The 2007 Nobel Prize in Chemistry for Surface Chemistry: Understanding Nanoscale Phenomena at Surfaces

Michael Bowker*

School of Chemistry, Cardiff University, Cardiff CF10 3AT, U.K.

ABSTRACT The 2007 Nobel Prize in Chemistry was awarded to Gerhard Ertl for his seminal work in the area of surface science, particularly at the gas–solid interface. Although Ertl began his career at a time when the term "nanotechnology" was not yet known, his contributions to the field have paved the way for many future scientists in this area and led to a deeper understanding of catalysis and other surface-specific processes at the nanoscale. Here, we summarize the scientific developments that guided early progress in surface science, and we explore the major advancements in Ertl's career, including his work on adsorption and oxidation of small molecules on metal surfaces. Significant contributions of other key scientists to this rich area are also presented.

Gerhard Ertl was awarded the 2007 Nobel Prize in Chemistry on October 10th;[1] this was, coincidentally, his birthday! The citations for this award include the following: "for groundbreaking studies in surface chemistry", "for his thorough studies of fundamental molecular processes at the gas−solid interface", and "for having laid the methodological foundations for an entire field of research".

This Nobel Prize was in recognition of major contributions to the development of the field of surface science, significant advances in which began around the mid-1960s, about the time that Ertl began in the field. His work has mainly focused on the adsorption of simple molecules such as CO and N_2 on well-defined surfaces and the relationship of the related surface structures/energetics to industrial-scale reactions, including ammonia synthesis and the removal of pollutants from car exhaust. Before going into this in detail, let us first define this field of surface science and briefly describe its evolution.

DEFINITION AND DEVELOPMENT OF SURFACE SCIENCE

In the context of this Nobel Prize, "surface science" is defined as the field concerned with the understanding of the nature of surfaces (physical and electronic structure) and of the interaction between gas-phase molecules and surfaces. This is rather a limited definition, since surfaces exist in a wide variety of environments; this point will be expanded further below.

There are several phases to the development of surface science, which we can arbitrarily define as follows:

(i) The Nobel Prize in Physics in 1937 was awarded to Davisson and Thomson and was arguably the first awarded for an achievement in surface science.[2] The award was nominally given for achievements in the field of electron diffraction; Davisson and his colleague Lester Germer were the first to obtain diffraction pattern data from a crystalline surface (in the 1920s),[3] which led to the publication of low-energy electron diffraction (LEED) patterns, a technique that is now in routine operation in hundreds (possibly thousands) of laboratories around the world. Their sample was an accidentally created, non-polycrystalline Ni on a Ni foil, which was being treated in a reasonably good vacuum system.

(ii) The development of ultra-high-vacuum (UHV) conditions was an essential step in the evolution of surface science. In turn, the two essential developments necessary to achieve UHV were (1) good pumping systems and (2) the recognition of the crucial importance of "bake-out" for removal of residual water contamination. The latter enabled pressures to be reduced from a minimum of $\sim 10^{-8}$ mbar to the $10^{-10}-10^{-11}$ mbar region, which is vital for study of *clean* surfaces. If the surface under study is a transition metal, then many of the background molecules in the system (*e.g.*, H_2, CO) adsorb on the surface with high efficiency (the so-called "sticking probability" is ~ 1). This in turn means that, since the collision rate with each atom at the surface is $\sim 1\ s^{-1}$ at 10^{-6} mbar pressure, it is

*Address correspondence to bowkerm@cardiff.ac.uk.

10.1021/nn700356g CCC: $37.00

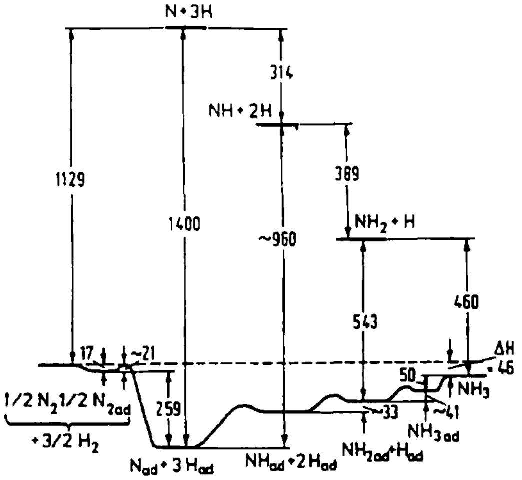

Figure 1. Potential energy profile for ammonia synthesis on iron catalysts from surface science data. Reprinted with permission from ref 16. Copyright 1983 American Institute of Physics.

