Heterogeneous Catalysis and Catalytic Processes

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Lecture – 16

Good morning, last time I was talking about transmission electron microscopy and we were just talking, electron microscopy rest pill. And, that was discussed that depending upon the characteristics of the primary beam which may have the 400 kilo electron volt of energy may start from 50 kilo electron volts; so high beam of energy. And, the electrons just a impinge on the surface and then it can be primary, secondary or backscattered electron. And, energy of these electrons which may diffract, which may transmit from the surface is measured.

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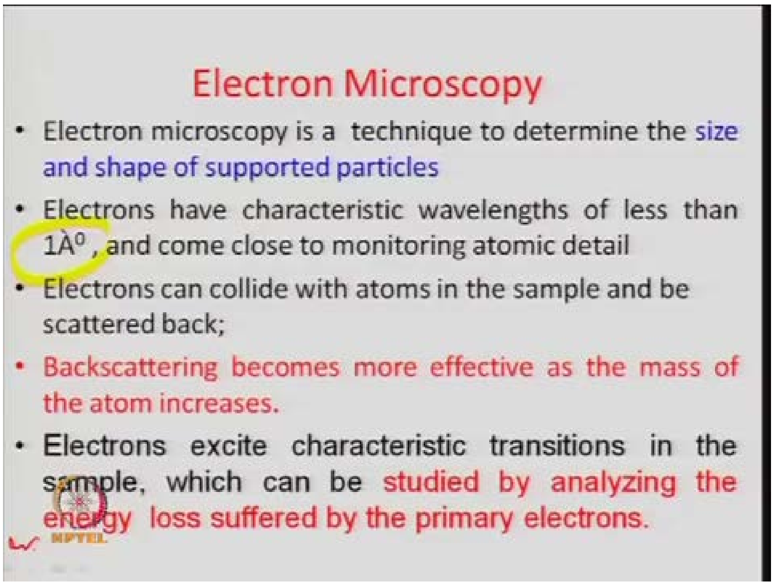

Electron Microscopy

- Electron microscopy is a technique to determine the size and shape of supported particles
- Electrons have characteristic wavelengths of less than 1À^0, and come close to monitoring atomic detail
- Electrons can collide with atoms in the sample and be scattered back;
- Backscattering becomes more effective as the mass of the atom increases.
- Electrons excite characteristic transitions in the sample, which can be studied by analyzing the energy loss suffered by the primary electrons.

So, electron which have wave length of roughly point approximately 1 Armstrong. So, that energy can be calculated and based on that one can determine the surface morphology. So, that was discussed.

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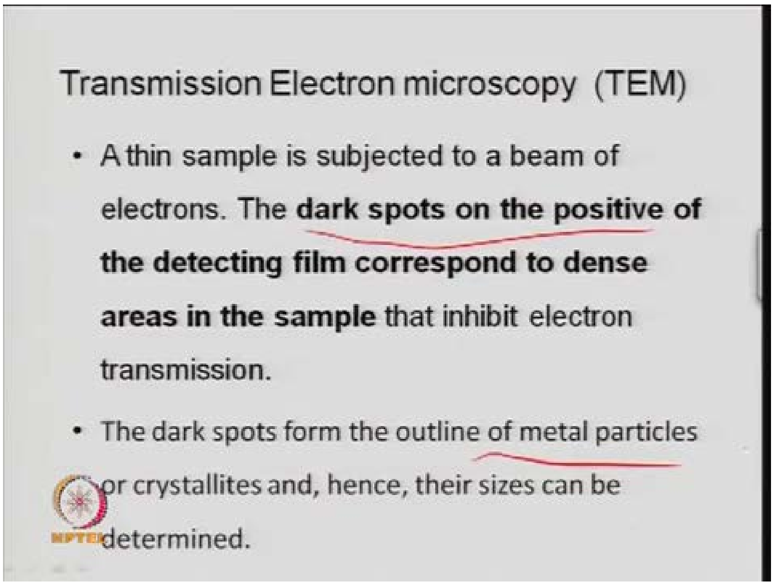

Transmission Electron microscopy (TEM)

- A thin sample is subjected to a beam of electrons. The **dark spots on the positive of the detecting film correspond to dense areas in the sample** that inhibit electron transmission.
- The dark spots form the outline of metal particles or crystallites and, hence, their sizes can be determined.

So, transmission electron microcopy as I said that something which transmits. So, if it a pore; so electron will transmit to the pore. If it a hard surface; so, it may not. So, that will come as a black spot. So, this is what the dark spot on the positive of the detecting film that correspond to the dense area. Suppose, there is a platinum then it will so black but if it is alumina, the metal will, electron will transfer to the pore of that. So, dark spot from the outline of the metal particles or crystalline, crystallite; so, that can be used to find out the composition. This can be used to find out the Morphology, Topology like SEM ((Refer Time: 02:08)) but time gives you 2 d lenses over mass of the solid; total mass of the solid.

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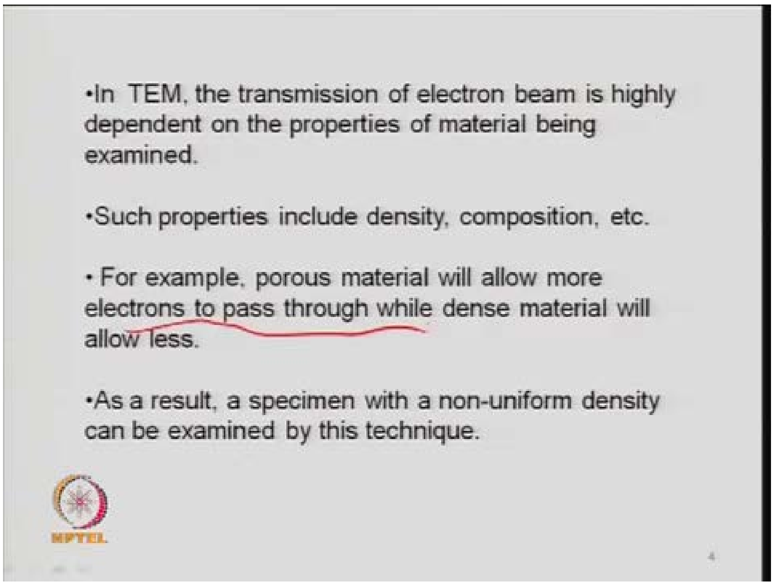

- In TEM, the transmission of electron beam is highly dependent on the properties of material being examined.
- Such properties include density, composition, etc.
- For example, porous material will allow more electrons to pass through while dense material will allow less.
- As a result, a specimen with a non-uniform density can be examined by this technique.

So, generally as we talked that the electron beams of highly; high energy electron beam that is depending upon the properties of the material examined the property includes density composition. So, based on this density of the solid and composition structural composition. So, metal part is there support is there different metal may be there; so the electronic configuration is different. So, depending upon you can distinguish between the metals. So, porous materials; suppose you have so it will allow more electrons to pass through while dense material will allow less. So, you can distinguish; so based on this the non uniform density can be examined. So, uniform of the surface or chemical composition of the surface can be traced by using this transmission electron microscopy.

