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Scientific Background on the Nobel Prize in Chemistry 2007

Chemical Processes on Solid Surfaces

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Introduction

The Nobel Prize in chemistry for 2007 is awarded to Gerhard Ertl for his thorough studies of fundamental molecular processes at the gas-solid interface. When a small molecule hits a solid surface from a gas phase there are a number of possible outcomes. The molecule may simply either bounce back or be adsorbed. It is the latter case that carries the most interesting possibilities. The interaction with the atoms of the surface can be so strong that the molecule dissociates into 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.

There are very important practical situations where these scenarios are the key chemical events. Heterogeneous catalysis has been a central process in the chemical industry for a century. The agriculture of the world has been supplied with fertilizers rich in nitrogen since 1913 due to the Haber-Bosch process, where the nitrogen of the air is converted to ammonia using an iron-based catalyst. Today every car produced has a catalyst system that converts carbon monoxide and hydrocarbons to carbon dioxide in the exhaust gases. Also the content of nitrous gases is reduced through the action of the catalyst. Thin semiconductor layers are produced by chemical vapor deposition (CVD) in large quantities in the microelectronics industry. Currently large resources are devoted to the development of efficient fuel cells that would enable the use of hydrogen as a standard vehicle fuel. Corrosion, which is caused by chemical reactions at surfaces, is a major problem both in everyday life and in more sophisticated industrial contexts such as in nuclear power plants and airplanes. 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. It is clear that chemical processes at surfaces play a central role in wide span of economically highly significant applications of chemical knowledge to the solution of practical problems.

The study of chemical processes at surfaces also plays a significant role from the perspective of basic chemical research. In our theoretical description of chemical reactions the formation of a molecule in the gas phase provides the conceptually most simple case. Here it is possible to consider a reacting species affected only by the encounter with the reaction partner. However, in most applications of practical importance reactions occur in more complex environments, where the reacting species are constantly exchanging energy and momentum with other neighboring molecules. In a solution the environment is disordered and dynamic. In the description of such systems one typically has to rely on considering the effect of the environment through its average properties. The gas-solid interfaces provide one 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 support, but in the most ideal cases the support has long-range order. The consequence is that the interaction between molecule and support is much more regular, which allows for more precise experiments and more detailed theoretical descriptions. Thus one can see the study of chemical reactions on surfaces as one route towards a deeper understanding of reactions in condensed phases in general.

Background

Due to its major importance in chemistry the study of chemical processes at surfaces and interfaces has a long history. In 1912 P. Sabatier was awarded one half of the Nobel Prize 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 in this method is the adsorption of hydrogen molecules on the metal surface, where it is dissociated into the constituent hydrogen atoms. The method, properly refined, still remains today a standard procedure for hydrogenation of organic molecules. Heterogeneous catalysis was also the central process behind the award of the Nobel Prize to F. Haber “for the synthesis of ammonia from its elements”. Even though technical improvements have been made, the same basic concept is used in the modern version of the process. In 1932 the chemistry prize was awarded to I. Langmuir “for his discoveries and investigations in surface chemistry”. Langmuir made a range of seminal contributions relevant to both heterogeneous catalysis and to processes at the air-water interface. His name is associated in the literature with the “Langmuir adsorption isotherm”, “the Langmuir through” and the “Langmuir-Hinshelwood scheme” for heterogeneous catalytic reactions. Since 1932 there has been no Nobel Prize in chemistry that specifically addresses the field of chemical processes on surfaces. In 1956, however, it was awarded to C.N. Hinshelwood and N.N. Semenov “for their research into the mechanisms of chemical reactions” and in 1986 the prize was given to D.R. Herschbach, Y.T. Lee and J.C. Polanyi “for their contributions concerning the dynamics of chemical elementary processes”. These latter prizes concern fundamental aspects of chemical reactions primarily occurring in the gas phase.

Following Langmuir’s work there was for some time a lack of seminal progress in the study of chemical processes at surfaces. There were two major difficulties to overcome. It was, and still is, notoriously difficult to prepare surfaces of controlled composition and morphology. Additionally, there was a lack of experimental techniques to enable the direct monitoring of the molecular events at the surfaces. Instead one usually relied 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 there emerged a number of new methods of studying surfaces under high vacuum conditions. This led to the establishment of a scientific area called “surface science”, which attracted scientists with a background in disciplines like 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 were available. It was further hoped that these tools would continue to improve to enable really detailed chemical studies.

