

Molecular Mechanism of Heterogeneous Catalysis

The 2007 Nobel Prize in Chemistry

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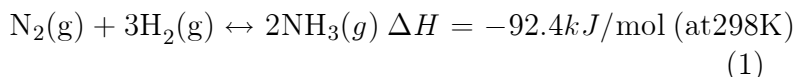
and Physical Chemistry, working with Prof. K L Sebastian. Her research interests include theoretical study of resonance energy transfer involving various donor-acceptor systems.

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Gerhard Ertl, the German physical chemist, was awarded the Nobel Prize in chemistry for the year 2007, for his contributions in the area of surface science. His painstaking work led to a microscopic understanding of heterogeneous catalysis in industrially important chemical reactions. These include the Haber–Bosch process for the production of ammonia, and the catalytic oxidation of carbon monoxide.

1. Introduction

Ammonia is an important chemical as it is used in the production of fertilizers and other chemicals. It is manufactured by the reaction of nitrogen with hydrogen. This has the advantage that nitrogen is very readily available, as it constitutes 78.1% of air. Further, the reaction between nitrogen and hydrogen,



is exothermic, and hence one might have expected it to occur easily, once you mix the two gases at room temperature. However, on mixing, the reaction does not occur at all, as the activation energy for the reaction is very large. The reason for the high activation energy is that the first step of the reaction is the breaking of the bond between the two nitrogen atoms. As it is a triple bond, this step needs a lot of energy, as a result of which the activation energy for the first step in the reaction is very large. Thus, even at the high temperature of 500°C , the reaction occurs with very low yield. As there is net reduction in volume when ammonia is formed (see

Keywords

2007 Chemistry Nobel Prize, heterogeneous catalysis, surface science experiments.



(1)), one expects high pressure to favor the formation of ammonia. In spite of this, at a temperature of 500°C and a pressure of 250 atmospheres, the yield is still low.

A breakthrough in the synthesis was made in 1909, when Fritz Haber, a German chemist, synthesized ammonia using the reaction represented by equation (1). He realized that the reaction occurs at appreciable rates, under conditions mentioned above, if a porous iron catalyst, prepared by reducing the iron oxide magnetite (Fe_3O_4) is used. In 1910 Carl Bosch, used this for the industrial production of ammonia. Using this process, ammonia was manufactured in Germany during the first World War, which was then used to produce the much needed ammonium nitrate, for use in explosives. At that time, all the natural sources of nitrate were under British control and if Haber had not developed the process, the course of history would have been very different! Haber and Bosch were awarded the Nobel Prize, for their work, in the years 1918 and 1931, respectively.

The iron catalyst is in the solid state, and the reaction occurs on its surface, where the two gases, nitrogen and hydrogen get adsorbed and then react. This reaction is an example of heterogeneous catalysis, a process of catalysis wherein the reactants and the catalyst are in different phases of matter. The reaction, even though commercialized, requires rather high temperature and pressure and it still remains a dream to have a catalyst which would work at lower temperatures and pressures. Osmium is a better catalyst, but has the disadvantage of being more expensive, and hence is not used for industrial production. It is interesting that bacteria called rhizobia can convert nitrogen into ammonia and then other compounds. The mechanism of this is not understood and is a very active area of research [1]. In order to develop a better catalyst for industrial production, it is necessary to have a clear understanding of the mechanism of the reaction, viz., the various steps involved in



Fritz Haber, who was responsible for demonstrating that ammonia can be produced using an iron catalyst, and later together with Bosch, pioneered its industrial production. He was awarded the Nobel Prize in chemistry for the year 1918.



Carl Bosch, who was awarded the Nobel Prize in chemistry for the year 1931 for pioneering the industrial production of ammonia.

Processes occurring on surfaces are very difficult to study both experimentally and theoretically, which led Fermi to exclaim: “God made the bulk but the Devil created the surface”.

the process, and how the catalyst works. In spite of the obvious importance of this reaction, such microscopic details remained unknown for a very long time. The reason was that processes occurring on surfaces were very difficult to study both experimentally and theoretically. In fact, the Nobel Prize winning physicist, Enrico Fermi, is reputed to have said: “*God made the bulk but the Devil created the surface*”.