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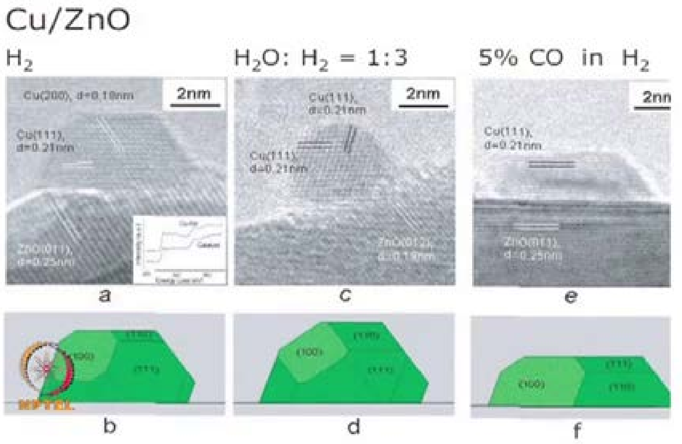
TEM images of a model catalyst for methanol synthesis, consisting of copper particles on a zinc oxide substrate.

[Adapted from P.L. Hansen, J.B. Wagner, S. Helveg, J. Rostrup-Nielsen, B.S. Clausen and H. Topsøe, Science, 295 (2002) 2053.]
Text Book Ref. : I. Chorkendorff, J.W. Niemantsverdriet Concepts of Modern Catalysis and Kinetics, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30574-2]



So, we were talking about this picture; as I said how much surfaces is created. So, this you can just if you look at here, the copper zinc oxide catalyst and the treatment or conditions are here it is treated with hydrogen, here it is in the environment of water and hydrogen; and in third case it is with carbon monoxide. So, you can see that when the treatment gases are different then, the surface which I created on the support is changed, that morphology has been changed. This you can very easily say here, the dark you can see here this and then here it appears to be centered one; the agglomerated.

So, how a surface is created that is again a different theory, that the free energy of the surface is measured. And, when the metal is interacting with the support; so free energy depending upon the faces or planes and the center of that crystal. So, the energy is calculated and that is known as surface free energy. So, wolf construction that is one of the important methods to determine the shape of a crystal or how does a crystal forms? Because as I said, it depends on the energy. So, d orbitals if you look at transition metals which have unpaired d electron they have highest energy and they will try to dissipate it. Because when the surface is created, the energy you have to provide certain kind of energy a large molecule it is to be ruptured. So, energy is increasing for the at the end for the given molecule.

So, this principle is used here. So, when you use the transmission electron micro graph, then you see the structures like this, depending upon the electron energy on different phases. So, this you can very easily if you look at the structure here which I showed here the different planes h c p structures hexagonal closed pack, body central cubic; so, faced centered cubic there can be different structure of a crystal plane, lattice plane. So, 1, 1, 1; 0, 0, 1 but I was talking earlier during X ray diffraction pattern you observe them. Because the diffraction at different diffraction and different positions the X ray which emits and their wave length is that is lambda is known. So, you can calculate the from the different planes. What is the crystal or phase? And, what is the orientation of that crystal? Because when the reaction takes place the orientation of that metal on the support is also important. So, this is what I was I am talking here is the orientation of these planes.

So, there are different structure here, we have 1 1 0 plane then 1 0 0 plane, 1 1 0, this 1 1 1 body. So, different orientations of a lattice when you see x y z plane and how these are arranged in that plane? How an atom has been arranged in an plane? So, that structure can be identified. So, when you have a 10 planes; so you can see here that this is a one kind of; this is a zinc oxide like this you can see a boundary here. So, zinc oxide; so you can measure the crystal size of zinc oxide also by just looking this distance; because this distance is 2 Nanometer. So, what is this distance is roughly here, the copper particle size is 0.21 nanometer.

And, if this is copper 2 0 0; it has a crystal size of roughly 0.18 nanometer. So, in this case, if you see it is 0.21 nanometer. In this case, again it is 0.21 nanometer. So, size has increased if you look at compared from this and this; this is because of the agglomeration. So, one can get the idea if you have a transmission electron micro graph. So, you can get the structure or you can get the idea about the composition of the matter.

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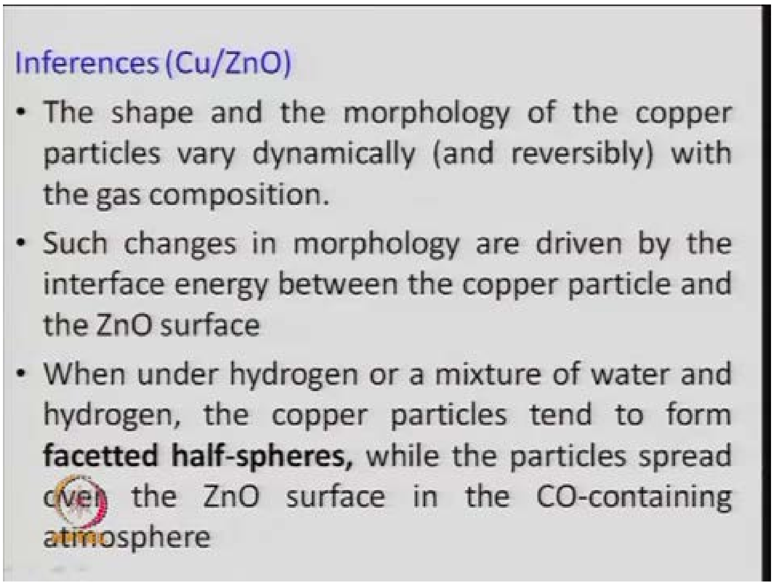

Inferences (Cu/ZnO)

- The shape and the morphology of the copper particles vary dynamically (and reversibly) with the gas composition.
- Such changes in morphology are driven by the interface energy between the copper particle and the ZnO surface
- When under hydrogen or a mixture of water and hydrogen, the copper particles tend to form **facetted half-spheres,** while the particles spread over the ZnO surface in the CO-containing atmosphere

So, this is what the inferences from this the shape and morphology of the copper particle that vary dynamically and reversibly with the gas composition. So, depending upon the gas composition it is changing; because the it is chemically reactive gases which have been gases which have been centroid. So, depending upon the adsorption or chemisorption stronger or weaker; so there can be a change in the surface structure. So, such changes in morphology are driven by the interphase energy. So, that is what related to the wolf construction and can be used to determine the structure. Because the gamma is proportional to the distance surface energy the structure if I say that formal something like this.

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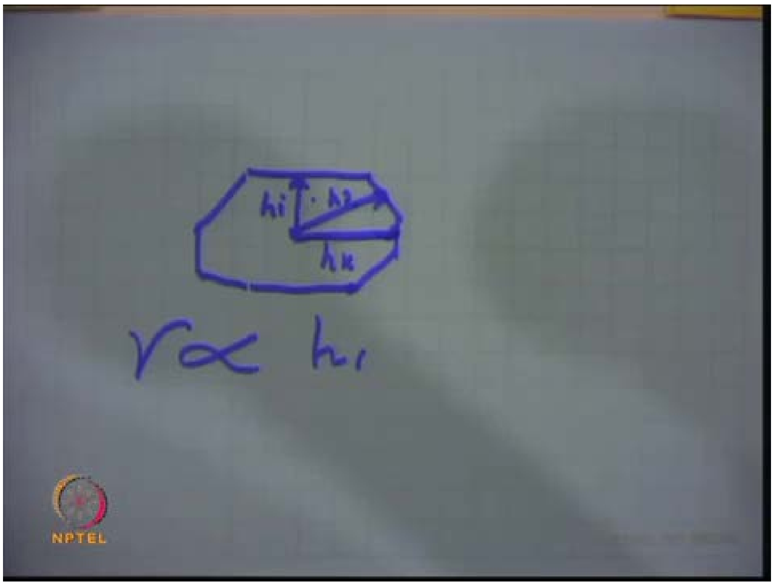

If you have a structure like this; so, are measuring distances from this, distance this, distance this? So, this is what if I am saying this is h i, this is say h j, this is say h k; so, energy, surface energy gamma is proportional to distance of this h i or h j or h k. So, if this distance is high; so you are larger. So, it means the gamma will be larger than this one and than this one. Then, you can have that how this surface is forming. So, depending upon these distances the surface energy is different of each plane; so this plane, this plane, this plane and so on, so on. So, you can get the idea about the crystal geometry. So, crystal geometry plays a very important role during catalytic activity. So, that is what the nano particles when you are saying its shape is changing basically.

