

The 2007 Nobel Prize in Chemistry



The Chemistry Laureate for 2007 was Gerhard Ertl, an Emeritus Professor and retired director of the Max-Planck Fritz Haber Institute in Berlin. The award recognises his successes in providing detailed descriptions of how chemical reactions take place on surfaces, studies that have laid the foundation of modern surface chemistry. He is awarded the prize for showing how reliable results can be obtained for such chemical processes.

Ertl, a German by birth, gained his PhD in physical chemistry in 1965 from the Technical University in Munich. In 1986 he succeeded Heinz Gerischer as director of the Department of Physical Chemistry of the Haber Institute and was appointed Scientific Fellow. His research focuses on structure and chemical reactions at solid surfaces. He has received more than 60 awards for his work, the latest being the Nobel Prize.

Introduction

Despite the stereotypical image of the chemist holding a test tube in which a number of chemicals have been mixed to produce a new compound, we know that much more information is needed to understand how a chemical reaction actually occurs. The branch of chemistry concerned with reactions on solid surfaces – *surface chemistry* – demands advanced dust-free laboratories and sophisticated electronic instrumentation, coupled with advanced methodology and great precision. It is neither straightforward nor cheap! But surface reactions play such a vital role in both chemical industry and natural systems that they demand to be studied. 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 chemical reactions on the surfaces of ice crystals in the stratosphere are causing the O₃ layer in the atmosphere to deteriorate. Knowledge about chemical reactions on surfaces helps to produce renewable fuels more efficiently and create new materials for electronics.

Surface chemistry: a brief history

Chemical processes at surfaces and interfaces have a long history. One half of the 1912 Nobel Prize was awarded to P. Sabatier for *his method of hydrogenating organic compounds in the presence of finely disintegrated metals whereby the progress of organic chemistry has been greatly advanced in recent years*. It was later realized that the crucial molecular event is the adsorption of H₂ molecules on the metal surface, where they are dissociated into the constituent atoms. Refined, the method remains a standard procedure for hydrogenation of organic molecules. Heterogeneous catalysis was also central to the award of the Nobel Prize to Fritz Haber in 1918 *for the synthesis of ammonia from its elements*. Despite technical improvements, the same basic concept is used in today's process. In 1932 Irving Langmuir was awarded the prize for *discoveries and investigations in surface chemistry*, in which he made a range of seminal contributions relevant

to both heterogeneous catalysis and to processes at the air-water interface.

After Langmuir, there was little progress in the study of chemical processes at surfaces because two major difficulties had to be overcome. Firstly, it was, and still is, notoriously difficult to prepare surfaces of controlled composition and morphology. Secondly, there were few experimental techniques that enabled the direct monitoring of molecular events at the surfaces. Instead, the researcher had to rely on measuring the chemical composition in the gas phase outside the surface. Inferences can be made about molecular surface events from such studies, but the information is uncertain. A transformation of the whole field was triggered by the emergence of semiconductor technology during the 1950s and 60s, when methods for handling surfaces under high vacuum conditions were developed. Furthermore, a number of new methods of studying surfaces under high vacuum conditions emerged. These developments led to the establishment of *surface science*, a research discipline that has attracted scientists with backgrounds in condensed matter physics, physical chemistry and chemical engineering. By the end of the 1960s a number of scientists had come to realize that useful tools for studying molecular processes at surfaces had become available. They hoped that these tools would continue to improve so as to enable really detailed chemical studies of reactions at surfaces to be undertaken.

Precisely because surfaces are so very chemically active, it is difficult to keep them clean enough to study a specific reaction – one of the reasons that precision combined with a high vacuum system is essential for success. In air, any surface is immediately covered by molecules from the gases present. Ertl displayed a unique understanding of how to make use of different experimental technologies, and he incorporated new technologies in his palette in order to produce as complete a picture as possible of the reaction under investigation. Apart from generating important knowledge about specific reactions, he constructed,

above all, a methodology that other researchers have been able to apply to completely different surface reactions. Initially, Ertl studied the behaviour of H₂ on metal surfaces and his studies of fundamental molecular processes at the gas-solid interface were particularly thorough.

