Module 8 : Surface Chemistry

Lecture 37 : Surface Characterization Techniques

Objectives

After studying this lecture, you will be able to do the following:

- Use the Langmuir's isotherm to calculate the surface area of adsorbent.

- Use the BET (after Brunauer, Emmett and Teller) equation is used to give specific surface area from the adsorption

- data.

- Use X-Ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Low Energy Electron

- Diffraction(LEED) to characterize surface structures.

- Use microscopic methods of characterization such as Scanning Electron Microscopy (SEM) and Scanning

  Tunneling Microscopy (STM) to analyse surface structures of materials.

37.1 Introduction

Surface characteristics of a material refer to the properties associated with its surface. Typically measurements of surface area, surface roughness, pore size, and reflectivity constitute surface characteristics. Information on surface characteristics is very important for the possible applications of surfaces as semiconductors, heterogeneous catalysts and also in biological research. Surface area is an attribute that is used by catalyst manufacturers and users to monitor the activity and stability of a catalyst. There are different methods used to measure different surface properties. Most methods are based on the isothermal adsorption of nitrogen. Many advances in surface science have made the methods surface sensitive, i.e., they are sensitive to the outermost atomic layers (depth of 2-3 atomic layers) of the bulk solids. These techniques could be classified into two categories: Classical Methods and Instrumental methods.

37.2 Classical Methods:

(a) Langmuir's model:

In adsorption systems where Langmuir's model is followed, the maximum amount of adsorbate adsorbed per gram of adsorbent for the formation of monolayer, X_m/(mg/g), is determined. Knowing the approximate contact area of an adsorbate molecule, surface area of adsorbent could be calculated using following equation:

Surface area of the adsorbent (m^2/g) = $\dfrac{X_m(mg/g) \times N \times S(m^2/molecule)}{M}$ (37.1)

Here, X_m = Maximum amount of adsorbate adsorbed per gram of adsorbent for monolayer formation, M = Molecular weight of the adsorbate(mg/molecule), N = Avogadro's number and S = Contact surface area by each molecules (m^2).

Example 37.1 : The volume of nitrogen gas at 1 atm and 273K required to cover 1g of the silica gel is 0.129 dm^3. Calculate the surface area of the gel if each nitrogen molecule occupies an area of 16.2 X 10^{20} m^2

Solution:

Number of moles of N_2 in 0.129dm^3

$$= 0.129/22.4 = 5.76 \times 10^{-3} \text{ moles of } N_2 \text{ gas}$$

Therefore, total number of N_2 molecules in 0.129 dm^3 of N_2

$$= 5.76 \times 10^{-3} \times 6.02 \times 10^{23} \text{ molecules } /22.4 \text{ } dm^3 = 34.67 \times 10^{20}$$

The total area of 1g of the silica gel = 34.67 x 10^{20} x 16.2 x 10^{-20} m^2

$$= 561.74 m^2$$

37.2 Classical Methods:

(b) BET equation

BET (after Brunauer, Emmett and Teller) equation is used to give specific surface area from the adsorption data. The BET equation is used to give the volume of gas needed to form a monolayer on the surface of the sample. The actual surface area can be calculated from a knowledge of the size and the number of the

adsorbed gas molecules. Nitrogen is used most often to measure BET surface, but if the surface area is very low, argon or krypton may be used as both give a more sensitive measurement, because of their lower saturation vapor pressures at liquid nitrogen temperature.

BET equation is as follows:

$$\frac{z}{(1-z)} \bullet \frac{1}{V} = \frac{(c-1)z}{cV_{mono}} + \frac{1}{cV_{mono}}$$
(37.2)

Where, V = volume of gas adsorbed at pressure p; V_m = amount of gas corresponding to one monolayer; z = p/p*, ratio of pressure of gas and pressure at saturation; c = a constant.

A plot of $\frac{z}{(1-z)V}$ vs z gives slope $\frac{(c-1)}{cV_{mono}}$ and intercept at $z = 0$, and cV_{mono} could be determined. The results can be combined to give c and V_{mono}.