So, as I discussed here also that under hydrogen or mixture of water and hydrogen the copper particles tends to form facetted half spheres; while the particle is spread over zinc surface in the carbon monoxide containing atmosphere. So, the gas environment also changes the structure of the metal; it can change the structure of the metal.

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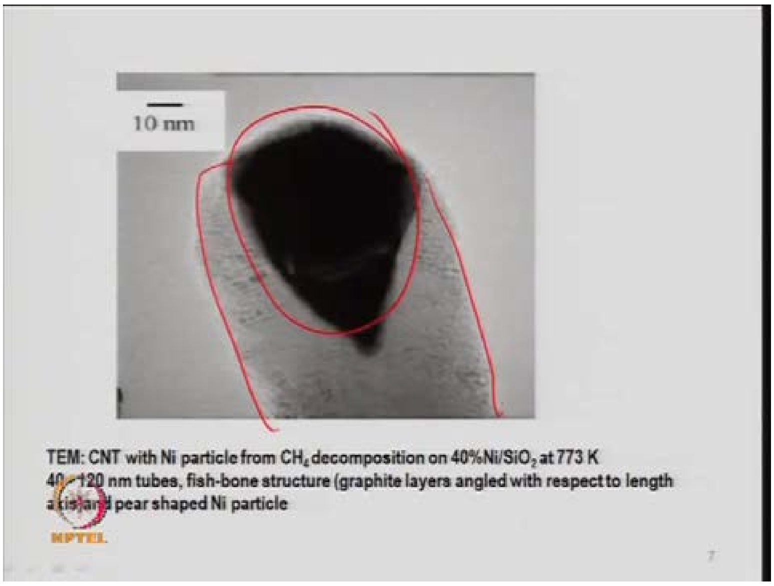

TEM: CNT with Ni particle from CH_4 decomposition on 40%Ni/SiO_2 at 773 K
40-120 nm tubes, fish-bone structure (graphite layers angled with respect to length axis) and pear shaped Ni particle

So, this again another picture just which shows that, this is a nickel particle. Basically, the catalyst which have been used here is nickel silica, nickel on silica support and then, the methane decomposition reaction has been carried out. So, after reaction also you can get that what structure has been formed. So, this is a nickel particle and you can see that it is not spherical in shape. So, the shape of the nickel; so, the nickel particle is here. Because it is so you are looking at a black and this is nothing but the carbon which is deposited on the nickel.

So, nickel on nickel the carbon is growing in the form of fiber. So, that is another interpretation which you can get from the transfer electrons spectroscopy that or microscopy. What surface or what type of carbon material has been formed after the reaction on a metal and how does it grow on the surface of the metal? So, topology and the morphology or structural composition of the catalyst before and after the reaction can be compared by using transmission electron microscopy.

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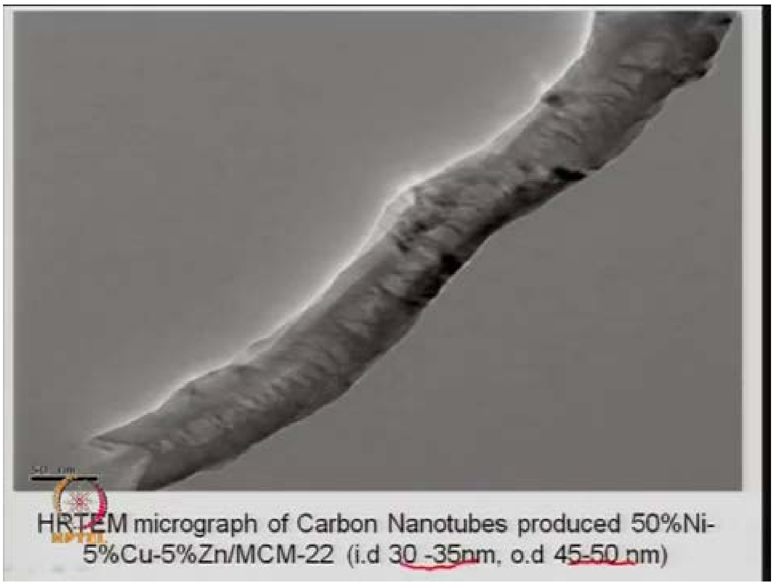

HRTEM micrograph of Carbon Nanotubes produced 50%Ni-5%Cu-5%Zn/MCM-22 (i.d 30 -35nm, o.d 45-50 nm)

This is another picture, if you have high resolution transmission electron microscopy at high energy. So, you can check the structure of the carbon which has been deposited on the catalyst. So, you can see here, that it is a kind of nano tubes; and it can be just that if you just look at the closer picture there are different layers of the carbon inside. So, that can give you the idea about that if you have one A type catalyst, B type catalyst; so you can get the idea about their i d, o d. So, this is the internal diameter of the carbon nano tube and this is the outer diameter of the carbon nano tube.

So, one can predict that there are two layers right or it can be a multi walled carbon nano tube; if you go further analysis of this fighting structure of the carbon. So, one can the idea about these kind of structural changes the morphology of the carbon formed during the reaction or similar other observation from transmission electron microscopy.

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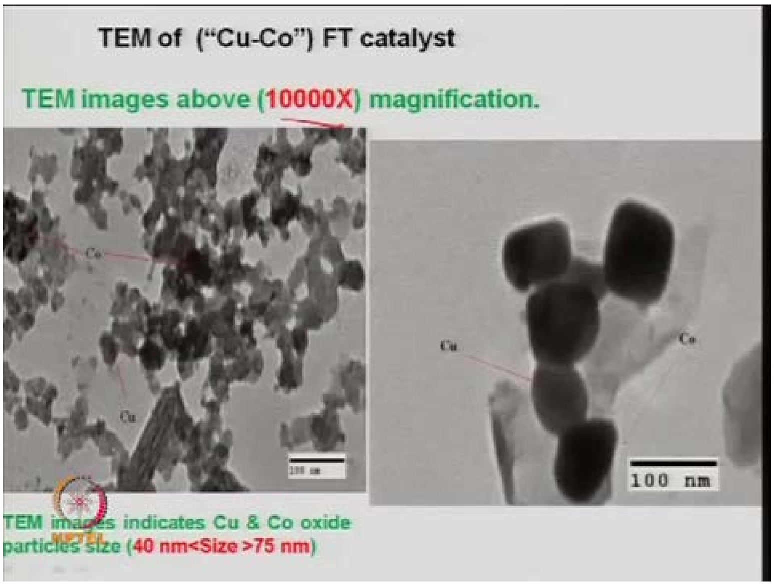

TEM of ("Cu-Co") FT catalyst

TEM images above (10000X) magnification.

TEM images indicates Cu & Co oxide particles size (40 nm<Size >75 nm)

This is the another example where the copper cobalt catalyst has been used for Fischer Trop reaction. So, by looking if you just go through that and then, take a closer picture at a higher magnification. So, this is your copper particle, these are your cobalt particle; so, copper has come in between in the cobalt particle if you look at. And, then can interpret that the dispersion is high or low if the cobalt particles are together, they may agglomerate during reaction which may not be good for the Fischer Trop reaction.