When a small molecule hits a solid surface from a gas phase there are two possible outcomes. The molecule may simply bounce back or it can be adsorbed. It is the latter case that raises the most interesting possibilities. The interaction with the atoms of the surface can be so strong that the molecule dissociates into its constituent groups or atoms. The molecule can also react directly with surface groups and change the chemical properties of the surface. A third possibility is that the adsorbed molecule encounters another previously adsorbed one and there is a binary chemical reaction on the surface.

Very important practical situations exist where these scenarios are the key chemical events; heterogeneous catalysis has been central to the chemical industry for more than a century. Since 1913, agriculture has been supplied with fertilizers rich in nitrogen, produced by the Haber-Bosch process in which N₂ gas is converted to NH₃ using an iron-based catalyst. These days, every car has a catalyst system that converts (toxic) CO and hydrocarbons to CO₂ in the exhaust gases; the catalyst also adsorbs the nitrous gases present reducing their quantity in the vehicle's emissions. Currently, large resources are devoted to the development of efficient fuel cells using H₂ as a standard vehicle fuel, where surface reactions between electrodes and H₂ are critical. Corrosion is caused by chemical reactions at surfaces; it is a major problem in everyday life and in sophisticated industrial contexts such as nuclear power plants and aircraft. Damage by corrosion may be reduced by adjusting the composition of the surface so that it is protected by an oxide layer formed in air. Thin semiconductor layers are produced by chemical vapor deposition in large quantities in the microelectronics industry. Chemical processes at surfaces are, therefore, central not only to a wide range of highly significant practical and economic applications of chemistry but also to the basic chemical research needed to unravel the details.

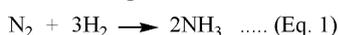
Our theoretical description of chemical reactions conceptually provides the simplest case for the formation of a molecule in the gas phase where the reacting species is affected only by encounter with its reaction partner. However, in most practical applications, reactions occur in more complex environments where the reacting species are constantly exchanging energy and momentum with other neighbouring molecules. For example, in a solution, the environment is disordered and dynamic and any description typically relies on considering the effect of the environment through its average properties. The gas-solid interface provides an example of an environment that is intermediate between the relative simplicity of the gas phase and the molecular complexity of the liquid phase. At the surface of a solid an adsorbed molecule can exchange energy and momentum with the surface material, but in the most ideal cases this support has long-range order. The consequence is that the interaction between molecule and support is much more regular, and this allows both

more precise experiments and more detailed theoretical descriptions. Thus, the study of chemical reactions on surfaces provides one route towards a deeper understanding of reactions in condensed phases in general.

Ertl's contributions to surface chemistry

Sabatier's work left a long-standing question of how H₂ is organized on metals like Pd, Pt and Ni. This question is relevant not only for understanding the hydrogenation of organic molecules, but also how hydrogen gas is used or produced at metal electrodes in many electrochemical processes. By combining experimental studies using low energy electron diffraction (LEED) with measurements of desorption, and also using modeling, Ertl was able to provide a quantitative description of how hydrogen is exposed on the metal surfaces.¹ This was highly relevant to the then current discussion of catalytic mechanisms. Ertl not only gave answers to a number of that had been posed for a long time, but also demonstrated how one could utilize the LEED method in combination with other experimental approaches. The most relevant chemical questions clearly needed more than one method. His approach to science is that when new opportunities appeared he revisits its fundamental problems that he had analyzed previously. Thus, his latest publication on H₂ adsorption on a metal surface concerns the vibrational spectrum.²

The next long-standing and industrially important problem that Ertl attacked concerned the molecular mechanism of the catalytic formation of NH₃ in the Haber-Bosch process (Eq. 1). Ertl's contribution was in providing detailed knowledge about how this process works. But above all, this study provides an example of systematic methodology applied to surface chemistry problems. In this way he has established an experimental school of thought for the entire discipline.



In order to obtain a suitable thermodynamic driving force for the Haber-Bosch process (Eq. 1), industrially it is performed under high pressure. The commonly used catalyst consists of Fe particles with added KOH on a support of alumina and silica. Owing to its economic importance, numerous investigations had been made by the time Ertl initiated his studies in the mid-1970s. Although it was understood from kinetic studies that the rate-limiting step was the chemisorption of N₂, the underlying mechanism and the nature of the reactive species were unclear. Alternative mechanisms had been suggested, based on either atomic or molecular nitrogen, but it was impossible to discriminate between these on the basis of kinetic data alone. Equipped with the tools of surface science Ertl took the opportunity to investigate aspects of the reaction in model systems, however far from the realities of the Haber-Bosch process these seemed.