Ertl’s contributions.

Since the work of Sabatier there was a longstanding question of how hydrogen is organized on metals like palladium, platinum and nickel. The question is relevant not only for understanding the hydrogenation of organic molecules but hydrogen gas is

also used or produced at metal electrodes in many electrochemical processes. By combining experimental studies using LEED (for explanations of acronyms see end of reference list) with measurements of desorption and also using modeling Ertl was able to provide a quantitative description of how hydrogen is exposed on these metal surfaces (Conrad et al., 1974; Christmann et al. 1974; Christmann et al. 1976; Christmann et al. 1979). This was a highly relevant issue for the current discussion of catalytic mechanisms. In the studies of hydrogen adsorption Ertl not only gave a number of answers to questions that had been posed for a long time, but he also demonstrated how one could utilize the LEED method in combination with other experimental approaches. In order to answer the most relevant chemical questions it was clearly insufficient to concentrate on one method only. It is a feature of Ertl's approach to science that when new opportunities appeared he would revisit fundamental problems that he had analyzed previously. Thus his latest publication on the hydrogen adsorption on a metal surface concerns the vibrational spectrum (Badescu et al. 2002; Badescu et al. 2003). The figure illustrates the organization of a monolayer of hydrogen atoms on a Pt(111) surface.

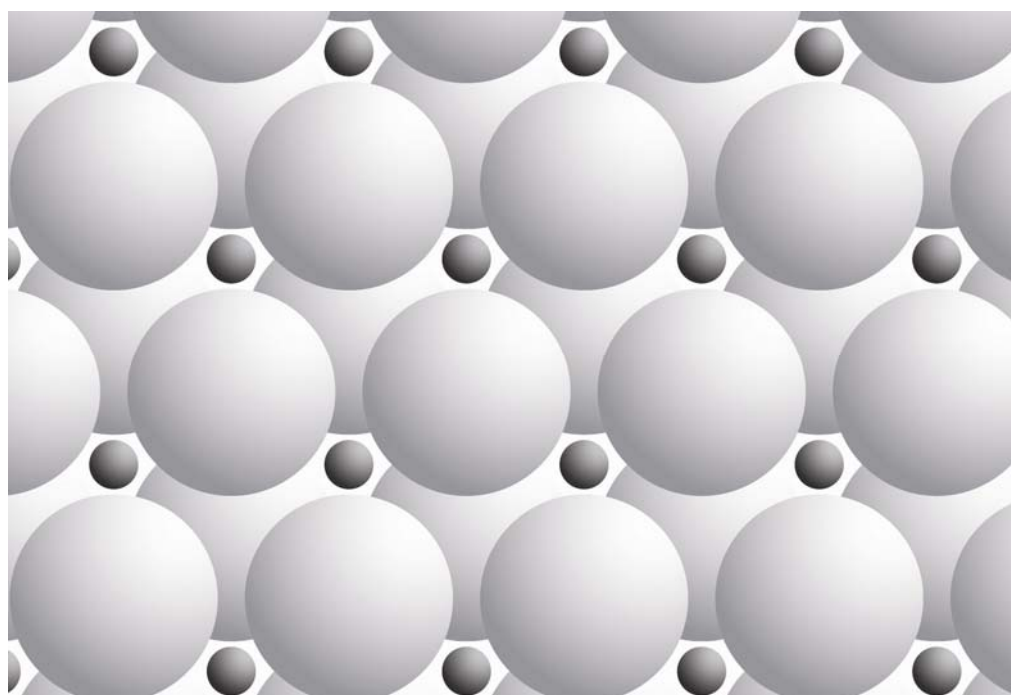
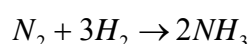


Illustration of how the hydrogen atoms, small spheres, are organized in a monolayer on a (111) platinum surface. (Adapted from Badescu et al. 2003)