But if you have the promoter copper which is acting here as a promoter; so, small concentration of copper may enhance that dispersion. So, one can interpret that why dispersion of cobalt increased in the addition of in the presence of copper on the catalyst. So, this kind of analysis can be provided by doing this transmission electron micro.

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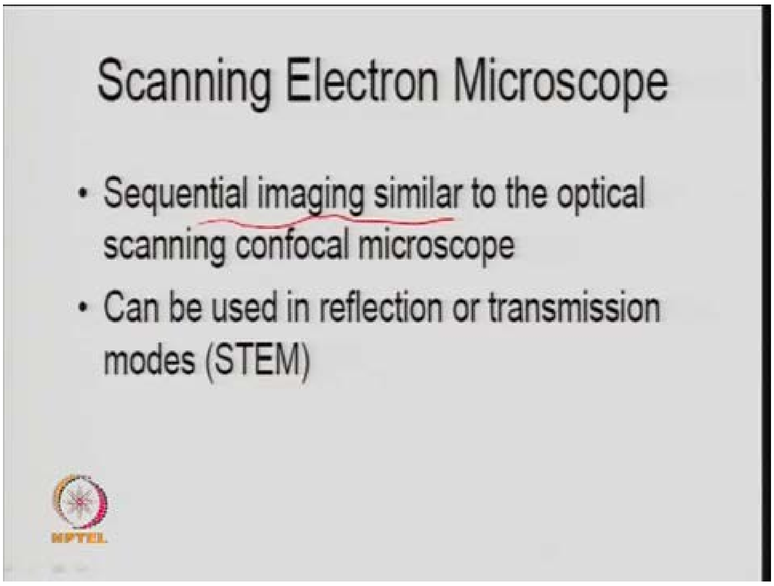

Scanning Electron Microscope

- Sequential imaging similar to the optical scanning confocal microscope
- Can be used in reflection or transmission modes (STEM)

Similarly, scanning electron micro graph; so, here again the fundamental things are same. That is again we are using the electron beam but these are secondary kind of electron or back scattered electron or it can be a X ray also. So, this can be associated with X ray diffraction also, we call it E D X energy dispersive X ray analysis. So, here again sequencer energy, which is similar to optical scanning confocal microscope. So, just like an your optical microscope you do you take a picture. So it is just a picture of that surface but using the electron not the light source photos of other low energy sources. So, this can be used in reflection or transmission mode; so, whatever different approaches can be used here.

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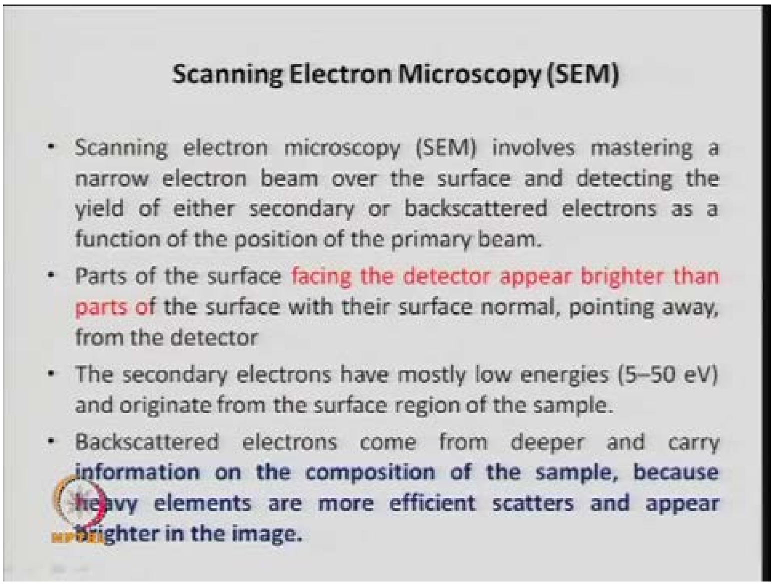

Scanning Electron Microscopy (SEM)

- Scanning electron microscopy (SEM) involves mastering a narrow electron beam over the surface and detecting the yield of either secondary or backscattered electrons as a function of the position of the primary beam.
- Parts of the surface facing the detector appear brighter than parts of the surface with their surface normal, pointing away, from the detector
- The secondary electrons have mostly low energies (5–50 eV) and originate from the surface region of the sample.
- Backscattered electrons come from deeper and carry **information on the composition of the sample, because heavy elements are more efficient scatters and appear brighter in the image.**

So, the principal wise if you look at the scanning electron microscopy involves mastering in narrow electron beam over the surface. And, detecting the yield of secondary or back stroke, back scattered electron as a function of the position of the primary beam. So, it may be a diffracted beam, depending upon the orientation of the metal on the catalyst and the beam which strikes on that. So, depending upon that the it may be diffract; so, the diffraction be energy can be measured it can be back scattered. So, the energy of these secondary beams or back scattered electron can be measured.

The part of the surface, facing the detector appears brighter than, the part of the surface with their surface normal pointing away from the detector. So, you will have something like a bright image, in the case of scanning electron micro graph. So, it is a diffracted from the surface of the matter; the secondary electrons roughly they have the energy between 5 and 50 electron volt; these originate from the surface region of the sample.

So, once you measure the energy this is same, fundamental thing is same; that we are using the energy of these beams, kinetic energy of the beam and then correlating. Because different metal have different property, depending upon their property or electronic configuration the energy of this refracted beam will change. So, back scattered electron; generally they come from deeper end carry information on the composition of the sample. Because heavy elements are more efficient scatters and appear brighter in the image. So, again when you have the beam, the electron beam; the diffraction or it comes from its secondary or the lower level of the atom.

So, back scattered electron, secondary electron; what you have seen the case of x space also. So, the electrons are here used other than the protons. So, x sphere, like x spheres or like your TEM, the SEM can also be used for determining the composition. But the TEM gives you whole mass of the sample 2 d image; you will not get here that kind of image in the scanning electron. So, it is because it is just like a picture pictorial diagram microscopic view of that surface.

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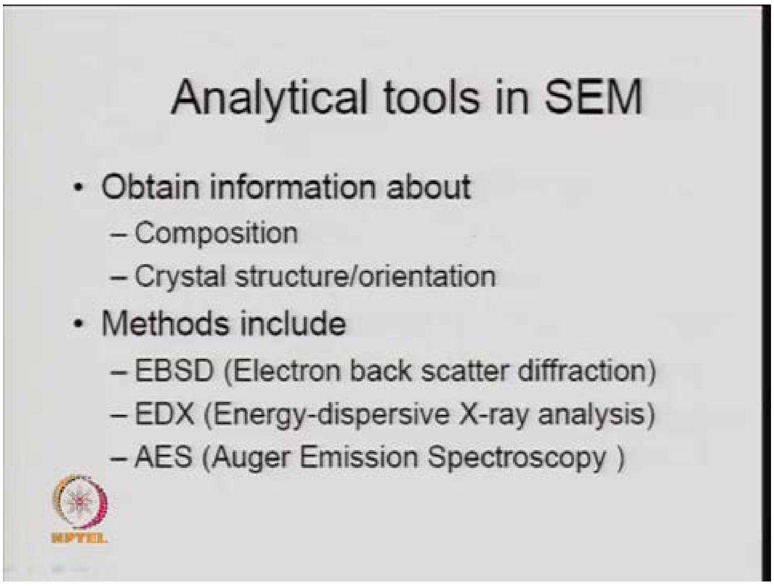

Analytical tools in SEM

- Obtain information about
  - Composition
  - Crystal structure/orientation
- Methods include
  - EBSD (Electron back scatter diffraction)
  - EDX (Energy-dispersive X-ray analysis)
  - AES (Auger Emission Spectroscopy)

So, the composition crystal structure orientation these can be obtained. And, these are based on as I said electron back scatter back scattered effects; E D X energy dispersive X ray analysis which can give you the composition of the surface only the point wise, a different points you can determine the surface composition. And, then you can just take the average; so, it can give you over all composition on the surface of the metal. If you have, a different locations otherwise it can be localized also; this may not be correct result if you use SEM E D X for determining the chemical composition. And, auger electron emission because again these are the second year back scattered electrons auger electrons. So, can you have the information regarding the auger electrons also?