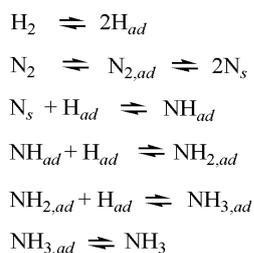
Ertl had previously studied H₂ on metal surfaces and it was straight-forward for him to show that, on the Fe of the Haber-Bosch process, the behavior of N₂ was qualitatively similar.³ He measured the concentration of nitrogen atoms on the iron surface while simultaneously adding *hydrogen* to the system. He saw that as he added more H₂, the concentrations of N-atoms on the surface diminished.

Ertl concluded that nitrogen atoms on the surface disappear as they react with hydrogen molecules. This showed that the first step in the Haber-Bosch-reaction takes place between hydrogen molecules and nitrogen atoms. If the reaction had taken place between molecular hydrogen and molecular nitrogen, atomic nitrogen would still form on the surface, but it would remain unperturbed by the amount of hydrogen added.

In the then current literature, the most controversial issue was whether nitrogen would dissociate on the surface. The N-N triple bond is one of the strongest known and it appeared counterintuitive for interaction with the surface to be sufficiently strong to cleave N₂ into atoms. Ertl showed that atomic nitrogen was, in fact, present on clean iron surfaces,⁴ and he deduced a detailed structural model for the iron-nitrogen structure on the surface.⁵ Moreover, it was possible to characterize the kinetics of the nitrogen adsorption in detail.⁶ The formation of atomic nitrogen occurs with a low activation energy but with a very small pre-exponential factor making the process slow. Ertl also discovered that although the activation energy was different for different crystal planes, the reaction proceeds on all of the three major crystal planes, (111), (110) and (100). Furthermore, the energy barrier increases with increasing surface coverage so that the kinetic difference between the crystal planes decreases.

Initially it was far from obvious that these model studies applied to the molecular events in the industrial Haber-Bosch process. To demonstrate the applicability, Ertl and Thiele⁷ analyzed the surface composition of a commercial catalyst using Auger Electron Spectroscopy (AES). They found that under ambient conditions the surface had a complex composition but, under the reducing conditions of the process, iron and potassium dominate at the surface. Through a characterization of adsorption energies, it was concluded that it is only the adsorbed atomic nitrogen that remains on the surface when the reaction chamber is emptied after a catalytic cycle at high pressures. By using AES to analyze how surface nitrogen coverage varied with H₂ pressure during the reaction, the high-pressure data were shown consistent with those for model measurements at low pressures. Furthermore, there was consistency between the observed rates of the elementary processes and the macroscopically measured kinetics. These studies, bridging what is called the *pressure gap*, were crucial in gaining acceptance of the *surface science approach* to catalysis by a community struggling with the realities of industrial processes involving heterogeneous catalysis.

Scheme 1



Having identified that the dissociation of N₂ into atoms was slow, and having demonstrated that the model systems were relevant for to the Haber-Bosch process, it was

comparatively easy to show that the mechanism was that of Scheme 1. Although this had been suggested previously, Ertl not only confirmed its correctness but also gleaned the energetic details of the individual steps, the later ones starting from NH₃ and monitoring the steps backwards (which is favoured at low pressures). Adsorption of NH₃ on Fe involves an energy gain of < 75 kJ/mol, small enough to ensure complete desorption at typical process conditions (T ≥ 400 °C). According to Scheme 1, the adsorbed NH₃ can dissociate on the surface. The presence of NH₂ could not be quantified spectroscopically but, by co-adsorbing NH₃ and D₂, Ertl was able to infer the dissociation and recombination rates for the reaction:



NH is present in quantities large enough for observation using methods like ultraviolet photoelectron spectroscopy, secondary ion mass spectroscopy, and high resolution electron energy loss spectroscopy.⁸ From these measurements, it then became possible to formulate the mechanism of Scheme 1 in energy terms.⁹