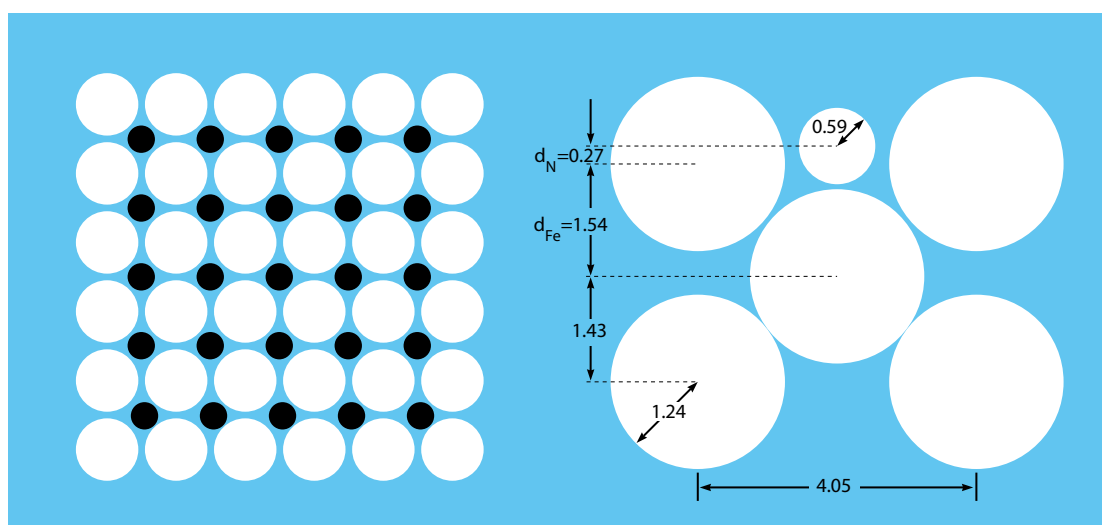
The next long-standing problem that Ertl attacked concerned the molecular mechanism of the catalytic reaction in the Haber-Bosch process. In the net reaction



nitrogen molecules react with hydrogen molecules to form ammonia. To obtain a suitable thermodynamic driving force for the reaction the industrial process is designed to occur with the reactants at high pressure. The commonly used catalyst consists of iron particles with added potassium hydroxide on a support of alumina and silica. Due to its economic importance this reaction had been the subject of numerous investigations by the mid 1970s when Ertl initiated his studies. Although it was

understood from kinetic studies that the rate-limiting step of the process was the chemisorption of nitrogen, the underlying mechanism was unclear, and even the nature of the reactive species. Alternative reaction mechanisms had been suggested, based on either atomic or molecular nitrogen, and it was clear that it was not possible to discriminate between these on the basis of kinetic data alone. Equipped with the tools of surface science Ertl had the opportunity to investigate aspects of the reaction in model systems. However, these would seemingly be very far from the realities of the Haber-Bosch process.

In accordance with the Langmuir-Hinshelwood scheme the first steps of the reaction would involve the adsorption of the hydrogen and nitrogen molecules on the surface. Ertl had previously studied hydrogen on metal surfaces and it was straightforward to show that on iron the behavior was qualitatively similar (Bozso et al 1977a). In the current literature the most controversial issue was whether nitrogen would dissociate or not on the surface. The triple bond of the nitrogen molecule is one of the strongest bonds known and it appeared counterintuitive that the interaction with the surface atoms could possibly be strong enough to cleave the nitrogen molecule into its constituent atoms. Even if it were energetically possible, one would expect high energy-barriers for the cleavage. Using photoelectron spectroscopy Ertl could demonstrate the presence of atomic nitrogen on clean iron surfaces (Bozso et al. 1977b; Ertl et al. 1981) and it was possible to deduce a detailed structural model for the iron-nitrogen structure on the surface (Imbihl et al. 1982).

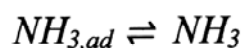
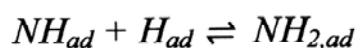
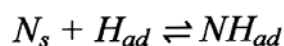
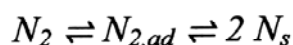
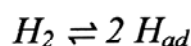


Structure of an overlayer of nitrogen atoms (small filled circles) on a (100) surface of iron (large open circles). Left: top view; right: side view. (Adapted from Imbihl et al. 1982)

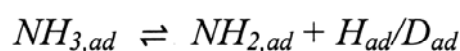
It was, moreover, possible to characterize in detail the kinetics of the nitrogen adsorption (Ertl et al. 1982). The formation of atomic nitrogen occurs initially with a low activation energy but with a very small prefactor making the process slow. Ertl also found that the activation energy was different for different crystal planes, but in such a way that the reaction could anyway proceed on all three major crystal planes (111), (110) and (100). Furthermore with increasing surface coverage the barrier increases in such a way that the kinetic difference between the crystal planes decreases.