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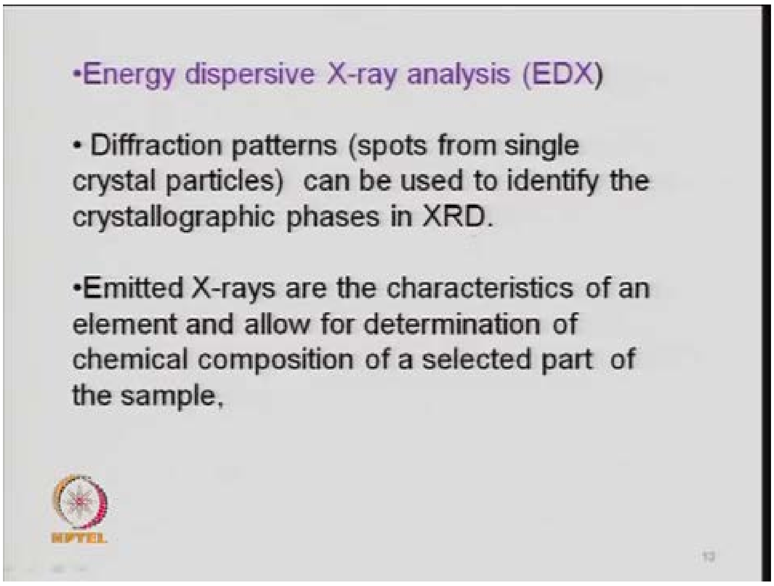

- Energy dispersive X-ray analysis (EDX)
- Diffraction patterns (spots from single crystal particles) can be used to identify the crystallographic phases in XRD.
- Emitted X-rays are the characteristics of an element and allow for determination of chemical composition of a selected part of the sample.

So, in E D X as I said, the SEM E D X can be connected together. And, because X ray sources which come from the surface that there energy and they can look at the diffraction from the surface at different wavelength. So, the diffraction pattern which is spots from single crystal particles can be used to identify the crystallography phases in X R D. So, just like your here you can use this information for determining the chemical composition in X R D you just get the phases.

So, the emitted X rays are characteristics of an element and allow for determination of chemical composition of a selected part of the sample so that is the difference. Because the intensity, light intensity which you have in X ray the wavelength is fixed. When you do the X ray diffraction you use a copper potassium for radiations 1.5 Armstrong in which to here, the wavelength can also be varied; so, in that energy dispersive reaction.

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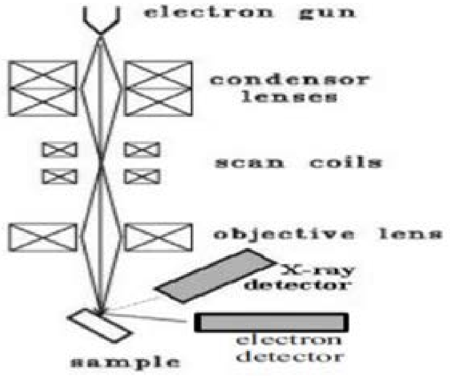

SEM / EDX

[Adapted from Text Book Ref. : I. Chorkendorff, J.W. Niemantsverdriet Concepts of Modern Catalysis and Kinetics, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30574-2]

Is just a picture that, the you have a source of energy beam, electron gun and there are condenser lens to get the monochromatic energy, mono energetic beam. And, then the scan coil which passes through the objective lens the sample is placed here. In TEM, you place samples somewhere here, but sample is placed here; so, the diffraction comes. So, which may be if it is a X ray then X ray detector like E D X electron detector. So, you measure the energy of these electrons and then information can be transmitted in terms of the phase composition, structural composition, particle size, morphology. So, that the particle is spherical in size or irregular right cylindrical in shape.

So, all this kind of information, agglomeration of the particle after reaction. So, these information can be obtained from SEM; if you do SEM E D X, then you can find out what is the percentage of position in your catalyst, what is the percentage of sodium or any other metal also? But as I said, it is a point or line enhancive not for the whole surface you cannot take just from one set of data. So, at one point the composition may be very high but at the other point it may be 0. So, then, the there may be error.

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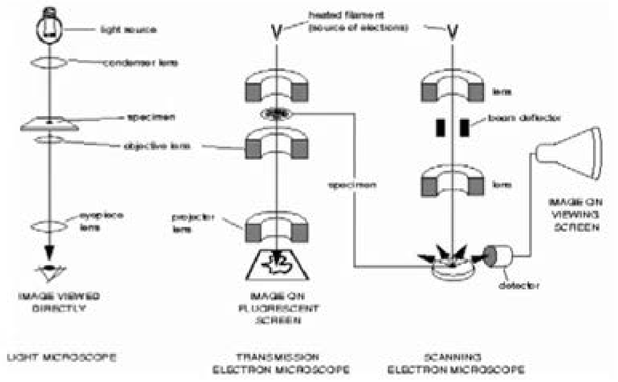
Transmission Electron Microscope



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So, this is just a comparison, among all these methods but SEM TEM and optical microscope. So, this is just an optical microscope you have a light source, where you have a condenser lens. And, then you have a specimen samples placed here; then, objective beam you have a eye piece here. So, you can look at your; the property of the sample which can be transmitted to a computer. And, you just take the data, you just picture, if your particle is larger in size it can do with certain magnification 50 times, 100 times something like that. So, just like a micro scope but here you use the electron beams whether it is TEM or SEM. So, this your TEM transmission electro micro graph and this is your SEM.

So, your sample and TEM is placed here. So, this is the sample spaceman and in this case the sample is placed here. And, the other things if you look at you have a lens here and another lens here also. You have a beam deflected here, because you are looking a deflection patterns of these. So, this is sent to here then diffracted or X ray beam and then, you have the star detector then image on view screen.

So, you can look at the composition of the particle and that can be a different magnification. So, in SEM or TEM can go up to magnification of 10 to the power five or 10 to the power 6 also? In the time also, you had the same thing specimen; so, then this is a projector here and then, you have the image on fluorescent screen. So, that can be viewed and you can get the composition of surface analysis.