only under UHV conditions that the surface can remain clean for a sufficient period of time to enable proper study. In this period (up until the early 1970s), most work was carried out in equipment built of Pyrex glass, and so glassblowers were an integral part of a research laboratory in this field. Much research in the 1950s was carried out on films, but significant advances were made in the understanding of *crystalline* surfaces by the inventions and application of the field emission microscope (FEM) and field ion microscope (FIM) by Erwin Müller in the 1930s, 1940s, and 1950s; this was the first true atomic-resolution microscope in use.[4,5] Work using the FIM was extended to adatom mobility studies by Gert Ehrlich and Robert Gomer from the 1950s into the 1970s.[6,7]

(iii) From the mid-1960s, stainless steel vacuum chambers began to dominate the field, and the invention of the knife-edge/copper gasket seal method ensured its wide adoption. This also enabled the much wider range of instrumentation that developed throughout the following period to be applied to surface studies. This began with retarding field analyzers, which enabled structural (LEED) and chemical (Auger electron spectroscopy) analyses of surfaces. The work in this period was based upon the use of very well-defined surfaces of known surface morphology, usually single crystals of metals with surfaces of known orientation. This has continued to the present day, though the range of materials investigated has expanded enormously.

ERTL'S WORK

In the context of the above developments in surface science, Ertl recognized the importance of this approach and set out to develop and exploit the new technology in the mid-1960s. He began his work in surface science at the Technical University in Munich, and his first papers concerned the kinetics of adsorption on Ge single crystals and the early use of LEED for Cu oxide structure determination.[8,9] He went on to be a Professor at the University of Hannover (1968–1973) and Ludwig Maximilians University, Munich (1973–1986), before joining the Fritz Haber Institute of the Max Planck Society in Berlin as Director of Physical Chemistry, succeeding Heinz Gerischer. The following describes the two main bodies of work for which Ertl was cited, though he has been, and still is, involved in a number of other developments in surface science and surface reactivity.

Nitrogen Adsorption on Iron and Its Relationship to Ammonia Synthesis. Ertl focused significant efforts into the study of the adsorption of simple molecules on Fe single crystals, and especially on those of relevance to ammonia synthesis (N_2, H_2, NH_3); his first publication in this field was in 1976; the work proceeded into the 1980s and was carried out in Munich.[10–16] He adsorbed N_2 on Fe and used Auger electron spectroscopy to determine the adsorption rate and extract energy barriers for the reaction.[10] As a result, a complete energy scheme for the reaction was described (Figure 1),[16] which showed the pathway for ammonia synthesis at the surface. Subsequently, others carried out molecular modeling of the synthetic reaction pathway using Ertl's scheme as input, an important aspect of which was a net zero activation barrier to dissociative nitrogen chemisorption. Nørskov and co-workers reported that calculations based on the potential scheme accurately predict industrial ammonia synthesis rates,[17–19] though this was challenged and explored by myself and co-workers;[20–23] an important aspect of the reaction is that dissociative nitrogen chemisorption presents a significant activation barrier that is rate-determining. Nevertheless, most of this pathway was correctly described by Ertl; he established the positive role of alkali promoters in the reaction[24,25] and identified the strong dependence of nitrogen dissociation on surface structure, with open surfaces being the most active (Figure 2).[26] Somorjai and co-workers at the University of California at Berkeley also found a similar structure dependence for the ammonia synthesis rate itself at high pressure (Figure 2).[27]

It seems very appropriate that Ertl went on to the Fritz Haber Institute, named after the founder of industrial ammonia synthesis and winner of the Nobel Prize in Chemistry for that work in 1918.[28]

CO Oxidation on Platinum Group Metals. One of the most significant pieces of work in this field was by Engel and Ertl, who carried out molecular beam studies on CO oxidation on Pd(111).[29–37] An important aspect of this reaction is the fact that there is light-off of the reaction at a particular temperature, giving a relatively sharp rise in rate, followed by a maximum, which then declines at

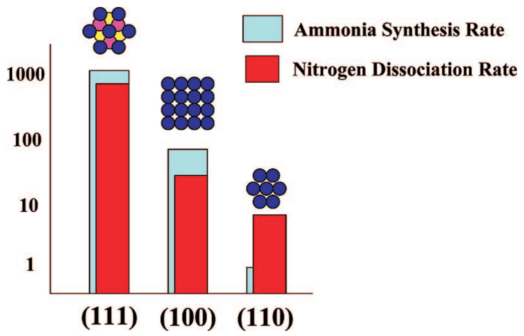

Figure 2. Adapted plot of the relative rates for nitrogen dissociation[15] and ammonia synthesis at high pressure,[16] showing the structure dependence for low Miller index surfaces.