2. A Bird’s Eye View of Ertl’s Contributions

The 2007 Chemistry Nobel Prize was awarded to Gerhard Ertl working at the Fritz Haber Institute in Berlin, for his studies which led to an understanding of the microscopic steps in the catalytic formation of ammonia as well as other important surface catalyzed processes [2]. He utilized very powerful experimental techniques to obtain a complete picture of the molecular processes involved in such catalytic reactions.

Surfaces are capable of catalyzing many chemical reactions. An understanding of any such catalytic process on a surface has far-reaching implications in both academic research and in the industrial development of chemical processes. For instance, the exhaust of motor vehicles contains highly toxic gases. Particularly undesirable is carbon monoxide (CO), which has to be removed from the exhaust before it is released into the atmosphere. The obvious procedure would be to oxidize it to carbon dioxide CO₂ and Pt was known to catalyze the oxidation. Ertl studied this reaction in detail and found the elementary steps involved in the process [3]. His work also focussed on the generation of artificial fertilizers and the study of reactions in fuel cells which occur on electrode surfaces. His other significant contributions include an understanding of the mechanism of formation of rust on an iron surface, the reasons for the depletion of ozone layer and how one could devise methods to prevent the depletion.



3. Surface Science Experiments

Surface science experiments are very difficult to perform. The reason is that surfaces easily get contaminated by the atmospheric gases. For example, each atom on a surface exposed to a pressure of 1 atm is struck about 10^8 times in one second. Even when the pressure is reduced to 10^{-4} Pa, each surface atom is hit 10 times in one second, which again gets contaminated very rapidly. Therefore, to study a chemical reaction happening on a surface, one has to keep the surface in almost near vacuum conditions. The conditions used involve pressures lower than about 10^{-7} Pa or 100 nPa ($\sim 10^{-9}$ Torr) and are known as ultra high vacuum (UHV) [4]. The techniques for generation of UHV became available only in the 1950s and 60s. UHV requires the use of special materials in creating the vacuum system, extreme cleanliness to maintain the vacuum system, and baking the entire system to remove water and other trace gases that are accumulated. At such low pressures the mean free path of a gas molecule is approximately 40 km. So the gas molecules will collide with the chamber walls many times before colliding with each other. Almost all the interactions therefore take place on various surfaces in the chamber. The experimental signatures of layers of adsorbed atoms and molecules are rather weak. Therefore, investigation of a particular chemical reaction on a surface needs a careful choice of experimental techniques. Ertl was among the pioneers in probing monolayers of atoms and molecules on pure surfaces. He made use of a variety of elegant techniques for this purpose. This included Low Energy Electron Diffraction (LEED), photoelectron spectroscopy, Infra red spectroscopy, work function measurements, and a variety of other techniques [5]. LEED gives us information on the patterns that adsorbates form on the surfaces. Adsorbate-surface interactions are probed by Fourier Transform Infrared Spectroscopy (FTIR). Adsorbate coverage can be quanti-

Surface science experiments are very difficult to perform.



fied by work function measurements. Another elegant technique is the Scanning Tunneling Microscopy (STM), which can be used to probe the atomic locations and the local electronic structure on a surface, and to manipulate atoms on surfaces. Ertl is very unique, in that he cleverly used all these techniques to get a complete picture of industrially relevant processes occurring on surfaces [6]. As a result of the systematic investigations he was able to give answers to certain fundamental questions in surface science that were unanswered for decades.

4. Catalytic Production of Ammonia

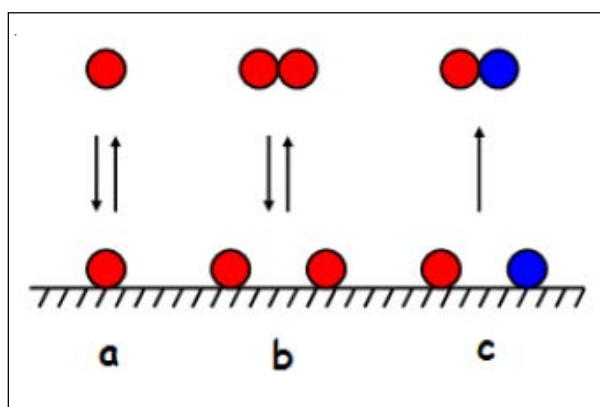
When a molecular species approaches a surface, it can undergo several processes near the surface. It may just bind to the surface by van der Waals interactions, a process that is known as physisorption. Alternatively, it may form chemical bonds with the surface atoms, leading to chemisorption. Sometimes a molecule may undergo dissociation at the surface and the constituent fragments form chemical bonds with the surface. If one of the fragments finds a suitable adsorbed species nearby, it may then react with such a species on the surface and form new products, which leave the surface in a process known as desorption. These possibilities are schematically shown in *Figure 1*.

