The Nobel Prize in Chemistry 2007

This year's chemistry laureate **GERHARD ERTL** *has succeeded in providing a detailed description of how chemical reactions take place on surfaces and has in this way laid the foundation of modern surface chemistry. He is awarded the prize for showing how reliable results can be obtained in this area of research.*

From artificial fertilizers to clean exhaust

The most stereotypical image possible of the chemist is probably one where he or she is holding a test tube in which a number of chemicals have been mixed to produce a solution of a new colour. And this is certainly one aspect of what chemistry is about. In general though, much more is needed to understand a chemical reaction. Several of the most important chemical reactions do not even take place in a solution but in completely different states. One specific branch of chemistry is concerned with reactions on solid surfaces and in this field test tubes are not particularly useful. Instead, advanced technical equipment like vacuum chambers, electron microscopes and cleanrooms are needed, combined with an advanced methodology and great precision.

It is neither straightforward nor cheap to investigate how molecules and atoms behave on solid surfaces. So why bother? Simply because surface reactions play such an important role in both the chemical industry and natural systems. Knowledge of surface chemistry can help explain such diverse processes as why iron rusts, how artificial fertilizers are produced, how the catalyst in a car's exhaust pipe works and why the ozone layer is deteriorating (through chemical reactions on the surfaces of ice crystals in the stratosphere). Knowledge about chemical reactions on surfaces will also help us produce renewable fuels more efficiently and create new materials for electronics.

Surface reactions are vital in many processes today
– in catalytic cleaning carbon monoxide oxidates on platinum,
– freons used in air conditioning systems, for instance, reduce the ozone layer by reacting on the surfaces of small ice crystals,
– rusting takes place when an iron surface is exposed to oxygen,
– surface reactions are used in the electronics industry to manufacture semiconductor materials for components,
– artificial fertilizers contain ammonia which is produced when nitrogen and hydrogen react on an iron surface,
– renewable fuels can be produced using catalytic surfaces.

The emergence of modern surface chemistry

Modern surface chemistry started to emerge in the 1960s thanks to vacuum technologies which were developed in the semiconductor industry. This year's Nobel Laureate in Chemistry, Gerhard Ertl, was one of the first to understand the potential of the new technology. He is awarded the Nobel Prize for having laid the methodological foundations for an entire field of research. The great reliability of Ertl's results is due to the meticulous precision in his work combined with an outstanding capacity to refine problems. He has painstakingly and systematically searched for the best experimental techniques to investigate each separate question.

Precisely because surfaces are so very chemically active it is difficult to keep them clean enough to study a specific reaction: this is one of the reasons that precision combined with a high vacuum system is essential for experimental success. In air, any surface is immediately covered by molecules from the gases present. Ertl has displayed a unique understanding of how to make use of different experimental technologies, and whenever possible he has been quick to incorporate new technologies in his palette – always in order to produce as complete a picture as possible of the reaction he has decided to investigate. Besides producing important knowledge about specific reactions, he has above all constructed a methodology that other researchers have been able to apply to completely different surface reactions.

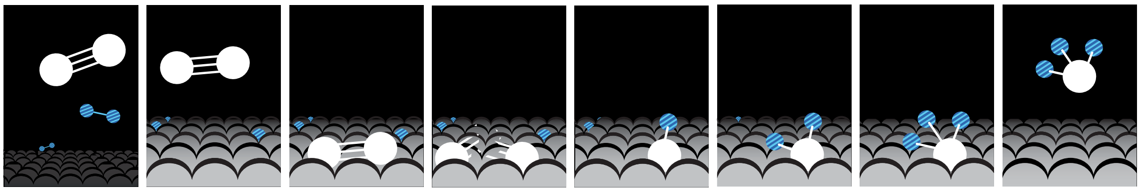
Gerhard Ertl first studied the behaviour of hydrogen on metal surfaces. Hydrogen gas can be produced at one of the electrodes in an electrochemical solar cell, and can then be used in the reverse reaction to generate electricity in a fuel cell – just to mention a couple of cases where the behaviour of hydrogen on solid surfaces is instrumental. There exist many more possible examples. Catalysis is, as we shall soon see, another area where this knowledge is important.

