interface between the gold and the oxide can react with atomic hydrogen produced by H_2 dissociation on the metal[6]. And surface-imaging experiments have suggested that H_2 can be dissociated on isolated palladium sites to promote hydrogenation reactions on copper surfaces[7]. These were all valuable studies, but Karim and colleagues' work might be the most convincing demonstration of spillover yet.

In their experiments, Karim *et al.* used a technique called nanolithography to prepare a series of model catalyst samples, and used spatially resolved X-ray absorption measurements to follow the progress of a reaction in which iron oxide particles were chemically reduced by hydrogen atoms to form metallic

50 Years Ago

Beginning with this issue of *Nature*, most subscribers to this journal in North America will be supplied each week with a copy which has been flown across the Atlantic by air freight and then distributed from New York by surface mail … The increasing pace of change of science, and the urgency of a good many scientific communications, would be in themselves sufficient reason why copies of a weekly journal should not at the beginning of their useful life be incarcerated for two weeks or more in the hold of a ship. But periodicals of all kinds are more than mere providers of information. They serve also to give those who read them something which can properly be called a sense of community … But those who see their periodicals late tend to feel excluded from an experience which others have enjoyed. This, certainly, is why out of date newspapers are so hard to read.
From *Nature* 7 January 1967

100 Years Ago

Readers who have copies, which they may be willing to spare, of advanced text-books, models, specimens, and apparatus for the study of geology are invited to communicate with the British Prisoners of War Book Scheme (Educational) at the Board of Education, Whitehall, S.W.
A request has just reached the committee of that war charity from Ruhleben for about fifty books, etc., to enable the camp school there to establish a general course in dynamic geology and crystallography … Books in almost every subject are urgently needed to meet the steadily increasing demands which are daily being received from British prisoners interned in enemy or neutral countries.
From *Nature* 4 January 1917

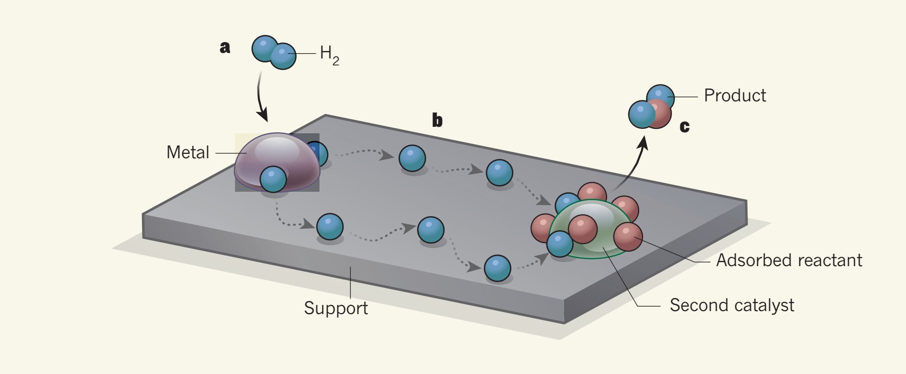

Figure 1 | Mechanism for hydrogenation reactions that involve spillover. Catalytic hydrogenations are reactions of hydrogen gas (H_2) with other atoms or molecules, and sometimes require two catalytic sites on a support. **a**, Gaseous H_2 molecules first adsorb onto a metal nanoparticle. The metal catalyses H_2 dissociation (break-up), forming adsorbed hydrogen atoms. **b**, The hydrogen atoms migrate along the surface of the oxide support (each curved arrow represents a 'step' taken along the surface), until they reach the second catalyst — a process called spillover. **c**, The second catalyst mediates the reaction of the hydrogen atoms with other adsorbed atoms or molecules, yielding the final product. Karim *et al.*[1] have studied spillover in a reaction in which the metal is platinum and the second catalyst is iron oxide. The iron oxide also acts as the reactant in their system; it is reduced to metallic iron and produces water on reaction with hydrogen atoms.

iron. The catalysts consisted of a support — a thin film of either titanium oxide or aluminium oxide — onto which the researchers deposited 15 pairs of nanoparticles. Each pair consisted of a platinum nanoparticle and an iron oxide nanoparticle (30 and 60 nanometres in diameter, respectively) separated by defined distances that ranged from 0 to 45 nm.

The authors then exposed these model catalysts to a hydrogen atmosphere under set conditions (1×10^{-5} millibars, 343 kelvin), and recorded X-ray absorption spectra before and after exposure to determine the degree to which each iron oxide nanoparticle was converted to metallic iron. They observed only slight conversion for systems on aluminium oxide, and only when the platinum and iron oxide nanoparticles were less than 15 nm apart. (Maximum reduction was observed for the pair of nanoparticles that overlapped on aluminium oxide, presumably because no migration of hydrogen atoms between catalysts is needed.)

By contrast, maximum iron oxide reduction occurred for all the iron oxide nanoparticles on titanium oxide, regardless of the distance between the paired particles. The authors also used X-ray absorption to show that, when reactions were performed on titanium oxide, titanium ions in the support are reduced during the process, from Ti^{4+} to Ti^{3+}. Therefore, they concluded that spillover requires the catalyst support to be a reducible oxide.

This better understanding of spillover should aid the design of catalytic hydrogenation processes. It may also help to explain the mechanisms of other important chemical reactions. For example, in the light-induced production of H_2 from water using semiconductor catalysts, the conventional wisdom has been that metal additives catalyse the required reduction of water by trapping excited electrons generated from light absorption. However, my co-workers and I have argued[8] that, instead, the role of the metal is to promote H_2 formation through the recombination of hydrogen atoms produced from the reduction of water at semiconductor sites. Our explanation hinges on the ability of hydrogen atoms to travel from the surface of the semiconductor to the metal — a reverse spillover effect[9]. Karim and colleagues' approach could potentially be adapted to test this hypothesis directly. Their experiments could also be expanded to quantify the kinetics of the spillover effect and to assess its contribution to the rates of many other hydrogenation reactions.

Karim *et al.* end their report with a molecular-level theory to explain why spillover takes place on titanium oxide, but not on aluminium oxide, on the basis of computational modelling. However, that modelling did not provide a direct comparison of the two systems, because it started at different points in the reaction pathway for each of the oxide films. Moreover, the energy diagram derived from their calculations suggests the existence of a viable, low-energy pathway for hydrogen spillover on aluminium oxide, even though this is not observed experimentally. Finally, the authors acknowledge, but do not fully resolve, the role that water may have in the spillover effect, which is crucial in many catalytic systems. These issues should be topics for future work. Nevertheless, Karim and co-workers' study reveals an innovative way to probe spillover, and opens fresh avenues of investigation to better understand and use this effect in catalysis. ■

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SYSTEMS BIOLOGY

Molecular memoirs of a cellular family

A system that introduces random modifications to barcode sequences embedded in cells' DNA allows lineage relationships between cells to be discerned, while preserving the cells' spatial relationships. SEE LETTER P.107

LAUREN E. BECK & ARJUN RAJ

Determining how large, multicellular organisms emerge from a single cell is a major goal for biologists, and a key to understanding many dynamic processes and diseases. A fundamental component of this goal is the mapping of cellular lineages, which is crucial for understanding not only embryonic development, but also processes such as the growth of cancers and stem-cell differentiation. Frieda *et al.*[1] describe a technique on page 107 that uses genetic engineering to embed lineage information in a cell's DNA. The results can then be read out by direct visualization — an advance that stands to transform our ability to build spatio-temporal cell lineages.

One of the landmark achievements in the field of lineage tracing has been the ability to resolve the complete developmental