

A Modest Attempt to Understand Something About Catalysis

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Surface science has been around for quite some time. Back in 1825 Faraday was studying the nature of adsorption of gases on surfaces. Catalysis has been occupying the talents of physical chemists since before the days of Haber and Bosch. More recently, the transistor is an application of surface science to the solid state physics of semi-conductors.

Predictably, engineers also are becoming involved in surface science. The electrical engineers must find new and better ways to design and build their integrated circuits. The mechanical engineers and material scientists must find alloys and composites which will withstand stress and corrosion better. The chemical engineers must learn more about fundamental surface phenomena in order to improve yield and productivity of their catalytic reactors.

The starting point is the interaction of gas phase atoms and molecules with a clean metal surface--the phenomenon which is generally called 'chemisorption'. By combining experimental results and theoretical calculations (mostly in the area of quantum mechanics) we hope to gain more precise knowledge of exactly what occurs in a heterogeneous catalytic reaction.

TECHNIQUES FOR STUDYING SURFACES

The first thing to realize is that there are many experimental tools available for studying surfaces. Each has a different name (usually an acronym), and each seems technologically more complicated than its predecessor. Many of them fall into the category of 'spectroscopy'--that is, the experimental determination of atomic and molecular energy levels by means of absorption or emission of energy.

For example, there is 'Auger' spectroscopy (pronounced oh-jhay) in which a surface is bombarded with high energy electrons which cause other electrons in the surface atoms to move to higher energy states. As these electrons decay back to their original levels, they cause the emission of secondary electrons which can be captured and analyzed according to their energy (and in some cases their direction). The energy distribution of these secondary electrons is unique for a given element. One can readily see, for example, whether a tungsten surface has oxygen, or carbon, or both (possibly carbon monoxide) attached to it. Auger spectroscopy is, so to speak, the opening salvo in the experimental effort to discover surface information. It returns information about the composition at the surface.

There is also ultraviolet photoemission spectroscopy (UPS). In this technique UV light strikes the surface and is responsible for the direct ejection of electrons according to Einstein's photoemission theory for which he won the Nobel Prize in 1905. These electrons can be energy-analyzed to give information about the valence electrons at the surface, and hence the status of the chemical bonding there.

Another form of photoemission spectroscopy uses X-rays in place of UV light (XPS or ESCA). X-rays are capable of exciting core level electrons from atoms within about 20 Angstroms of the surface. Energy analysis of these electrons can yield information about the "valence states" (Pt^{++} vs. Pt^{++++} for example) in addition to composition. One advantage of XPS is that X-rays do not damage the surface as much as the high energy electrons used in Auger so that surfaces which are easily decomposed can be studied with XPS. XPS, however, is a much more difficult experiment to perform than Auger.

The surface structure of a single crystal with an adlayer can be determined using low-energy-electron diffraction, LEED, in which low energy electrons are back reflected by the surface onto a phosphorescent screen. The diffraction pattern on the screen and spot intensity vs. electron energy is then used to deduce the surface structure. This experiment differs from X-ray diffraction in that the low-energy electrons are not able to penetrate more than a few atomic layers beneath the surface so that they do not carry bulk structure information which may be considerably different.

It is also possible to bombard the surface with some very heavy projectiles such as argon or cesium ions. These cannonballs literally tear a small area of the surface apart and scatter the pieces into the surrounding atmosphere. This shrapnel can then be picked up and analyzed with a mass spectrometer. The result is a plot of concentration as a function of depth beneath the surface. This technique is known as SIMS (secondary ion mass spectroscopy).

Because of our interest in surface reactions, we have incorporated into the apparatus a molecular beam 'doser' with which we can aim reactive molecules (nitrogen, oxygen, carbon monoxide, methane, etc.) at the metal surface for a given length of time. During the bombardment we can measure the gas phase composition with the mass spectrometer. After the molecular beam is shut off we can use Auger, UPS, or XPS to detect any changes in the surface which have accompanied the molecular 'dosing'.

After a sample has been dosed with a gas, information about the binding energy and surface states can be gained using thermal programmed desorption, TPD. In TPD the sample's temperature is increased linearly while the system pressure and gas phase composition are monitored. Peaks in these spectra are due to desorbing species, and the lower the desorption temperature, the lower the binding energy.

HIGH VACUUM TECHNOLOGY

The bell jar is a stainless steel chamber which holds the sample. It is equipped with many different side and top ports for viewing the sample, moving it about, and subjecting it to the various tests described above. To the left of the bell jar is the electronic section, and to the left of that, the computer system used to monitor and control the experiments.

To obtain meaningful results from this type of apparatus it is necessary that the sample surface be free of debris. This is no easy task. A clean metallic surface exposed to ordinary air would be hopelessly contaminated in nanoseconds by virtue of bombardment by oxygen, nitrogen, and carbon dioxide molecules. In order to gain time to do any of the experiments discussed here it is necessary to go to pressures of the order of .0000000001 mm of mercury where there are only a few hundred thousand molecules per cubic centimeter in the gas phase. Such a pressure will allow about a half-hour to do experiments after the sample surface is cleaned by heating to a high temperature.