Nitrogen becomes artificial fertilizer

Next Ertl decided to study the Haber-Bosch-process, which is the basic step in the production of artificial fertilizer as it is used to capture nitrogen from air. This reaction is of enormous commercial importance since lack of nitrogen is often what limits crop yields. Lightning strikes and the activity of certain earth bacteria found at the roots of leguminous plants are two of the very few natural mechanisms that can bind nitrogen. For the invention of the Haber-Bosch process as such, Fritz Haber was awarded the Nobel Prize in Chemistry in 1918. Ertl's contribution has been to provide detailed knowledge about how the process works. But above all, his work with the Haber-Bosch process should in this context be regarded as an example of the systematic methodology he has applied to surface chemistry problems. In this way he has established an experimental school of thought for the entire discipline.

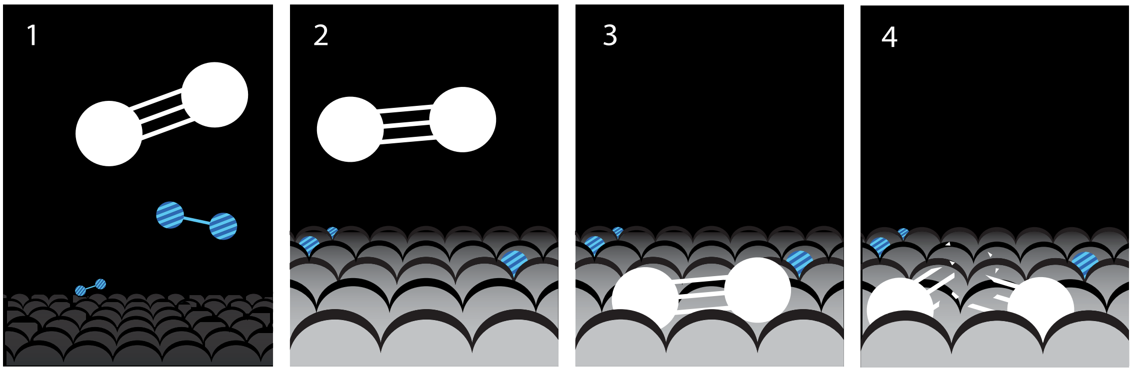
In the Haber-Bosch process, nitrogen – which is an important constituent of ordinary air – reacts with hydrogen to form ammonia. This is the first and most challenging step in the production of artificial fertilizer. It is necessary to use a catalyst for this reaction to take place, and this is where surface chemistry plays a role. The catalyst used in the Haber-Bosch process is finely dispersed iron: the reaction takes place using the surface of the grains of iron as support. Nitrogen and hydrogen both attach to the iron surface: in this manner they react more easily with one another. One of the crucial questions which Ertl addressed is which step in the reaction is the slowest. In order to improve the process as a whole it is the slowest step one needs to speed up – much like traffic in a city, where one slow traffic light may produce a total gridlock.

The Haber-Bosch process step-by-step



In the Haber-Bosch process nitrogen (white) reacts with hyrogen (striped) on an iron surface to then form molecules of ammonia which are released from the surface. This reaction, which extracts nitrogen from air, is an important step in the production of artificial fertilizer.

In order to investigate the Haber-Bosch process, Ertl used an idealised system – a clean and smooth iron surface in a vacuum chamber into which he could introduce well controlled amounts of the different gases. When nitrogen lands on the iron surface, it first attaches as a molecule (1–3) consisting of two nitrogen atoms. The bond between the two nitrogen atoms is among the strongest in chemistry. When the molecule has finally attached itself to the iron surface, the two nitrogen atoms may however release one another and bind to iron instead, although this takes some time (4). One of the first questions Gerhard Ertl posed was whether nitrogen reacts in its molecular or in its atomic form with hydrogen to finally form ammonia. From earlier work Ertl already knew that the hydrogen molecule immediately dissociates and attaches in atomic form on the surface (1–2).