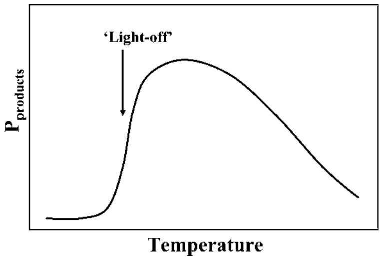

Figure 3. Schematic diagram of light-off as seen for CO oxidation on platinum group metals.

higher temperatures (Figure 3). Ertl showed clearly that this effect was due to poisoning of the surface sites by adsorbed CO, so that product creation begins once significant desorption of CO occurs, and once *both* adsorbed CO and adsorbed O atoms are present on the surface, a Langmuir–Hinshelwood-type reaction (Nobel Prizes in Chemistry in 1932[38] and 1956,[39] respectively) is the dominating process. He extended the work to a number of different surface planes and different metals. However, it quickly became clear to Ertl and his colleagues that the reaction was even more complicated than initially imagined. The reaction exhibits "spatio-temporal" variations in rate.[40] Simple oscillations and, also, more chaotic oscillations in the reaction rate could be identified. Most startlingly, he used the technique of photoelectron–electron microscopy (PEEM, invented by Brüche in the 1930s,[41] but much improved at the Fritz Haber Institute itself) to display this spatio-temporal variation visually (Figure 4). This demonstrated the beauty and complexity of nature at the molecular and atomic levels and showed that reactions could take place in waves propagating on the surface, a two-dimensional analogue to the Belousov–Zhabotinsky reaction.[42] Depending upon the exact conditions, the length of these waves could be in the nanoscale range.

OTHER KEY FIGURES IN THE FIELD AND IMPORTANT NEW CONCEPTS

No major subject like this develops through one person alone, and a number of others have contributed significantly. Here we highlight the work of two other surface scientists, though a number of others could also be cited, in terms of their contributions to new concepts in surface science. Several important ideas were developed in the middle period of surface science, especially in the 1970s and 1980s. These include the following:

Structure Sensitivity of Reactivity. Besides the work of Ertl on Fe described above, Somorjai used single crystals of different orientations to show that structure strongly affects selectivity of hydrocarbon reactions,[43] while David King (then of the University of Liverpool, now at the University of Cambridge and the UK Chief Scientific Adviser) showed that nitrogen dissociation on W surfaces was greatly enhanced by the presence of steps there.[44,45] In fact, the general description of this reactivity pattern is that surface coordination dictates activity; the lower the average surface coordination, the higher the reactivity of the surface. Surface reactivity is actually somewhat more complex than that, but this general description remains a useful starting point for understanding the trends.

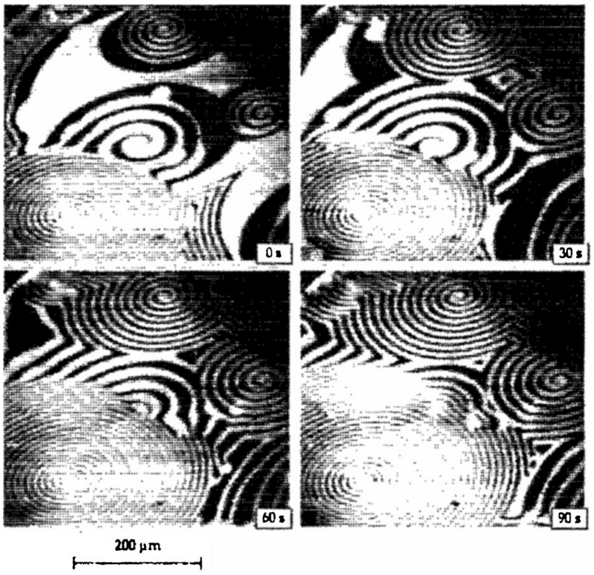

Figure 4. Spatio-temporal variations in the reaction of CO on Pt. Reprinted with permission from ref 40. Copyright 1993 American Institute of Physics.