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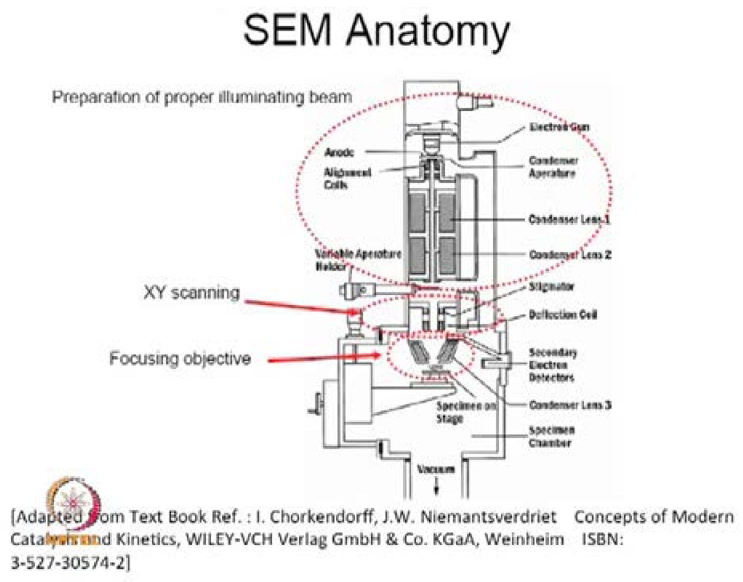

SEM Anatomy

[Adapted from Text Book Ref. : I. Chorkendorff, J.W. Niemantsverdriet Concepts of Modern Catalysis and Kinetics, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30574-2]

Anatomy, the structure wise; the, again; so, electron gun the source may be cathode rays or different type of beams, anode, condenser lens; the condenser lens 1 condenser lens 2 to get the monochromatic beam, energy beam and then, you have a variable aperture here. This is connected to vacuum; so, vacuum is very high 10 o minus 5; 10 above minus 10 o minus 5 to 10 o minus 6 milli bar very low vacuum. And, this is the specimen placed here, so diffraction takes place and these are the measured deflection cells to measure that. So, secondary electron beam detector condenser lens 3 whatever the diffraction transmission from here; so, you can measure the different properties of the secondary electron back scattered electron or X ray. So, energy of these or intensity can be measured and that can be collated for the surface composition.

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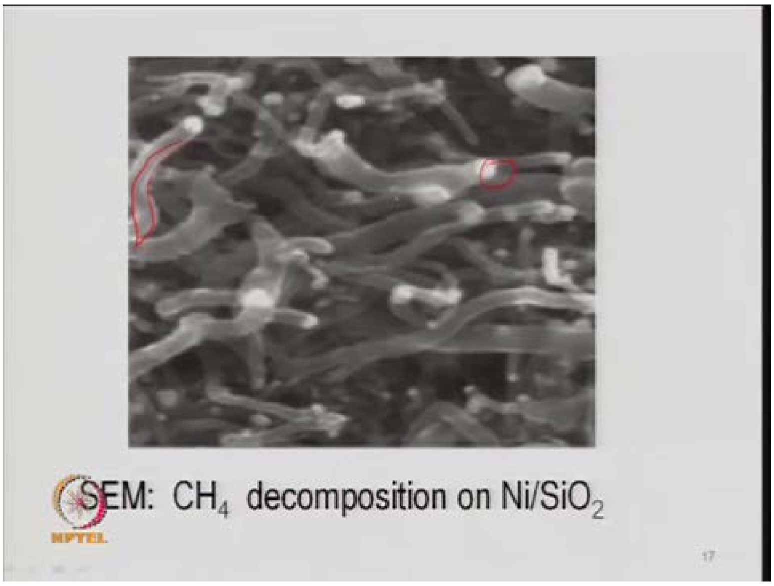

SEM: CH_4 decomposition on Ni/SiO_2

So, this is just what kind of information you get; on the same catalyst nickel earlier, the transversal electron micrograph. So, this is the scanning electro micrograph picture. So, these are the nickel particles and this growth which has taken place like this is your carbon fiber; carbon nano tube is grow on the metal surface. So, white spot is nickel because I said here; you get a brighter image, in TEM it was the darker image. So, then, the growth of this diameter can you find out, particle size can be find out; so, these information can be obtained from scanning electron micrographs.

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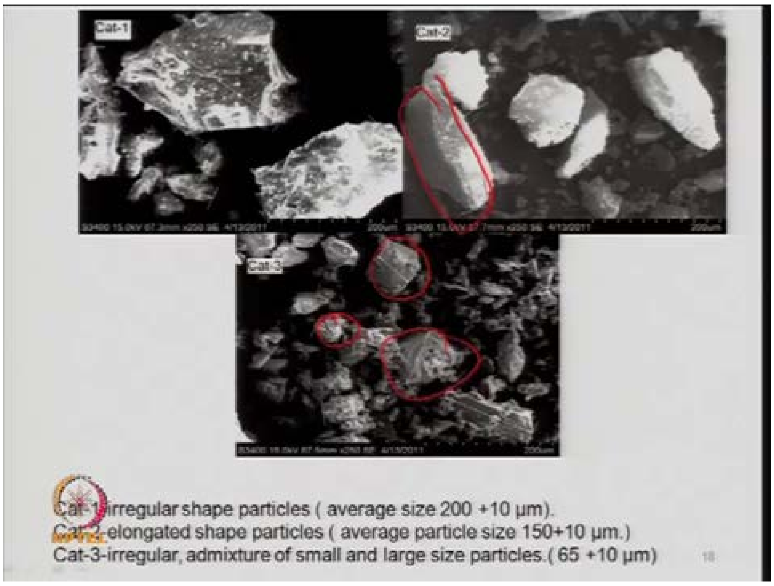

Cat-1-irregular shape particles (average size 200 +10 µm).
Cat-2-elongated shape particles (average particle size 150+10 µm.)
Cat-3-irregular, admixture of small and large size particles.(65 +10 µm)

So, similarly this, you can see the different catalyst and they can compare their structure; so, it is mentioned here that irregular shape particles here; you cannot see any crafted shape here; so, these are the irregular shape particles of the catalyst. The second one is something like elongated, in lengthwise it has increased like this, elongated shape particles; which is average size particle of 150 micron. Third one is again, irregular at mixture of a small end large particle. So, there are some particles small in size; but there are other particle which are larger in size. So, one can interpret these information from the scanning electron micro plier ((Refer Time: 23:05)).

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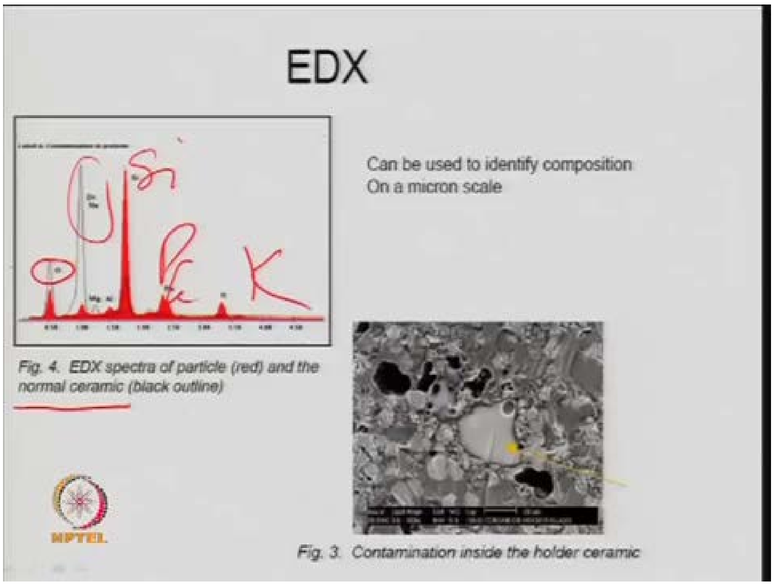

EDX

Can be used to identify composition
On a micron scale

Fig. 4. EDX spectra of particle (red) and the normal ceramic (black outline)

Fig. 3. Contamination inside the holder ceramic

When you do E D X; then, you can have the composition also like oxygen, zinc, sodium, silicon like this lead, potassium. So, this is for a ceramic material like red particles which have been showed here the E D X spectra of the particle; so, one can end this black out line these are just for the normal ceramic material this it. So, by doing this sum E D X you can distinguish from the original material or original support and the when the metal has been impregnated. And, you can compare what changes have occurred on the surface? When those metals have been loaded or compositions of the different metals have been loaded. So, compression can be made but as I said that this will be just a point analysis or a line analysis; it cannot be taken considered for the whole surface. You have to do this at different point or different position and then take the average.