It was far from obvious that the studies of model surfaces had a clear applicability to the molecular events in the industrial Haber-Bosch process. To demonstrate this Ertl (Ertl and Thiele, 1979) analyzed, using AES, the surface composition of a commercial catalyst. They found that at ambient conditions the surface had a complex composition but at the reducing conditions of the process iron and potassium dominate at the surface. Through a characterization of adsorption energies Ertl could also conclude 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 the surface nitrogen coverage varied with hydrogen pressure during the reaction he was able to demonstrate that the high-pressure data were consistent with those found for model measurements at low pressures. Furthermore there was a 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 for establishing acceptance of the “surface science” approach to catalysis among the community struggling with the realities of industrial processes involving heterogeneous catalysis.

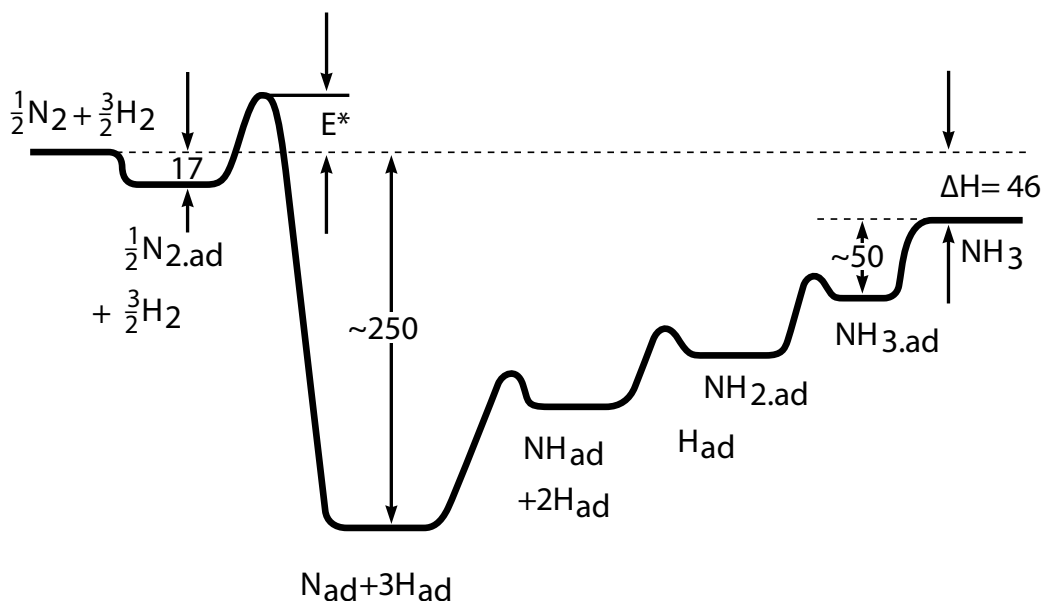
Having identified the dissociated nitrogen atoms, determined that the formation of this species was slow and demonstrated that the model systems were relevant for the conditions of the Haber-Bosch process it was straightforward to establish the reaction mechanism:



This reaction mechanism was one of those suggested previously, but Ertl did not only show to its correctness but he was also able to provide details of the energetics of the individual steps. To obtain information on the later steps in the reaction Ertl chose to start from ammonia and monitor the steps in the “backward” direction, which is favored at low pressures. Ammonia adsorbs on iron with an energy gain of less than 75kJ/mol which is small enough to ensure complete desorption at typical process conditions (temperature $\geq 400^\circ\text{C}$). According to the reaction scheme the adsorbed ammonia can dissociate on the surface. The presence of the state NH_2 could not be quantified by spectroscopic methods, but instead by co-adsorbing NH_3 and D_2 Ertl could infer dissociation and recombination rates for the reaction



NH_3 , on the other hand, occurs in large enough quantities to be observable using a number of different methods like UPS, SIMS, HREELS (Weiss et al. 1979; Drechsler et al.1979). Thus the reaction mechanism as shown above could be formulated also in energy diagram as shown below (Ertl 1983)



An energy diagram showing the progression of the reaction from the reactants N_2 and H_2 to the product NH_3 . Energies are given in units of kJ/mol. (Adapted from Ertl 1983)

Although the figure illustrates the reaction in quite some detail, one essential feature of the industrial process remained to be explained. Empirically it had been found that the presence of potassium ions in the catalyst improved the rate of the catalytic cycle. Ertl had also found that the potassium remained on the surface of the catalyst under process conditions. So why does potassium act as a promoter of the reaction? Since the cleaving of the nitrogen molecule is the rate-limiting step in the process, the potassium has to affect this step in order to enhance the rate. It was found that in the presence of potassium the nitrogen molecules adsorbed more readily on the surface and that the adsorption energy increased by 10 to 15 kJ/mol. The effect was attributed to the fact that potassium would donate electrons to neighboring iron atoms (Ertl et al. 1979).