The Role of Precursor States. King showed how significant the role of weakly held molecular states can be for dictating reactivity at surfaces, because they can diffuse over long distances in the weakly held state before reaction, thus effectively "seeking out" active sites for adsorption on an otherwise unreactive surface.[47,48] This is now recognized as a general form of behavior in adsorption and surface reactions.

Surface Reconstruction. Somorjai, King, and others revealed the fact that not all clean surfaces simply present the bulk termination at the surface, but that many rearrange their surface atoms in an attempt to present a lower-energy interface.[49]An example of this is the reconstruction of the Pt(100) surface, which presents a hexagonal overlayer that has nearly close-packed atoms, while a number of (110) face-centered cubic metal surfaces reconstruct to give a "missing row" conformation. Researchers now recognize that such reconstructions occur widely and that even bulk-terminated surfaces often reconstruct in the presence of gas molecules, while reconstructed clean surfaces can revert to the bulk termination in the presence of gas.

In these respects, the Nobel Committee lost an opportunity to recognize the contributions of others to the field of surface science.

THE NEW ERA OF SURFACE SCIENCE

Necessarily, the Nobel Prize recognizes past achievements, and surface science is advancing quickly into new realms of endeavor. These include surface science at the liquid–solid interface (especially surface electrochemistry, something with which Ertl has been heavily involved in recent years). If, however, we focus on the gas–solid interface, developments are proceeding apace and include the following:

Nanoparticles and Model Catalysts. Although single-crystal metals can be good models of some catalyst surfaces, many catalysts comprise very small nanoparticles, and their reactivities may be different from that of the bulk metal. Thus, critical developments in this field have occurred in the past couple of decades and have become a significant area of work in the field. Since catalytic reactivity usually involves a metal oxide interface, much work has been devoted to the surface structure and reactivity of oxides; fabricating nanoparticles on such oxides and measuring their reactivity has now become the cornerstone of much of this work.

In Situ Studies—Out of UHV, into the Ambient. With the advent of many new techniques that are capable of providing surface information without the necessity of UHV (*e.g.*, scanning probe microscopies, vibrational spectroscopies), there is an increasing body of work focusing on the structures of surfaces under ambient or even high-pressure conditions. Somorjai, Goodman, and others have been instrumental in developing this area of surface science.

Nonetheless, the foundations laid by Ertl and the other significant contributors to surface science from the mid-1960s and on are fundamental to our understanding of surface phenomena under new conditions, with new materials, and often for very complex surface species and reactions. Further, essential work still needs to be done and is continuing to be done on the "simple" systems of which surface scientists have established first principles.

Additionally, the field of surface science has laid the foundation for nanoscience by developing techniques, by provoking thought, and by pointing to the key roles played by nanoscale phenomena in important surface processes. It must be remembered that, as we enter ever deeper into the nanoworld, so the properties of the surface layer become ever more significant, as the surface to bulk ration becomes very high.