Ertl measured the concentration of nitrogen atoms on the iron surface while simultaneously adding hydrogen to the system. He saw that the more hydrogen he added, the more the concentration of nitrogen atoms on the surface diminished. Ertl's conclusion was that nitrogen atoms on the surface disappear as they react with hydrogen. This shows that the first step in the Haber-Bosch-reaction takes place between hydrogen and atomic nitrogen. If instead the reaction had taken place between hydrogen and molecular nitrogen, atomic nitrogen would still form on the surface but remain unperturbed by the amount of hydrogen added.

Surface measurement difficulties

Measuring the concentration of nitrogen on the iron surface is however by no means simple. To distinguish atomic nitrogen from molecular nitrogen Ertl used different spectroscopic methods. The basis for all these methods is that the surface is bombarded by particles (either light-particles, that is photons, or free electrons). Electrons in the atoms at the surface will be forced to move when they are hit by this stream of particles, much as a billiard ball is set in motion when it is struck by another ball. Either the electrons will be totally removed from the atoms, in which case it is possible to measure their energy directly. Or it is possible to measure the energy indirectly by registering the light which is emitted when the electron, after being hit, quickly returns to its original position. In both cases this measurement will reveal the type of atom that has been struck and something about what the chemical environment of that atom looks like – for instance if it is attached to another atom to form a molecule or if it lies on its own on the surface. The energy of the atoms varies according to these different circumstances.

Another way to investigate the concentration of nitrogen at the surface is to study the structure of the surface itself, because this structure is modified slightly when iron binds to nitrogen. In this case Ertl used a method which involved bombarding the surface with electrons that are scattered in a specific pattern. This pattern reveals the structure of the iron surface.

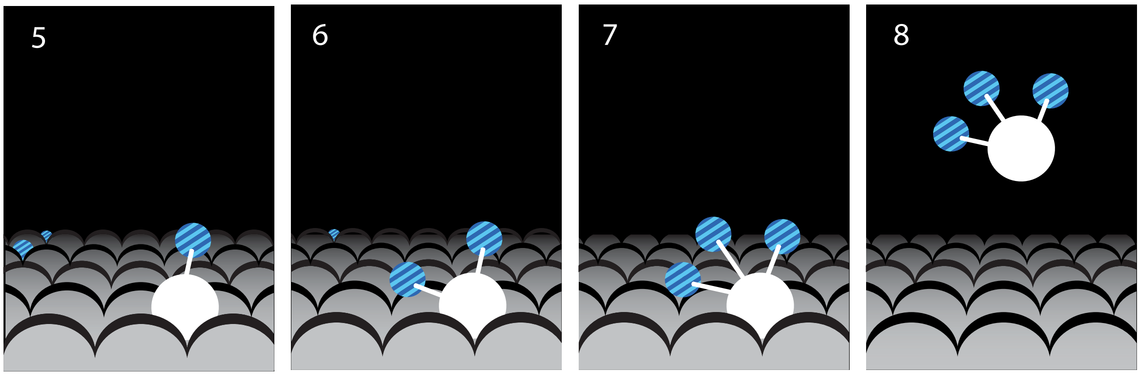
The point of using all these different methods together is that in this type of surface chemistry it is very difficult to be really sure of what one sees. Any minute impurity in the system will immediately attach itself to the surface; it will not be diluted as in a solution. In other words the surface must be investigated in many different ways to make sure that the picture is not distorted by contamination. The signal from each experimental technique will also be very weak because only a single atomic layer at the surface is being observed. In more traditional chemistry the reaction takes place in the whole solution simultaneously, with several "layers" of atoms and molecules that yield much larger signals.

Nitrogen split takes longest

Using different ways of determining which molecules are present at the iron surface during the course of the reaction, Ertl also discovered that the step that limits the rate of the whole Haber-Bosch process is actually the splitting of the nitrogen molecule into its constituent atoms. Once the nitrogen atoms are free from each other they quickly collect enough hydrogen atoms to form ammonia. If one wants to improve the process therefore, this nitrogen split has to be speeded up. It was already known that adding potassium to the catalyst is a way of improving the Haber-Bosch process. Ertl could show not only that the addition of potassium did in fact hasten the reaction but also why.