Ertl's investigations of the reactions in the Haber-Bosch process serve as a model of how sophisticated experimental methods can be used to study a phenomenon of utmost practical relevance. He started by identifying the crucial features of the reaction in the industrial context. He then demonstrated how, and in what way, studies of model systems were relevant for the understanding of the more complex practical situation. He then isolated a number of elementary steps that were targets of focused studies. These steps were characterized both from a structural, an energetic and a kinetic point of view using state-of-the-art methodology. This involves the use of many different methods with highly sophisticated equipment. For each question there is, at any given time, an optimal method and it is clear that throughout Ertl's ambition has been to use that method.

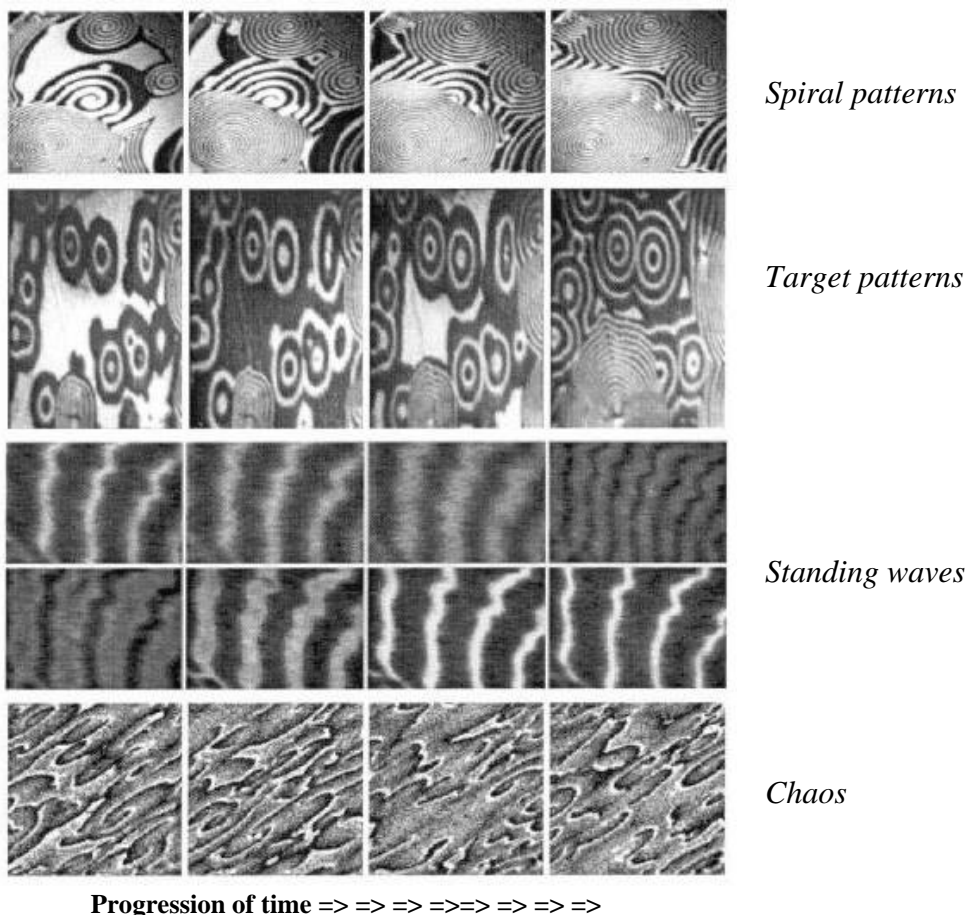
Ertl not only clarified the molecular events of the Haber-Bosch process, but he also demonstrated what it takes to unravel mechanisms of a catalytic process in general. This has had a lasting influence on the field of heterogeneous catalysis.