REFERENCES AND NOTES

1. http://nobelprize.org/nobel_prizes/chemistry/laureates/2007.
2. http://nobelprize.org/nobel_prizes/physics/laureates/1937.
3. Davisson, C.; Germer, L. H. Diffraction of Electrons by a Crystal of Nickel. *Phys. Rev.* **1927**, *30*, 705–741.
4. Müller, E. W. Elektronenmikroskopische Beobachtungen von Feldkathoden. *Z. Phys.* **1937**, *106*, 541–550.
5. Müller, E. W. Das Feldionenmikroskop. *Z. Phys.* **1951**, *131*, 136–142.
6. Ehrlich, G. Modern Methods in Surface Kinetics. In *Advances in Catalysis*; Eley, D. D., Pines, H., Weisz, P. B, Eds.; Academic Press: San Diego, CA, 1963; *Vol. 14*, pp 347–391.
7. Gomer, R.; Wortman, R.; Lundy, R. Mobility and Adsorption of Hydrogen on Tungsten. *J. Chem. Phys.* **1957**, *26*, 1147–1164.
8. Ertl, G. Über die Kinetik der Katalytischen Oxidation von Wasserstoff an Germanium-Einkristallen. *Z. Phys. Chem.* **1965**, *5*, 49–62.
9. Ertl, G. Untersuchung von Oberflächenreaktionen an Kupfer mittels Beugung langsamer Elektronen (LEED). *Surf. Sci.* **1967**, *6*, 208–232.
10. Ertl, G.; Grunze, M.; Weiss, M. Chemisorption of N_2 on an Fe(100) Surface. *J. Vac. Sci. Technol.* **1976**, *13*, 314–317.
11. Bozso, F.; Ertl, G.; Grunze, M.; Weiss, M. Interaction of Nitrogen with Iron Surfaces. I. Fe(100) and Fe(111). *J. Catal.* **1977**, *49*, 18–41.
12. Bozso, F.; Ertl, G.; Weiss, M. Interaction of Nitrogen with Iron Surfaces. II. Fe(110). *J. Catal.* **1977**, *50*, 519–529.
13. Ertl, G.; Lee, S. B.; Weiss, M. Kinetics of Nitrogen Adsorption on Fe(111). *Surf. Sci.* **1982**, *114*, 515–526.
14. Ertl, G. Surface Science and Catalysis—Studies on the Mechanism of Ammonia Synthesis: The P. H. Emmett Award Address. *Catal. Rev.—Sci. Eng.* **1980**, *21*, 201–223.
15. Ertl, G. Reaction Mechanisms in Catalysis by Metals. *Crit. Rev. Solid State Mater. Sci.* **1982**, *10*, 349–372.
16. Ertl, G. Primary Steps in Catalytic Synthesis of Ammonia. *J. Vac. Sci. Technol., A* **1983**, *1*, 1247–1253.
17. Stoltze, P.; Nørskov, J. K. Bridging the "Pressure Gap" between Ultrahigh-Vacuum Surface Physics and High-Pressure Catalysis. *Phys. Rev. Lett.* **1985**, *55*, 2502–2505.
18. Stoltze, P.; Nørskov, J. K. An Interpretation of the High-Pressure Kinetics of Ammonia Synthesis Based on a Microscopic Model. *J. Catal.* **1988**, *110*, 1–10.
19. Stoltze, P.; Nørskov, J. K. Comment on 'The Application of Surface Kinetic Data to the Industrial Synthesis of Ammonia' by M. Bowker, I. Parker and K.C. Waugh. *Surf. Sci.* **1988**, *197*, L230–L232.
20. Bowker, M.; Parker, I. B.; Waugh, K. C. Extrapolation of the Kinetics of Model Ammonia Synthesis Catalysts to Industrially Relevant Temperatures and Pressures. *Appl. Catal.* **1985**, *14*, 101–118.
21. Parker, I. B.; Waugh, K. C.; Bowker, M. On the Structure Sensitivity of Ammonia Synthesis on Promoted and Unpromoted Iron. *J. Catal.* **1988**, *114*, 457–459.
22. Bowker, M.; Parker, I.; Waugh, K. C. The Application of Surface Kinetic Data to the Industrial Synthesis of Ammonia. *Surf. Sci.* **1988**, *197*, L223–L229.
23. Bowker, M. Nitrogen Dissociation on Fe: Activated, Non-Activated or Both. *Top. Catal.* **1994**, *1*, 265–271.
24. Ertl, G.; Weiss, M.; Lee, S. B. The Role of Potassium in the Catalytic Synthesis of Ammonia. *Chem. Phys. Lett.* **1979**, *60*, 391–394.
25. Ertl, G.; Lee, S. B.; Weiss, M. Adsorption of Nitrogen on Potassium Promoted Fe(111) and (100) Surfaces. *Surf. Sci.* **1982**, *114*, 527–545.
26. Strongin, D. R.; Carrazza, J.; Bare, S. R.; Somorjai, G. A. The Importance of C_7 Sites and Surface Roughness in the Ammonia Synthesis Reaction Over Iron. *J. Catal.* **1987**, *103*, 213–215.
27. Jacobs, P. W.; Somorjai, G. A. Conversion of Heterogeneous Catalysis From Art to Science: The Surface Science of Heterogeneous Catalysis. *J. Mol. Catal. A: Chem.* **1998**, *131*, 5–18.
28. http://nobelprize.org/nobel_prizes/chemistry/laureates/1918.
29. Engel, T.; Ertl, G. A Molecular Beam Investigation of the Catalytic Oxidation of CO on Pd (111). *J. Chem. Phys.* **1978**, *69*, 1267–1281.
30. Engel, T.; Ertl, G. Surface Residence Times and Reaction Mechanism in the Catalytic Oxidation of CO on Pd(111). *Chem. Phys. Lett.* **1978**, *54*, 95–98.
31. Engel, T.; Ertl, G. Elementary Steps in the Catalytic Oxidation of Carbon Monoxide on Platinum Metals. In *Advances in Catalysis*; Eley, D. D., Pines, H., Weisz, P. B, Eds.; Academic Press Inc.: San Diego, CA, 1979; *Vol. 28*, pp 1–78.
32. Ertl, G.; Norton, P. R.; Rüstig, J. Kinetic Oscillations in the Platinum-Catalyzed Oxidation of CO. *Phys. Rev. Lett.* **1982**, *49*, 177–180.
33. Cox, M. P.; Ertl, G.; Imbihl, R. Spatial Self-Organization of Surface Structure during an Oscillating Catalytic Reaction. *Phys. Rev. Lett.* **1985**, *54*, 1725–1728.
34. Rotermund, H. H.; Engel, W.; Kordesch, M.; Ertl, G. Imaging of Spatio-Temporal Pattern Evolution during Carbon Monoxide Oxidation on Platinum. *Nature* **1990**, *343*, 355–357.
35. Ertl, G. Oscillatory Catalytic Reactions at Single Crystal Surfaces. In *Advances in Catalysis*; Eley, D. D., Pines, H., Weisz, P. B., Eds.; Academic Press Inc.: San Diego, CA, 1990; *Vol. 37*, pp 213–277.
36. Ertl, G. Dynamics of Reactions at Surfaces. In *Advances in Catalysis*; Gates, B. C., Knözinger, H., Eds.; Academic Press, Inc.: San Diego, CA, 2000; *Vol. 45*, pp 1–69.
37. Starke, J.; Reichert, C.; Eiswirth, M.; Rotermund, H. H.; Ertl, G. Fluctuation-Induced Pattern Formation in a Surface Reaction. *Europhys. Lett.* **2006**, *73*, 820–825.
38. http://nobelprize.org/nobel_prizes/chemistry/laureates/1932.
39. http://nobelprize.org/nobel_prizes/chemistry/laureates/1956.
40. Nettesheim, S.; von Oertzen, A.; Roterman, H. H.; Ertl, G. Reaction Diffusion Patterns in the Catalytic CO-oxidation on Pt(110): Front Propagation and Spiral Waves. *J. Chem. Phys.* **1993**, *98*, 9977–9985.