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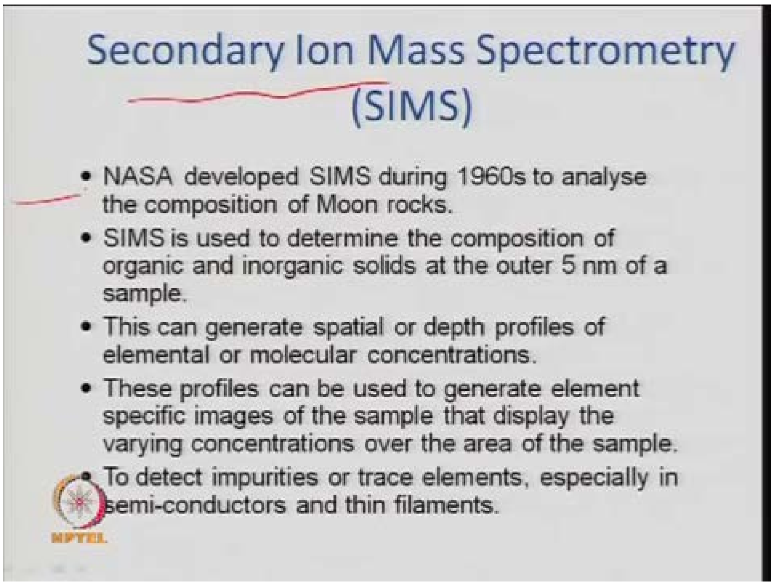

Secondary Ion Mass Spectrometry (SIMS)

- NASA developed SIMS during 1960s to analyse the composition of Moon rocks.
- SIMS is used to determine the composition of organic and inorganic solids at the outer 5 nm of a sample.
- This can generate spatial or depth profiles of elemental or molecular concentrations.
- These profiles can be used to generate element specific images of the sample that display the varying concentrations over the area of the sample.
- To detect impurities or trace elements, especially in semi-conductors and thin filaments.

The another characterization is based on ion technique. And, the important one is the secondary ion mass spectrometry. So, the first this one we were talking so far same time based on electron guns earlier we were talking about photons or X rays beams. So, this is another one and had become one of the most important tools for the characterization of the catalyst; again it can talk about oxidation state also, just like mass above spectroscopy.

So, this was first developed by NASA in 1960 just to analyze the composition of the moon rock. So, the composition may be different silicates, calcium, aluminates; so, this kind of composition. So, later on this has been used or developed for the catalyst also. So, secondary ion mass spectroscopy as the word says secondary ions not the primary ions; which have just from the lower surface of the atom; the ions which have come from the lower.

So, it is used to determine the composition of organic and inorganic solids at the outer 5 nanometer of a sample to that duct is flew 50 Armstrong, 5 nanometer; this can generate a special or duct profile of element or molecular concentration. So, information can be obtained for a catalyst up to certain depth and the profiles can be used to generate element specific of the sample. Then, display the varying concentration over the area of the sample. So, different locations you can find out the compositions or the oxidations states of the catalyst or whatever the surface which is formed or created during the preparation. So, the imputation can be determined. So, semiconductors and thin filaments if you have materials like that then, you can find out the impurity also.

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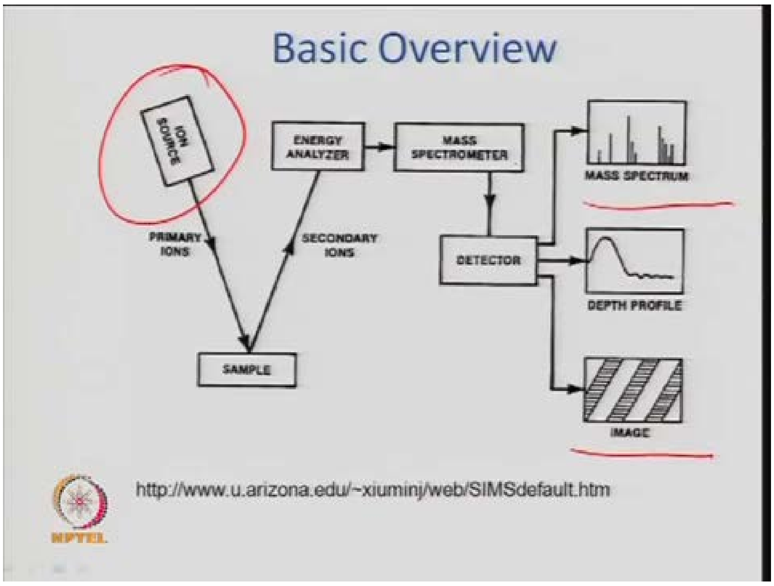

Basic Overview

http://www.u.arizona.edu/~xiuminj/web/SIMSdefault.htm

So, principal as moral as same that in instead of the electron beams your SEM ion source which is primary ions they just strike on the sample. And, then you have some secondary ions like those, like backscattered ions and detracted ions. And, then they are taken to an energy analyzer and which is connected to a mass spectrometer and mass spectrometer is connected to the detector. And, then you can have the spectrum of those compounds the ions which have been eradicated from the surface of a solid or catalyst. So, you can see the depth profile also, you can see the image also. So, all these information can be used from this.

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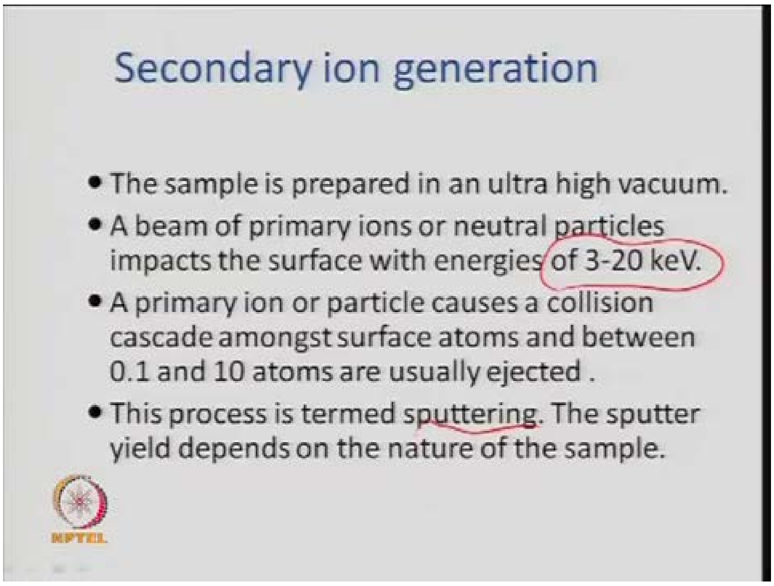

Secondary ion generation

- The sample is prepared in an ultra high vacuum.
- A beam of primary ions or neutral particles impacts the surface with energies of 3-20 keV.
- A primary ion or particle causes a collision cascade amongst surface atoms and between 0.1 and 10 atoms are usually ejected .
- This process is termed sputtering. The sputter yield depends on the nature of the sample.