When the coefficient c is large, the isotherm takes the simpler form as follows.

$$\frac{V}{V_{mono}} = \frac{1}{1-z}$$
(37.3)

This is applicable to unreactive gases on polar surfaces, for their c is $\simeq 10^2$. Higher value of c will mean mainly monolayer formation. The value of V_{mono}, the volume of gas required to form monolayer, is of considerable interest because it helps in the calculation of surface area of a porous solid. The surface area occupied by a single molecule of adsorbate on the surface can be calculated from the density of the liquefied adsorbate. For example, the area occupied by a nitrogen molecule at -195° C estimated to be 16.2×10^{-20} m² assuming molecules to be spherical and close packed in the liquid. Thus, from the value of V_{mono} obtained from the BET theory, surface area of the adsorbent could be determined.

37.2 Classical Methods:

(b) BET equation

Example 37.2 : The data given below are for the adsorption of nitrogen on alumina at 77.3 K. Show that they fit in a BET isotherm in the range of adsorption and find V_{mono} and hence surface area of alumina (m²/g). At 77.3 K, saturation pressure, P* = 733.59 torr. The volumes are corrected to STP and refer to 1g of alumina.

P/ (torr)	37.67	74.20	114.54	142.0	185.34
V (cm³/g: STP)	23.14	28.1	33.1	36.35	41.49

Solution:

From the above data, we have

$10 \times Z = 10 \times (P/P^*)$	0.51	1.01	1.56	1.94	2.53
$x = 10^3 Z/(1-Z)$ (V/cm³)	2.32	3.99	5.58	6.62	8.16

From BET equation , $\frac{z}{(1-z)} \bullet \frac{1}{V} = \frac{(c-1)z}{cV_{mono}} + \frac{1}{cV_{mono}}$

A plot of z/(1-z) against z will give a straight line with intercept z = 0 as equal to $\frac{1}{cV_{mono}}$ **and slope will be**

$\frac{(c-1)}{cV_{mono}}$

Intercept of the plot is 0.987×10^{-3} cm^{-3} where as slope = 2.88×10^{-2} cm^{-3}

Intercept = $\frac{1}{cV_{mono}}$ **= 0.987×10^{-3} cm^{-3} = 9.87×10^{-4} cm^{-3}**

37.2 Classical Methods:

(b) BET equation

Example 37.2:

Slope $= \dfrac{(c-1)}{cV_{mono}} = 2.88 \times 10^{-2}$ cm^{-3}

2.88×10^{-2} cm$^{-3} = (C\text{-}1) \times \dfrac{1}{cV_{mono}}$

$\qquad\qquad = (C\text{-}1) \times 9.87 \times 10^{-4}$ cm^{-3}

$(C\text{-}1) = 2.88 \times 10^{-2} / 9.87 \text{x} 10^{-4} = 29.18$

$\qquad C = 30.18$

Further , $\dfrac{1}{cV_{mono}} = 9.87 \times 10^{-4}$ cm^{-3}

$V_{mono} = 1 / C \times 9.87 \times 10^{-4}$ cm^{-3}

$\qquad = 1/ 30.18 \times 9.87 \times 10^{-4}$

$\qquad = 33.57$ cm^3

$\qquad = 0.03357$ dm^3

Number of N$_2$ molecules $= (0.03357/22.4) \times 6.02 \times 10^{23}$

$\qquad\qquad\qquad = 9.022 \times 10^{20}$ molecules

The total area $= 9.022 \times 10^{20} \times 16.2 \times 10^{-20}$ m^2

$= 146.156$ m^2/g (contact area of one N$_2$ molecule $=16.2 \times 10^{-20}$ m^2)

Now we shall consider the instrumental methods. These may be further classified as spectroscopic methods and microscopic methods.

37.3 Spectroscopic methods:

These methods make use of the principle that when a beam of electrons or high-energy radiation (usually X-rays) are bombarded at the surface, the surface electrons from the upper layer of are ejected. These electrons are called secondary electrons. Since the energy of these electrons is very low, these are assumed to be produced from only a few layers of the surface. Electrons of this energy (10-30 eV) cannot reach the surface from underlying layers. In spectroscopic methods, surfaces are analyzed by capturing secondary electrons of different energies, which are characteristic of their environment. Based on spectroscopic theory some of the techniques are discussed below.