Techniques for attaining such low pressures are fascinating in themselves. One must scrupulously avoid touching any internal parts with the bare skin. Any oils, natural or otherwise, in the system will carbonize during the high-temperature cleaning period. The resulting carbon will adsorb all kinds and numbers of molecules, making it impossible to pump down to the required pressure. Mechanical pumps followed by an ion pump combined with cryopumping and a titanium sublimation pump (a sort of molecular fly-paper) are used to scavenge unwanted molecules from the system.

THE COMPUTER SYSTEM

With only a short time in which to perform the actual experiments, it is essential that they be tightly controlled and the results be logged as accurately as possible. The digital computer is the device which adapts itself most readily to these requirements.

The computer is programmed to start and stop the experiments, monitor and control them as they are running, collect the data rapidly, massage the data into a usable form, and plot the results on graphs suitable for publication.

We are using the LSI 11/03 (Digital Equipment Co.) microprocessor for the computer CPU. This is a fast and versatile 16-bit unit capable of addressing 32K words (64K bytes) of random access memory. Peripheral units are a typewriter (Decwriter LA-36) for hard copy, a video terminal (Heath H-9) for direct communication with the computer, a video plotter (Tektronix 4006-1), a hard-copy X-Y plotter (Tektronix 4662), a pulse counter designed and built locally, a 512K floppy disk unit (Heath H-27), and a digitally programmable power supply (Hewlett-Packard 6131C). All of these have been interfaced together either with software purchased from the Heath Company or with small machine language subroutines written expressly for the purpose.

To give some idea of how the computer is, let us look at a typical XPS experiment. We wish to record the electron energy distribution resulting from X-ray bombardment of a surface. To do this, we must apply a specific voltage to the analyzer (a double-pass cylindrical mirror analyzer (CMA) which passes only those electrons having a band-pass energy corresponding to the applied voltage) and record the number of electrons passing through in a given time.

The computer monitors the 60Hz line clock (one pulse every 17 msec). After the first pulse is received it sets the voltage on the power supply attached to the CMA. By the time the next pulse is received everything is stable and the computer signals the counter to begin. Each electron passing through the CMA creates a pulse. These pulses are counted for a very accurate time determined by the computer. When this time is up and the counter is finished, it signals the computer, which then reads and stores the count. This all occurs between the second and third 60Hz pulse. The third pulse tells the computer to restart the cycle with a new voltage. Thus in one second the computer scans 30 voltages and records the electron count at each. A 100-volt scan at increments of 0.1 volt takes about 35 seconds.

In some cases it may be necessary to control the temperature of the sample. The computer has plenty of time in the above routine to read the sample temperature and turn a heater current up or down. Further, electron counts cannot be made while the heater is on since the fields caused by the heater current will disturb the emitted electrons. The computer will have to turn off the heater momentarily while counting is being done.

After the scan is over, the computer can execute another program which takes the recorded data and puts it in a form suitable for printing out and/or plotting.

In the above description it should be obvious that the computer lends a great deal of versatility to the system operation. After a given run we may discover that the pulse-counting time was too short or too long, or that the wrong energy range was scanned, or any of several other parameters were incorrectly chosen. To correct for such mistakes is merely a matter of changing the computer program. This is usually much simpler than changing hardware, and is another reason for applying computer control to this type of operation.

WORK IN PROGRESS

The work which is underway in our laboratory involves several different phases of study. The first phase is an extension of the work of W.H. Weinberg and R.P. Merrill published in Surface Science in 1972. The basis of this work was a LEED study of the nitrous oxide-tungsten (100) chemisorption surface done in conjunction with thermal programmed desorption. A clean tungsten (100) surface was dosed with nitrous oxide, and no change was observed in the LEED pattern. As the sample was heated, three peaks were observed in the TPD spectrum; a low temperature molecular peak, and then

two peaks supposed to be nitrogen. This left an oxide coating on the surface which could be removed by flashing to a high temperature. A surface structure model was then proposed which is consistent with the observed LEED patterns taken at different temperatures. In this early experiment the vacuum system did not contain Auger, UPS, a mass spectrometer, a beam doser or XPS. These experiments are being extended using these capabilities, four different nitrogen oxides and a broad temperature range so that both atomic and molecular adsorption can be studied. The knowledge gained in this study will be applied to catalysts which may realistically perform as NOX decomposition catalysts.

Another study is underway to understand catalysts in an industrially useful form and to relate this data to single crystal data. Industrial catalysts consist of small metallic crystallites supported on a porous structure of some substance such as silica or alumina. Recently it has been realized that the catalyst-support interaction plays an important role in determining the catalytic properties. The support can influence the "valence state" of the metal much like a promotor. If one can find procedures and substrates which optimize the catalytic activity per metal atom (turnover number) then fewer metal atoms (usually precious metals) can be used.

Our studies focus on platinum crystallites supported on a planar substrate. We intend to modify the surface through various means such as ion sputtering or chemical exposure. The surface then will be characterized using the various spectroscopies. Finally a reactive molecular beam study will allow us to relate the catalytic activity of the surface to the "state of the surface".

SUMMARY

The techniques described here for the study of surfaces are anything but slapdash. They represent a very high form of technology. All of the equipment--mechanical and electronic--must be highly sophisticated. The experimenter, above all, must be dedicated to quality rather than quantity. However, surface science is proving rapidly to be a rewarding undertaking for chemical engineers interested in catalysis and corrosion.