Figure 1. Possible processes that atoms/molecules can undergo near a surface:

a. An atom is adsorbed onto a surface.

b. A molecule gets dissociatively chemisorbed onto the surface.

c. Two chemisorbed atoms on the surface undergo a reaction, form a new product which finally desorbs from the surface.



In the production of ammonia, nitrogen and hydrogen molecules get adsorbed on the surface of the iron catalyst that is used. Then they react easily as a result of staying in proximity with each other. The reaction occurs in several steps. The bottleneck in such a process is the slowest step. It determines the overall speed of the process and hence is known as the rate determining step. If one can devise a methodology for speeding up the slowest step of the reaction, the rate of the reaction can be increased.

Ertl used a clean iron surface in a vacuum chamber and introduced nitrogen and hydrogen gases into the chamber. It was already known that the hydrogen molecule immediately dissociates into its constituent atoms on attaching to the surface. But, it was unlikely that the nitrogen molecule with very strong triple bond would dissociate into nitrogen atoms and form bonds with iron. So, an interesting question that Ertl asked was whether hydrogen reacts with the atomic form of nitrogen or its molecular form leading to the formation of ammonia. So, the first task at hand was to distinguish between the atomic and molecular nitrogen on the iron surface. When a surface is bombarded with photons of appropriate energy, they can knock off the electrons in the atoms which are present on the surface. The kinetic energies of the electrons that are knocked off can be measured, and the technique is known as photoelectron spectroscopy [7]. From the experimental data, it is possible to understand the chemical environment of the atom to which the electron belongs. It is possible to distinguish if the atom exists on its own on the surface or is part of another molecule that is adsorbed onto the surface. Thus one can find the concentration of nitrogen atoms on the iron surface. In an experiment, during the process of adding the hydrogen to the system, the concentration of nitrogen atoms was monitored. If the reaction was with molecular nitrogen, the concentration of nitrogen atoms

Photoelectron spectroscopy can be used to investigate whether nitrogen exists on the surface as atoms or as molecules.

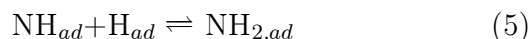
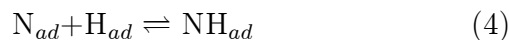
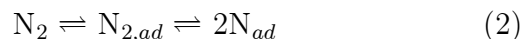


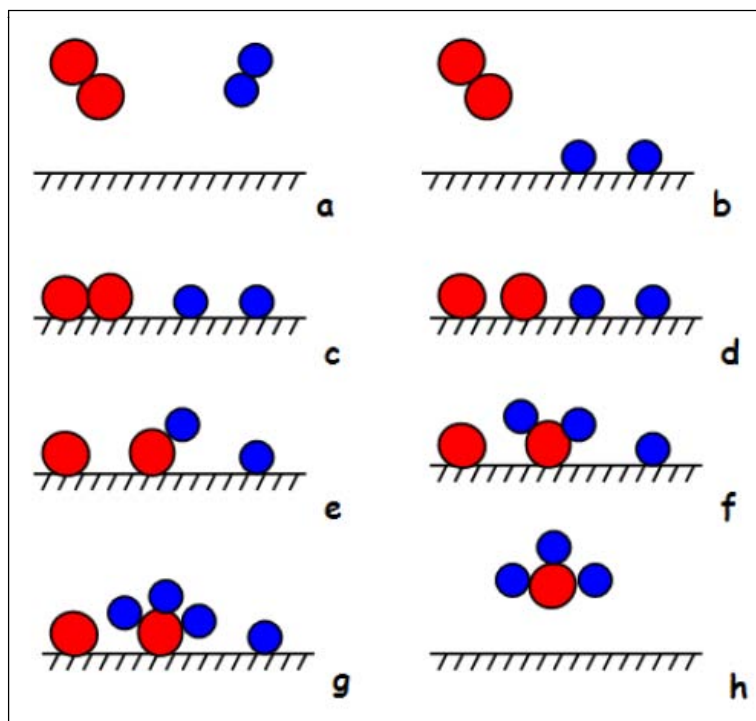
Ertl then concluded that the three hydrogens actually add up one by one to the nitrogen to generate ammonia.

should not change as one adds hydrogen gas. But, a decrease in the concentration of the nitrogen atoms was observed confirming that the reaction is actually between dissociated hydrogen atoms and nitrogen atoms. So, the slowest step of the reaction is the dissociation of nitrogen molecule into its constituent atoms.