(a) X-Ray Photoelectron Spectroscopy (XPS):

X-ray photoelectron spectroscopy (XPS) was developed in mid 1960 by K. Siegbohn and his colleagues. Later on, K. Siegbohn was awarded Nobel Prize for physics in 1981 for the work on XPS. This technique provides a wide range of information regarding atomic composition, oxidation states, and chemical structures. Because of its versatility it is also called Electron Spectroscopy for Chemical Analysis (ESCA). Basic principle of this technique is based on phenomenon called photoelectric effect, rationalized by Albert Einstein in 1905. When photons of known energy (usually X-rays) knock the surface, an electron from K-shell is knocked out; kinetic energy of this electron is measured in the spectroscopy. The spectrum is given as the binding energy as function of electron counting rate. Binding is one unique character of different elements. Binding energy of an atom can be calculated from the following equation.
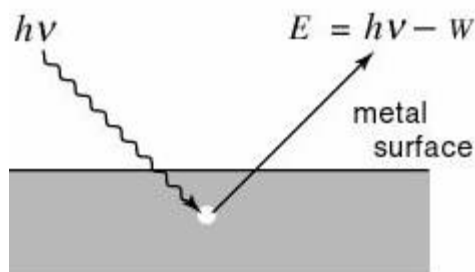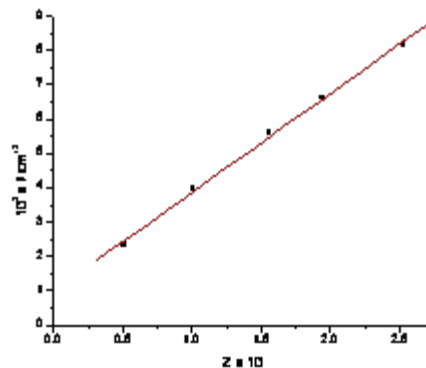

Figure 37.1 Photoelectric Effect

Binding Energy (eV), B.E. $= h\upsilon - $ K.E $- W$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (37.4)

where, $h\upsilon$ = Incident energy, K.E = Kinetic Energy of the ejected electron and W = Work function.

In the XPS spectrum, the innermost orbital appears a at higher binding energy than the outer orbital. Binding energies of 1s orbitals increase with atomic number.

37.4 Microscopic methods of characterization

Even microscopic methods make use of more or less the same principles, but these methods are generated by bombarding the surface with high-energy electrons, which are then multiplied several times so as to produce a magnified image of the surface on the fluorescent screen.

Few methods like STM, AFM work based on quantum mechanical principles.

(a) Scanning Electron Microscope (SEM):

This method takes advantage of the wave nature of light to attain higher magnification. It has nothing to do with the electron microscopy principles, only the magnification is comparable. In SEM a beam of electrons is generated in vacuum which is collimated by electromagnetic condenser lenses and scanned across the sample surface by an electromagnetic deflection coil. Primary imaging is done by collecting secondary electrons that are released by the sample. Then, the secondary electrons are magnified and finally made to fall on fluorescent screen to obtain final image.

Instrumentation and working:

1. **Electron source:** The electron source in SEM is an electron gun, a tungsten wire bent in 'V' shape, and applied

   voltage is as high as 10 keV, which then produces electrons from the tip. This whole set up is also called Wehnelt cylinder. The electrons so produced are accelerated and converged by applying anodic potential at a slight distance from the Wehnelt apparatus.
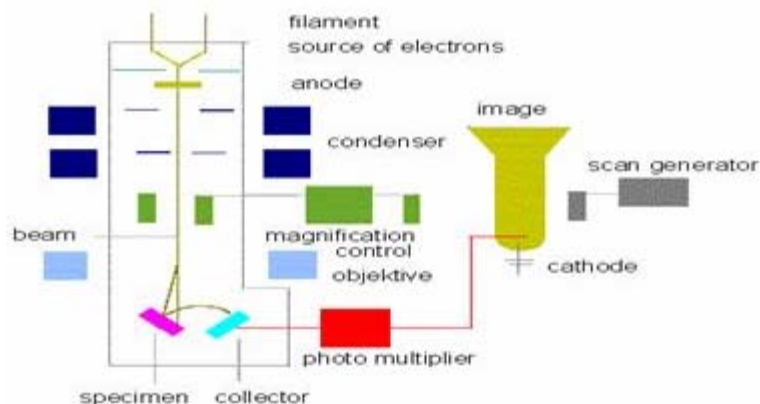

Figure 37.4 Block diagram of Scanning Electron Microscope

2. **Electromagnetic lenses:** Unlike in typical microscopes, SEM electromagnetic lenses are used to collimate the electron beam. Here, a magnetic field is used to perform the job of condenser and objective lenses which finally focuses the beam on the sample.