Whatever one does, however, the splitting of the nitrogen molecules will always be much slower than the other steps of the reaction. This means it is difficult to find any way to study the subsequent steps. Once nitrogen has split up, everything else happens at such a speed that it is impossible to "see" anything at all until ammonia has been formed and leaves the surface.

Bur Ertl did not give up. He wanted to chart the entire reaction and once again he showed both creativity and perseverance in reaching his goal: he realised that he could study the reaction backwards instead. The Haber-Bosch process is a reversible reaction, which means each step looks the same in both directions. The direction of the reaction is governed solely by which gases are pumped into the system, either ammonia or hydrogen plus nitrogen. So Ertl started to study how ammonia attaches to the iron surface, and how it subsequently dissociates step-wise into its building blocks of nitrogen and hydrogen. In this manner he managed to observe the two missing intermediate steps (5 and 6). Adding heavy hydrogen (which in some measurements will give a different signal from ordinary hydrogen) he could measure the speed at which the ammonia molecule releases one of its (ordinary) hydrogen atoms and subsequently collects a new (heavy) hydrogen. In this manner he found a way to study the rate of the final step in the reaction (7).



Ertl's investigation of the Haber-Bosch process offers a typical picture of his experimental methodology. Using a well controlled model system he manages to measure rates and activation energies for each step of the reaction. These values can then be used as a basis for calculating how the reaction proceeds in more realistic applications, using much higher pressures. This is why Ertl's methodology has great importance not only in basic research but also for the modelling of processes in industry.

Exhaust cleaning

Yet another surface reaction which has great practical importance is the oxidation of carbon monoxide on platinum. One important role of the catalyst in the exhaust pipes of cars is to ensure the efficiency of this reaction. Carbon monoxide is toxic and must be converted to carbon dioxide before leaving the exhaust pipe. Ertl has also studied this reaction in great detail. He has shown that the rates of different steps in the reaction will vary over time. Some of the steps oscillate between different rates, and the reaction proceeds differently depending on the coverage of the platinum surface. Sometimes these variations lead to a chaotic course of events: the reaction is therefore not reversible and much more difficult to study than the Haber-Bosch process. Ertl has shown the great complexity of a seemingly simple reaction, where carbon monoxide collects an extra oxygen atom to become carbon dioxide. This illustrates how his methodology also serves to shed light on highly complicated surface reactions.

Recently, Ertl has again chosen to study hydrogen on metal surfaces in order to make use of the new experimental technologies which are constantly emerging. In this way new pieces are gradually incorporated into his experimental methodology to provide an increasingly complete picture of surface reactions.

Illustrations: Typoform

LINKS AND FURTHER READING

More information about this year's prizes, including a scientific background article in English, is to be found at the Royal Swedish Academy of Sciences' website, *www.kva.se* and at *http://nobelprize.org*. You can also see the press conference there as web-TV. Further information about exhibitions and activities concerning the Nobel Prizes is available at *www.nobelmuseum.se*.

Scientific review articles in English

Imbihl, R., Ertl, G. Oscillatory Kinetics in Heterogeneous Catalysis. Chemical Review **1995**(95) 697–733

Ertl, G. Primary Steps in Catalytic Synthesis of Ammonia. Journal of Vacuum Science and Technology **A 1**(2) 1247–1253 (1983)

Scientific review articles in German

Ertl, G. Elementarschritte bei der heterogenen Katalyse. Angewandte Chemie **102**(11) 1258–1266 (1990)

Ertl, G. Elementarprozesse an Gas-Metall-Grenzslächen. Angewandte Chemie **88**(13) 423–433 (1976)

Link

Animation: Oxidation of carbon monoxide on platinum
Fritz-Haber-Institut, Max-Planck-Gesellschaft
www.fhi-berlin.mpg.de/surfimag/arts.htm

THE LAUREATE

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