After confirming that the reaction is between the hydrogen and nitrogen atoms adsorbed on the surface, the next step was to understand the reactions leading to the formation of ammonia from these atoms. But, once the slowest step (dissociation of nitrogen molecule into its atoms) occurred, the other steps were very fast. Hence it was not possible to study the other steps, with the time resolution of the techniques available. Here again, Ertl reasoned that as the reaction is reversible, one could start with ammonia and try to look at its dissociation on the surface. The idea worked quite well and he could study the dissociation process and he measured the rates at which the ammonia molecule releases its hydrogen atoms. NH_2 as such could not be identified spectroscopically. But, by letting NH_3 and D_2 on the iron surface, he could observe hydrogen atoms on the surface indicating the dissociation of NH_3 . The presence of NH was confirmed by several spectroscopic techniques like ultraviolet photoelectron spectroscopy (UPS), secondary ion mass spectrometry (SIMS), high resolution electron energy loss spectroscopy (HREELS). He then concluded that the three hydrogens actually add up one by one to the nitrogen to generate ammonia.

Thus, the Haber-Bosch process occurs in several steps, given below:





The first step is the adsorption of nitrogen and hydrogen molecules onto the iron surface. Nitrogen at first physisorbs as a molecule, and then dissociates into atoms, which remain chemisorbed on the surface. On the other hand, hydrogen molecule chemisorbs dissociatively, to give hydrogen atoms on the surface. The chemisorbed nitrogen atom then immediately picks up three hydrogen atoms, *one by one* leading to the formation of ammonia. Finally the ammonia molecule desorbs from the surface. The whole process is shown in *Figure 2* and the corresponding energetics of the process is shown in *Figure 3*. Thus, he developed a complete picture of the catalytic formation of ammonia, one of the most important industrial chemical processes.

Attempts were made to speed up the slowest step, viz., the dissociation of N_2 into atomic nitrogen. It was found that the addition of potassium to the catalyst actually

Figure 2. Steps involved in the Haber–Bosch process (the red balls denote the nitrogen atoms and the blue ones, the hydrogen atoms): a. N_2 and H_2 approach the iron surface.

b. H_2 undergoes dissociative chemisorption leading to hydrogen atoms on the surface.

c. N_2 gets physisorbed onto the surface.

d. N_2 undergoes dissociation on the surface and the nitrogen atoms bind to the iron atoms.

e. Atomic nitrogen picks up a hydrogen atom on the surface forming NH .

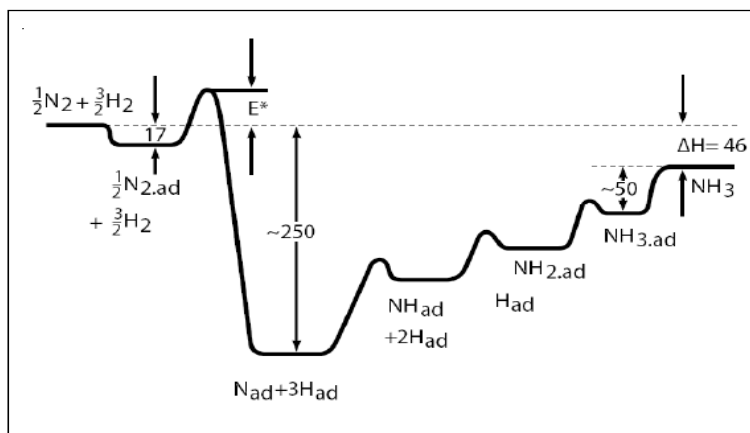
f. NH combines with another H atom forming NH_2 .

g. NH_2 picks up another hydrogen atom to form NH_3 .

h. Ammonia desorbs from the iron surface.