3. **Deflection coils:** The role of deflection coil is simply to scan the sample surface, which is mounted to sample platform by shifting the beam position. This is accomplished by applying positive potential to these coils. Normally solid sample can be glued directly on the platform, but powdered samples should be made into paste and then tapped on platform.

4. **Secondary Electron detector:** Secondary electrons are generated from the surface after colliding the surface with high-energy electron beam. These are received by a net like secondary electron detector, to which a positive potential of magnitude 10 keV is applied to grab the slightest emission of secondary electrons. Since strength of secondary electrons from the surface is very low, it is necessary to apply such large positive potential.

37.3 Spectroscopic methods:

(b) Auger Electron Spectroscopy (AES)

Unlike ESCA Auger (pronounced as OJ) Electron Spectroscopy is based on a two step process. In AES, the source is electron beam unlike x-rays in XPS. Electrons of energy 3-20 keV are incident upon a conducting sample. These electrons cause core electrons from the atoms contained in the sample to be knocked out, giving photoelectrons and atoms with a core hole. The atom then relaxes when electrons from higher level drop into the core hole, some energy is released in this transition, this released energy ejects another electron from the next higher level, which is called auger electron. The kinetic energy of auger electron is the difference between the energy released in relaxation of excited ion and energy required to remove the second electron from its orbit. The energy of auger electron is characteristic of the element that emits it and can be used to identify the element.

Auger electron spectroscopy is a popular technique for determining the composition of the top few layers of the surface. Except Hydrogen and Helium it is sensitive for all other elements. But it is more sensitive to lighter elements than heavy elements.

Auger electron emission is described as KLL, LMM, and MNN etc. For example KLL process involves initial removal of a K electron followed by a transition of an electron from L or higher levels to K. The energy released in this process ejects second electron from L Shell, which is called auger electron. This process occurs almost simultaneously. Auger electron emission is purely a surface phenomenon. Since auger electrons are very weak, only electrons from the surface of a few atomic layers can reach the detector.

Instrumentation:

It is somewhat similar to XPS except for the electron source. A common electron gun is the source of electrons. Its basic mechanism involves the application of a high voltage of about 50keV applied to "V" Wehnelt cylinder which produces electrons. These produced electrons are converged to a spot by positive potential. This spot is used to scan the surface.
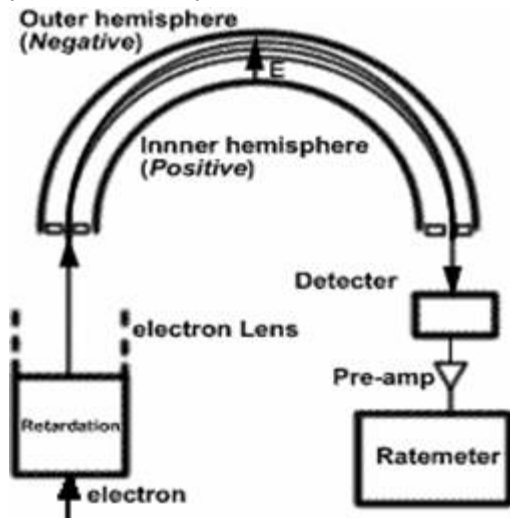

Figure 37.3 Auger Electron Spectroscopy

Applications of AES
1. Qualitative analysis of solid surfaces
2. Depth profiling of solids
3. Line scanning (Characterizing surface composition of solid as function of distance along the line)

(c) **Low Energy Electron Diffraction(LEED)**

This technique is especially used in crystallography. If a crystal is cut along a certain plane, then the atoms near the surface may be disturbed from their equilibrium positions. Such changes can be explored with LEED. The surface crystallography structures can be determined by bombarding the surface with low energy electrons (10-200eV) and diffracted electrons are observed as spots on a phosphorescent screen. The relative position of the spots on the screen shows the surface crystallographic structure.