Despite this success, one essential feature of the industrial process remained to be explained. Empirically, it had been found that the presence of K⁺ ions in the catalyst improved the rate of the catalytic cycle. Ertl had found that the potassium remained on the surface of the catalyst under process conditions. Since N₂ cleavage is rate-limiting, the potassium must influence this reaction step. It was then found that in the presence of potassium ions N₂ is adsorbed more readily on the surface and the adsorption energy increases by 10-15 kJ/mol; this is attributable to potassium donating electrons to neighbouring Fe atoms.¹⁰

Ertl's investigations serve as a model of how sophisticated experimental methods can be used to study a phenomenon of the utmost practical relevance. He began by identifying the crucial features of the reaction in the industrial context, demonstrated the relevance of model studies, and then identified a number of elementary steps that became the targets of focused studies. The steps were characterized from structural, energetic, and kinetic points of view using state-of-the-art methodology that involved the use of many different techniques with highly sophisticated equipment. For each question there is, at any given point in time, an optimal method. It is clear that, throughout his career Ertl's ambition has been to use that method.

Ertl not only clarified the molecular events of the Haber-Bosch process, but he also demonstrated what it takes to unravel mechanisms of catalytic processes in general. This has had a lasting influence on the field of heterogeneous catalysis.

In the Haber-Bosch process, the observed macroscopic kinetics of NH₃ production are related to the kinetics of the individual steps of the reaction observed under idealized conditions. For some heterogeneously catalyzed reactions it had been found earlier that the macroscopic kinetics indicated an oscillatory rate, a clear sign of non-linear dynamic behaviour. Challenged by such observations, Ertl also made an in-depth study of another *classical* catalytic reaction - the oxidation of CO by O₂ on Pt. This reaction is

important to the catalytic converter in a car's exhaust system. The crucial questions *What is the mechanism behind the non-linear kinetics?* and *What other phenomena can be inferred in addition to the kinetic oscillations?* led to this reaction illustrating a range of phenomena typical of non-linear kinetic reactions. Ertl showed that the rates of different steps in the reaction vary over time. Some 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 so that the reaction is not reversible and, as a consequence, becomes much more difficult to study than the Haber-Bosch process.

A series of imaginative studies¹¹ led Ertl to the microscopic causes of the observed non-linear behaviour. Again, he demonstrated how the full spectrum of surface physics/chemistry methods can be combined to yield a comprehensive understanding of important and complex catalytic processes. High pressure *in situ* methods, FTIR, and X-ray diffraction gave information on the state of the catalyst itself. These methods are generally much less precise than high vacuum techniques, but they gave invaluable corroborating information and helped close the pressure gap. In the study of sensitive oscillatory reactions on surfaces, the energy input must be controlled and minimized, and this is an added constraint. Thus, the use of AES, although powerful for the Haber-Bosch studies, is not feasible. Instead, low energy methods such as LEED were employed to directly monitor structural changes, and photoemission electron microscopy (PEEM) to monitor the local work function with high spatial resolution. These studies enabled Ertl to demonstrate that his methodology applies not only to systems where the kinetics are dominated by a single rate-limiting step, as for the Haber-Bosch process, but also to systems where non-linear dynamics prevail.

Ertl's lasting contribution to the understanding of surface chemistry

The 2007 Laureate, Gerhard Ertl, was one of the first to understand the potential of the new technology and he laid the methodological foundations for an entire field of research. The great reliability of Ertl's results can be

attributed to his meticulous precision combined with an outstanding capacity to refine problems. He painstakingly and systematically searched for the best experimental techniques to investigate each separate question.

His methodology sets a standard for how chemical processes on surfaces can be studied and elucidated.