Figure 3. Energetics of the steps involved in the Haber-Bosch process. The energies are given in kJ/mol. Note that the first step is the physisorption of nitrogen, and that this is not activated. The next step is the dissociation of nitrogen into two nitrogen atoms, which are chemisorbed on the surface. E^* is the activation energy for this step. Overall value of ΔH under the conditions of the synthesis is -46 kJ/mol.

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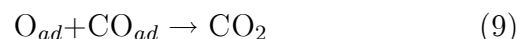
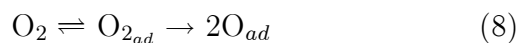


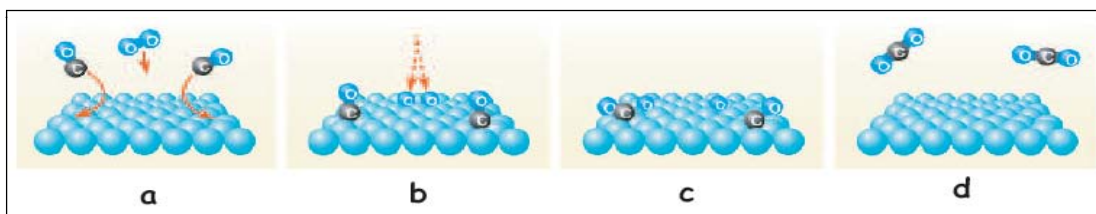
increases the rate of this process. But, the mechanism was not understood. Ertl came up with an explanation as to why potassium speeds up the reaction. The adsorption energies of nitrogen on an iron surface with and without the potassium were measured and the adsorption energy was found to increase by 10 – 15 kJ/mol on adding potassium [8]. Therefore, the reaction occurred faster in the presence of potassium. Further, potassium donates electrons to the neighboring iron atoms thereby leading to the facile dissociation of the nitrogen molecule. Thus potassium acts as a promoter for the catalytic reaction.

Ertl demonstrated unambiguously that the reaction involves atomic nitrogen adsorbed on the surface of iron and the slowest step in the process is the formation of chemisorbed atomic nitrogen by the dissociation of molecular nitrogen.

5. Catalytic Oxidation of CO to CO₂

Ertl's research was always concerned with the understanding of fundamental science. Around 1980, Ertl became interested in the oxidation of CO to CO₂. The reaction is catalyzed by platinum. The oxidation of carbon monoxide to carbon dioxide occurs in presence of a platinum catalyst via the following elementary steps [3]:





The CO molecule first chemisorbs onto the metal surface. Oxygen molecule undergoes dissociative chemisorption on the surface. The chemisorbed oxygen atoms combine with CO molecule on the surface, leading to the formation of carbon dioxide, which then desorbs. A schematic of the process is shown in *Figure 4*.

When Ertl started working on it, it was already known that the rate of catalytic oxidation of CO on a platinum surface was not constant, but oscillated as a function of time. Ertl placed the reactants in UHV with a single crystal of platinum. He observed that the arrangement of atoms on the surface changes to accommodate the CO molecules that are adsorbed on it. This reconstruction of the surface in turn increases the amount of oxygen that can be adsorbed on the surface, as a result of which the rate of the reaction increases. As CO is consumed in the reaction, the coverage of CO eventually drops, and the surface goes back to its original structure, and the rate of oxidation decreases. This cycle repeats, leading to the oscillatory behavior of the rate.

The analysis of Ertl led to the conclusion that certain regions of the surface would be covered mainly by CO while other regions would be covered by oxygen. To verify this, Ertl redesigned a photoemission electron microscope so as to obtain images of the surface, with sub-micron resolution. The images showed dark and light regions, corresponding to CO and oxygen rich areas. Further, these regions were quite organized and formed traveling waves on the two dimensional surfaces. Although such non-linear waves were well known in solution, it was the first time that they were observed on

Figure 4. The process of catalytic conversion of carbon monoxide to carbon dioxide.

a. Carbon monoxide and oxygen molecules approach the metal surface.

b. Both the molecules chemisorb onto the surface.

c. Oxygen molecule undergoes dissociation and the chemisorbed oxygen atoms interact with carbon monoxide.

d. Carbon dioxide is formed and then gets desorbed from the metal surface.