The diffracted spots move as the energy of the incident electron changes and the intensity of the spots as a function of incident electron energy reveals much about surface reconstruction. In order to determine the true structure, much computer analysis is to be done.

Applications:

This instrument is basically used for crystallographic surface analysis.

37.4 **Microscopic methods of characterization**

(a) **Scanning Electron Microscope (SEM):**

Instrumentation and working:

5. **Photomultiplier tube:**

The secondary electrons are made to fall on the surface of a photosensitive plate a in a photomultiplier tube (PMT), and then, the strength of these electrons is increased to several hundred of times.

6. **Phosphorescent screen:**

Thus, amplified electrons are made to fall on a phosphorescent screen, which provides magnified image of the

surface.

Applications:

1. Materials: Microphotography and chemical analysis to determine failure mechanisms of metals and ceramics due to erosion and corrosion.

    *   High resolution imaging.

    *   Elemental mapping.

    *   Quantitative point and area analysis.

    *   Automated point analysis of corrosion products.

    *   Environmental: Particles automated particle sizing and typing of combustion ash residues, dust, and other

    *   particulate matter.

    *   Particle size and shape.

    *   Fly ash resistivity for electrostatic precipitator performance.

    *   Particle classification or typing based on composition — used to determine the source of particles.

    *   Imaging — high resolution images.

3. Deposits and wear debris analysis.
4. Particle sizing and characterization.
5. Failure analysis.
6. Contaminant analysis.
7. Metallurgical studies.

37.4 Microscopic methods of characterization

(b) Scanning Tunneling Microscope (STM):

STM is widely used in both industrial and fundamental research to obtain atomic scale images of metal surfaces. It provides a three dimensional profile of the surface, which is useful for characterizing surface roughness, observing surface defects and determining the size and conformation of molecules and aggregates on the surface.

It works on the principle of a record player. A sharp needle, called tip, is used to scan the surface and kept close to the surface. The voltage is applied between the metallic tip and the surface of the specimen typically between millivolts to a few volts. Current flow between metallic tip and the specimen is called tunneling current. The surface is scanned, keeping the distance between tip and specimen constant, so that the tunneling current is constant. This total set up is connected to a feed back loop which keeps the distance constant. Even a decrease in distance by 1 nm brings 10 times reduction in tunneling current. By perceiving all these changes, the feed back loop keeps the distance constant. When the tip encounters an elevation on the surface, instantly there is reduction in tunneling current; the feed back loop identifies this change and ensures the distance between tip and surface. This scanning pattern is drawn on computer screen, which looks like a contour map, which gives a 3-D view.

Instrumentation and detail working of atomic force microscope is very complex and beyond the scope of our present study and a schematic diagram of an STM is shown below.
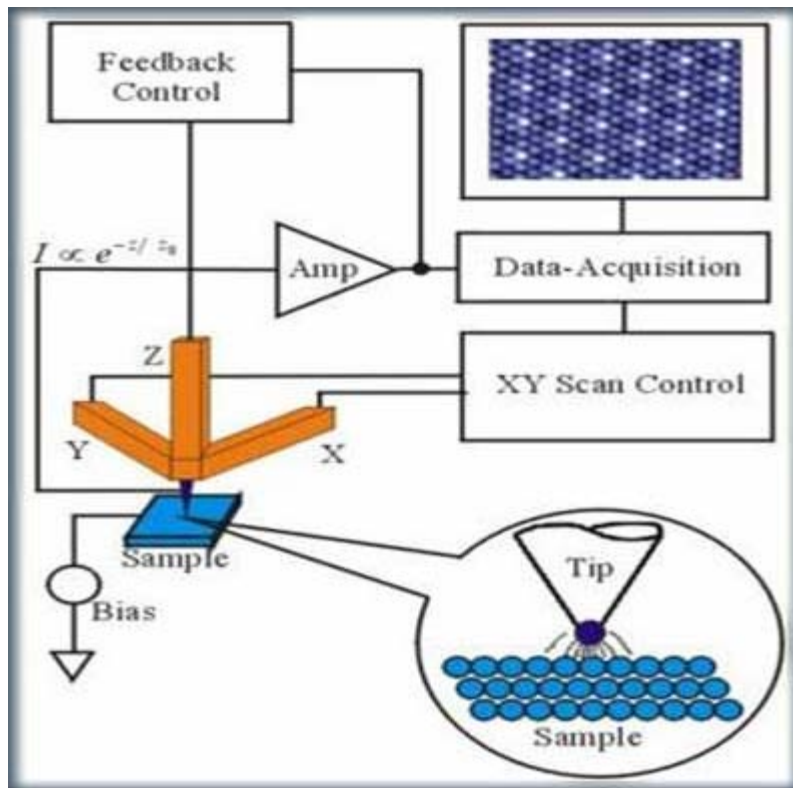
$I \propto e^{-z/z_0}$