41. Brüche, E.; Johannson, H. Einige Neue Kathodenuntersuchungen mit dem Elektrischen Elektronenmikroskop. *Z. Physik.* **1932**, *33*, 898–899.
42. Zhabotinsky, A. M. A History of Chemical Oscillations and Waves. *Chaos* **1991**, *1*, 379–386.
43. For a review of part of this work see: Davis, S. M.; Somorjai, G. A. Hydrocarbon Conversion over Metal Catalysts. In *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier Science Publishing Company, Inc.: New York, 1982; pp 217–364.
44. King, D. A.; Wells, M. G. Reaction Mechanism in Chemisorption Kinetics: Nitrogen on the {100} Plane of Tungsten. *Proc. R. Soc. London A* **1974**, *339*, 245–269.
45. Singh-Boparai, S. P.; Bowker, M.; King, D. A. Crystallographic Anisotropy in Chemisorption: Nitrogen on Tungsten Single Crystal Planes. *Surf. Sci.* **1975**, *53*, 55–73.
46. King, D. A. The Influence of Weakly Bound Intermediate States on Thermal Desorption Kinetics. *Surf. Sci.* **1977**, *64*, 43–51.
47. Cassuto, A.; King, D. A. Rate Expressions for Adsorption and Desorption Kinetics with Precursor States and Lateral Interactions. *Surf. Sci.* **1981**, *102*, 388–404.
48. For a review of this area, see: Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons, Inc.: New York, 1994; pp 36–270.
49. See, for instance: Titmuss, S.; Wander, A.; King, D. A. Reconstruction of Clean and Adsorbate-Covered Metal Surfaces. *Chem. Rev.* **1996**, *96*, 1291–1305.