The figure is reproduced with permission from Prof. Ertl's home page.





Gerhard Ertl, Professor at the Fritz Haber Institute in Berlin.

Ertl thoroughly investigated the complex kinetics involved in the catalytic oxidation of CO on the surface of Pt, and showed that it leads to a variety of non-linear phenomena, like oscillations, spiral waves, and chaotic patterns.

a surface. Several non-linear phenomena like [9] rotating spirals and chaotic patterns, which were known in other contexts, in areas like behavior of weather, formation of galaxies, and the dynamics of the heart were observed on the surface, as a result of this reaction. (A beautiful video of these patterns accompanied by music composed by Philip Mayers is available for download [10]) The work of Ertl led to a very detailed understanding of the mechanism of oscillations, a long standing puzzle in the area.

6. Brief Biographical Sketch of Ertl

Ertl was born in 1936, at Bad Cannstadt, a part of the German city Stuttgart. As a boy he had a keen interest in science, and grew up taking radios apart, performing chemical reactions in his bedroom, and playing the piano, his great love. He switched over to physics, when his mother objected to the smells that always were coming out of the bedroom! At the University he was a student of physics and at that time supported himself by joining a band that played at weddings and dance halls. He joined the Technical University of Munich as a doctoral student in 1962. His adviser was Heinz Gerisher, a well known physical chemist. Ertl apparently asked him in which field he should work and Gerisher told him that the whole field of air-solid interface has not yet been studied and that anything that one could do in the area would be fascinating. Ertl started working in the area, and was soon hooked.

In 1968, at the young age of 32, Ertl became a professor at the University of Hannover. He attracted a large number of excellent students - the students, on their part were very dedicated to him, so that when he moved to Ludwig Maximilians University in Munich in 1973, all the ten members of his group moved with him. In 1986, Ertl moved to the Fritz Haber Institute as the Director of the Department of Physical Chemistry, and again his



group of 30 moved with him! He retired from this position in 2004, and is presently an Emeritus Professor at the same Institute.

In 1974, Ertl listened to a talk by Paul Emmett, one of the great men of catalysis, and in that talk, Emmett pointed out that the mechanism of ammonia synthesis was not known. Inspired by the talk, Ertl decided to work on the problem, and soon it became his life long passion. He established the mechanism after long years of hard work. It was a time at which newer and newer techniques were being introduced in the field of surface science, and whenever he was able to set up a new tool, Ertl would take a new look at the problems that he had studied earlier, particularly, ammonia synthesis. This is typical of Ertl, who always wanted to have perfect understanding of all the phenomena, and his investigations always stood the test of time.

The Nobel Committee focused on Ertl's contributions to uncovering the mechanism of catalytic reactions. Another scientist, who has made important contributions to the area of surface science is Gabor Somorjai of the University of California, Berkeley. It was expected that Ertl and Somorjai together would win the Nobel Prize in the area of surface science. In fact, the 1998 Wolf prize in chemistry was awarded jointly to Ertl and Somorjai. On October 10, 2007, which was Ertl's 75th birthday, he was informed by the Nobel Committee that he had won the prize. The last time that the prize was given in the area of surface science was in the year 1932, when it was won by the American physical chemist, Irving Langmuir.

7. Final Remarks

The winning of the Nobel Prize by Ertl was not because of a chance discovery or luck. He started working on an area, which was totally unexplored at the time

The problems that Ertl worked on were the most important in the field, unsolved for a long time, of great industrial importance, and he worked very hard to understand the fundamental scientific aspects of the problem.



he got into it. The problems that he worked on were the most important in the field, unsolved for a long time, of great industrial importance, and he worked very hard to understand the fundamental scientific aspects of the problem. He pursued them with the characteristic German thoroughness and tenacity, using the best techniques, even redesigning his equipment so as to look at one particular aspect of the problem. It is for this painstaking effort to understand the science behind industrially important surface chemical processes that Ertl was awarded the Nobel Prize for chemistry in 2007.

Suggested Reading

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- [2] For more information on the prize announcement and related information, log on to www.nobelprize.org.
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- [10] <http://www.fhhi-berlin.mpg.de/surfimag/arts.htm>
A video named “On Platinum”, composed by P Mayers showing the variety of patterns that are formed on the Pt surface may be downloaded from here.

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