References

1. Conrad, H.; Ertl, G.; Latta, E.E. *Surface Sci.* **1974**, *41*, 435; Christmann, K.; Schober, O.; Ertl, G.; Neumann, M. *J. Chem. Phys.* **1974**, *60*, 4528; Christmann K.; Ertl, G.; Pignet, T. *Surface Sci.* **1976**, *54*, 365; Christmann, K.; Behm, R. J.; Ertl, G.; Van Hove, M.A.; Weinberg, W. H. *J. Chem. Phys.* **1979**, *70*, 4168.
2. Badescu, S.C.; Salo, P.; Ala-Nissila, T.; Ying, S. C.; *et al.* *Phys. Rev. Lett.* **2002**, *88*, 136101; Badescu, S.C.; Jacobi, K.; Wang, Y.; Bedürftig, K.; *et al.* *Phys. Rev. B* **2003**, *68*, 205401.
3. Bozso, F.; Ertl, G.; Grunze, M.; Weiss, M. *Appl. Surface Sci.* **1977**, *1*, 103.
4. Bozso, F.; Ertl, G.; Grunze, M. *J. Catalysis* **1977**, *49*, 18; Ertl, G.; Huber, M.; Lee, S.B.; Paál, Z.; Weiss, M. *Appl. Surface Sci.* **1981**, *8*, 373.
5. Imbihl, R.; Behm, R.J.; Ertl, G.; Moritz, W. *Surface Sci.* **1982**, *123*, 129.
6. Ertl, G.; Lee, S.B.; Weiss, M. *Surface Sci.* **1982**, *114*, 515.
7. Ertl, G.; Thiele, N. *Appl. Surface Sci.* **1979**, *3*, 99.
8. Weiss, M.; Ertl, G.; Nitschke, F. *Appl. Surface Sci.* **1979**, *2*, 614; Drechsler, M.; Hoinkes, H.; Kaarmann, H.; Wilsch, H.; Ertl, G. *Appl. Surface Sci.* **1979**, *3*, 217.
9. Ertl, G. *J. Vac. Sci. Tech.* **1983**, *A1*, 1247.
10. Ertl, G.; Weiss, M.; Lee, S.B. *Chem. Phys. Lett.* **1979**, *60*, 391.
11. Behm, R.J.; Thiel, P.A.; Norton, P.R.; Ertl, G. *J. Chem. Phys.* **1983**, *78*, 7437; Cox, M.P.; Ertl, G.; Imbihl, R. *Phys. Rev. Lett.* **1985**, *54*, 1725; Imbihl, R.; Cox, M.P.; Ertl, G.; Mueller, H.; Brenig, W. *J. Chem. Phys.* **1985**, *83*, 1578; Imbihl, R.; Cox, M.P.; Ertl, G. *J. Chem. Phys.* **1986**, *84*, 3519; Eiswirth, M.; Moller, P.; Wetzl, K.; Imbihl, R.; Ertl, G. *J. Chem. Phys.* **1989**, *90*, 510; Jakubith, S.; Rotermund, H.H.; Engel, W.; von Oertzen, A.; Ertl, G. *Phys. Rev. Lett.* **1990**, *65*, 3013; Kim, M.; Bertram, M.; Pollmann, M.; von Oertzen, A.; *et al.* *Science* **2001**, *292*, 1357; Beta, C.; Moula, M.G.; Mikhailov, A.S.; Rotermund, H.H.; Ertl, G. *Phys. Rev. Lett.* **2004**, *93*, 188302.

Compiled by Brian Halton and Peter Hodder from material freely available from the Nobel Foundation. Further details may be obtained from: <http://nobelprize.org>

Chemistry Behind the News

Drugs and Toys

Two children being admitted to hospital caused a popular children's toy to be pulled from shop shelves. They became ill from swallowing beads that were part of the toy.

The toy is a craft kit made up of multicoloured beads that when sprayed with water, stick to each other so they can be used to make pictures and other items.

1,5-pentanediol is used in the toys' manufacture, but it appeared this had been substituted with 1,4-butanediol.

In the liver, 1,4-butanediol (C₄H₁₀O₂) is broken down by alcohol dehydrogenase and aldehyde dehydrogenase into metabolic products including gamma-hydroxybutyr-

ate (GHB). GHB is abused as a recreational drug. It is also found naturally in the brain where it is thought to be a neuromodulator. GHB also seems to affect dopamine levels in the brain.

1,4-butanediol is mostly used in the manufacture of polyurethanes such as surface coatings, foam and adhesives.

The chemical that was meant to be used in manufacture was pentamethylene glycol or 1,5-pentanediol (OHCH₂(CH₂)₃CH₂OH). It is a water miscible liquid that is used as a hydraulic fluid as well as in the manufacture of polyester and polyurethane resins.