In the Haber-Bosch process it turned out to be possible to relate the observed macroscopic kinetics of ammonia production with the kinetics of the individual steps

of the reaction as observed under idealized conditions. For some heterogeneously catalyzed reactions it was found at an early stage that the macroscopic kinetics indicated an oscillatory reaction rate. This was a clear sign of non-linear dynamic behavior. Such phenomena have been much studied for chemical reactions in bulk and in 1977 I. Prigogine was awarded the Nobel Prize “for his contributions to non-equilibrium thermodynamics, particularly the theory of dissipative structures”. Challenged by observations of oscillatory rates Ertl chose to make an in-depth study of another “classical” catalytic reaction; the oxidation of carbon monoxide by oxygen on platinum. The crucial questions were: What is the molecular mechanism behind the non-linear kinetics? What other phenomena can be inferred in addition to the kinetic oscillations? It turned out that the system can be used to illustrate a range of phenomena typical of systems with non-linear kinetics.

Through a series of imaginative studies (Behm et al,1983; Cox et al. 1985; Imbihl et al. 1985; Imbihl et al. 1986; Eiswirth et al 1989;Jakubith et al. 1990; Kim et al. 2001; Beta et al. 2004) Ertl could establish the microscopic causes of the observed non-linear behavior. Again, Ertl demonstrated how the full spectrum of methods of surface physics and surface chemistry could be combined to yield comprehensive understanding of important and complex catalytic processes. High pressure *in-situ* methods include work function measurements that can be used to study changes in adsorbate coverage, FTIR that gives information on adsorbate-surface interaction and X-ray diffraction that yields information on the state of the catalyst itself. These methods are generally much less precise than high vacuum techniques, but they yield invaluable corroborating information to help close the pressure gap. In the study of sensitive oscillatory reactions on surfaces, the energy input must be controlled and minimized, and this is a further constraint. The use of AES that proved such a powerful tool in the studies of the Haber-Bosch process is, for example, not feasible. Instead, low energy methods must be employed, such as LEED that directly monitors structural changes and PEEM that that monitors the local work function with high spatial resolution.

For the oxidation of CO on Pt, there are several mechanisms operating but the most spectacular effects were caused by a surface reconstruction. For the bare metal surfaces (100) and (110) there is a reconstruction to reduce the surface strain. However, CO adsorbs more readily on the unmodified surface and at a certain coverage the difference in adsorption energy is sufficient to cause a reversal of the surface reconstruction. Now oxygen is also more chemisorbed on the reverted surfaces. Then the rate of the catalytic process increases leading to a lower coverage and a possibility for a surface reconstruction. This can in addition to an oscillatory kinetics also lead to a spatial organization on the surface with domains rich in CO and O₂, respectively. Illustrations of adsorption patterns observed by PEEM are shown in the illustrations below.



Platinum surface imaged by photoemission electron microscopy. Dark areas are rich in CO while light areas are O₂ rich. Note the oscillatory behavior of the domain extensions. Time scale ~10s, length scale ~0.1mm (The Surface Imaging Group, Dept. of Physical Chemistry, Fritz-Haber-Institute of the Max-Planck-Society, www.fhi-berlin.mpg.de/surfimag)

Through these studies Ertl has demonstrated that his methodology is applicable not only to systems where the kinetics are dominated by a single rate-limiting step as is the case in the Haber-Bosch process, but also to systems where non-linear dynamics prevail. His methodology sets a standard for how chemical processes on surfaces can be studied and elucidated.

Concluding remarks

Ertl has developed a general methodology that can be applied to the important problems in molecular surface science. He has applied the methodology to some of the most central previously unanswered questions concerning molecules on surfaces. The investigations have been carried out with the greatest elegance in the experimental approach. His work is characterized by the ambition to always use the method best suited to solve the problem at hand. Ertl is never satisfied with an isolated interesting observation. Instead the studies are brought to their logical conclusions. Through his accurate studies he has provided a firm basis for our thinking about molecular processes at surfaces.

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Acronyms used in the text:

AES	Auger Electron Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
HREELS	High Resolution Electron Energy Loss Spectroscopy
LEED	Low Energy Electron Diffraction
PEEM	PhotoEmission Electron Microscopy
SIMS	Secondary Ion Mass Spectroscopy
UPS	Ultraviolet Photoelectron Spectroscopy

Illustrations: Typoform