Figure 37.5 Schematic diagram of Scanning Tunneling Microscope

Applications:

Analysis of atomic arrangements.

Surface analysis of nano materials.

Membrane surface analysis.

37.4   Microscopic methods of characterization

(c)   Atomic Force Microscope (AFM)

AFM is simply a modified version of a scanning tunneling microscope. Unlike STM, it is applicable to both conducting and insulating surfaces. AFM works by scanning similar to STM. In AFM the tip is positioned at the end of a cantilever, a flap shaped much like a diving board. The tip touches the surface while scanning. The tip is repelled or attracted by the surface of the specimen and the cantilever beam deflects. The magnitude of the deflection is captured by a laser beam that reflects at an oblique angle from the very end of cantilever. A plot of laser deflection versus tip position on the sample surface provides the resolution of hills and valleys that constitute the topography of the surface. AFM works with the tip touching the sample (constant mode), or the tip can tap across the surface (tapping mode). The other measurements can be made using modifications of AFM. These include variation in surface micro friction with a lateral force microscope (LFM), orientation of magnetic domains with magnetic force microscope (MFM), deflection in elastic modulii on micro scale with force modulation microscope (FMM) and obtaining the differences between chemical formulations across the surface area with chemical force microscope (CFM).

Instrumentation and detail working of atomic force microscope is very complex, its schematic diagram is shown below.
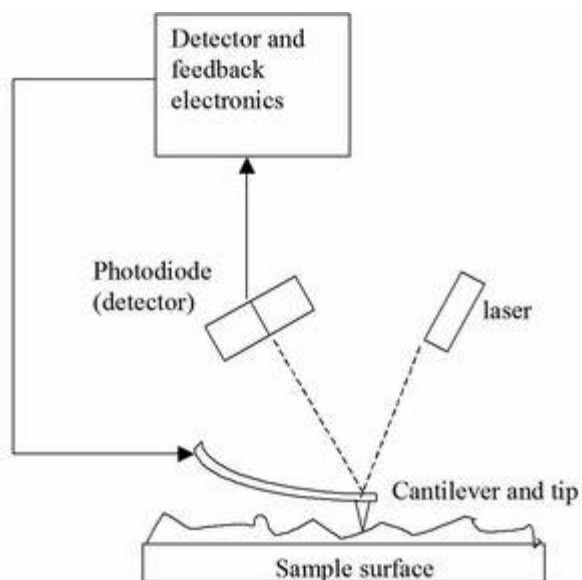
Figure 37.6 Schematic diagram of Atomic Force Microscope

Applications:
1. For studying surface derivatization of biosensors.
2. For defect inspection.
3. For nano material texture and roughness.
4. For polymer analysis.
5. For surface analysis of metals in metallurgy.
6. For nano structures and nano particle analysis.

Summary

In the present lecture, you have been introduced to adsorption isotherms and instrumental methods to characterise surface areas and structures. The Langmuir's isotherm and the BET (after Brunauer, Emmett and Teller) equation were used to calculate the surface areas of adsorbents from the adsorption data. We distinguished between the spectroscopic methods and microscopic methods for studying surface structures.

X-Ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED) methods were analysed and their use in characterizing surface structures was outlined. In the last section, the use of microscopic methods of characterization such as Scanning Electron Microscopy (SEM) and Scanning Tunneling Microscopy (STM) to analyse surface structures of materials was presented.