So, generation of the secondary ion that is the first thing. So, sample is prepared in a ultra high vacuum; very high vacuum is required for the process; the beam of primary ions or neutral particles they impact on the surface with energy 3 to 20 kilo electron volts. So, roughly the primary ions have the energy of ordered or from vary from the 3 to 20 kilo electron volt. So, primary ion particles cause collision; cascade among a surface atom and between 0.1 and 10 atoms are usually ejected; roughly 10 percent of the atoms are ejected from the surface or which are the secondary ions.

Because it depends on the type of the surface, it depends on the energy of the primary ion. And, then these are a kind of backscattered ion which comes from the top first top layers. So, first, second, a third layer of the atoms and the process is known as sputtering; the sputter is depend on the nature of the sample. So, depending upon the nature of the sample; you have different kind of secondary ions and once, you measure their energy or their intensity then, you can correlate with the surface or the metal.

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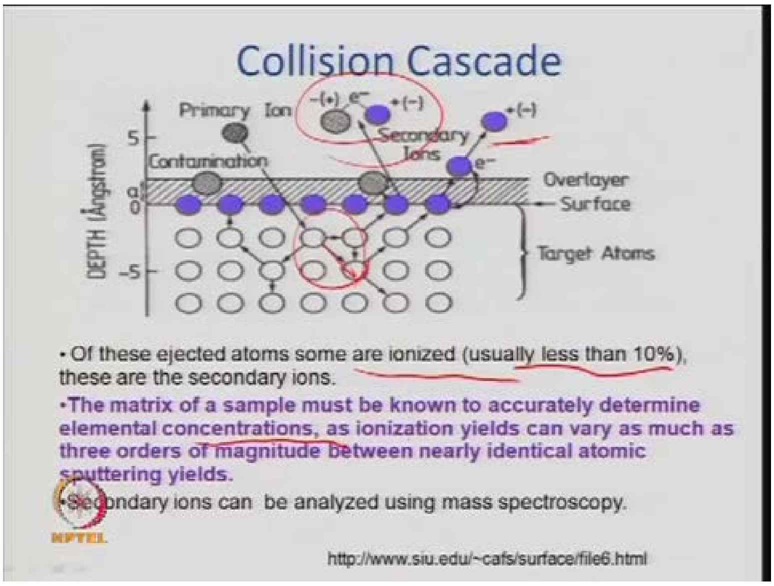

Collision Cascade

- Of these ejected atoms some are ionized (usually less than 10%), these are the secondary ions.
- **The matrix of a sample must be known to accurately determine elemental concentrations, as ionization yields can vary as much as three orders of magnitude between nearly identical atomic sputtering yields.**
- Secondary ions can be analyzed using mass spectroscopy.

http://www.siu.edu/~cafs/surface/file6.html

This is just a picture of collision cascade. So, primary; and so, this is the surface over layer or surface and these are the atoms; so, when it strikes they collide among themselves. So, this is what the kind of collision. And, then you get secondary ions because of the collision among these atoms; and then these atoms leave the surface. So, negative electron and then this positive.

So, these secondary ions and these energies which come from the primary ions, because of the primary ion; we strikes on the surface and collide. So, they come out and energy is measured. So, this is what the target atom; so up to this 5 nanometer depth; one can measure the information on the surface or metal. So, of these ejected these atoms some are ionized which are roughly less than 10 percent as I said; and these are known as secondary ions.

So, the energy which is of the energy of these ions which are roughly not more than 10 percent; the matrix of the sample must be known to accurately determine elemental concentration. So, you should know some priory information about the metal; because that you know based on your preparation. But metal has been taken what salt have been, salts have been taken for the preparation of the catalyst. So, these are known based because it is a kind of dictionary from where you have to short list; which component is like you do in your GCMS also, gas chromatography, mass spectrometry or any other chromatography.

So, you should have some prior information about the sample and this can because once you know that. So, you can get the idea about the elemental concentration as ionization yield can vary as much as 3 orders of magnitude between nearly identically atomic sputtering field. Because the; that is what the very crucial that, you have to differentiate, you should be able to differentiate between the closer atoms or closer ions which come out. Because once if you have 2 very close atoms; the property of the second hand will also be similar.

Then, you should be able to distinguish them; same thing in the any analysis. When you have a just like an X ray also I told you that JCPDS is generally one of the package which is used. But there also, that B value will be very closer you have to just ensure. And, you have to be very careful when you identify; same thing in GCMS also and same thing here also. So, secondary ions can be analyzed by using the mass spectroscopy.

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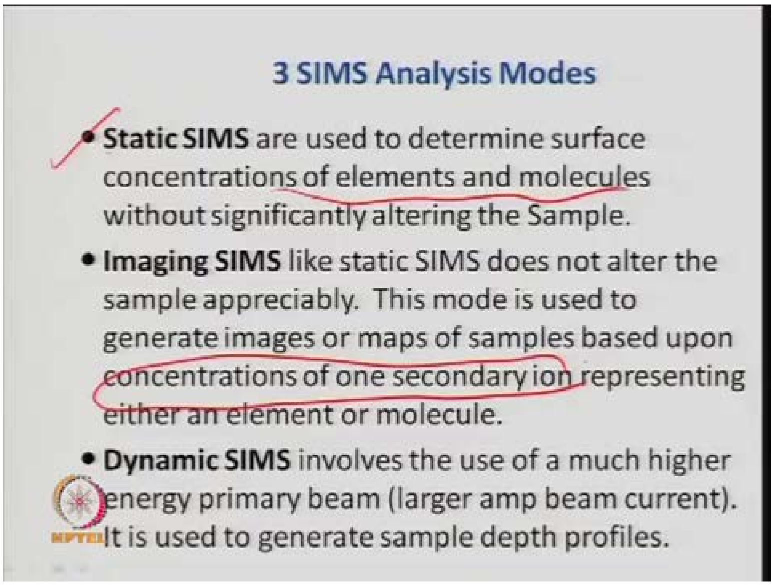

3 SIMS Analysis Modes

- **Static SIMS** are used to determine surface concentrations of elements and molecules without significantly altering the Sample.
- **Imaging SIMS** like static SIMS does not alter the sample appreciably. This mode is used to generate images or maps of samples based upon concentrations of one secondary ion representing either an element or molecule.
- **Dynamic SIMS** involves the use of a much higher energy primary beam (larger amp beam current). It is used to generate sample depth profiles.

There can be different types of SIMS; so, static SIMS, imaging SIMS or dynamic SIMS. So, imaging the name says that, basically this imaging will give you the picture; just like an MRI image it talks about the picture of that structure of the surface; it takes the image.

But static SIMS; this is used to determine the surface concentration of elements, molecules without significantly altering the sample. So, you can get the composition by using this method; static SIMS; so, most of the time we use this for the catalytic purpose. Imaging SIMS like static SIMS does not alter the sample too much; this mode is used to generate images or maps of the samples based upon concentration of one secondary ion representing either an element or molecule. So, it takes the image of that surface rather talking in terms of p which you get in the form of concentration; it will image that just like your transmission electron micrograph.

So, you can look at the composition or you can get the idea about the morphology or topology of the surface. Dynamitic it in SIMS involves the use of much high energy primary beam which is a larger ampere beam current; and it is just used to generate sample depth profiles. If you need in depth analysis then, the dynamic secondary ion mass spectroscopy method is used; most of the time the static SIMS is used to determine the concentration or composition of the surface.

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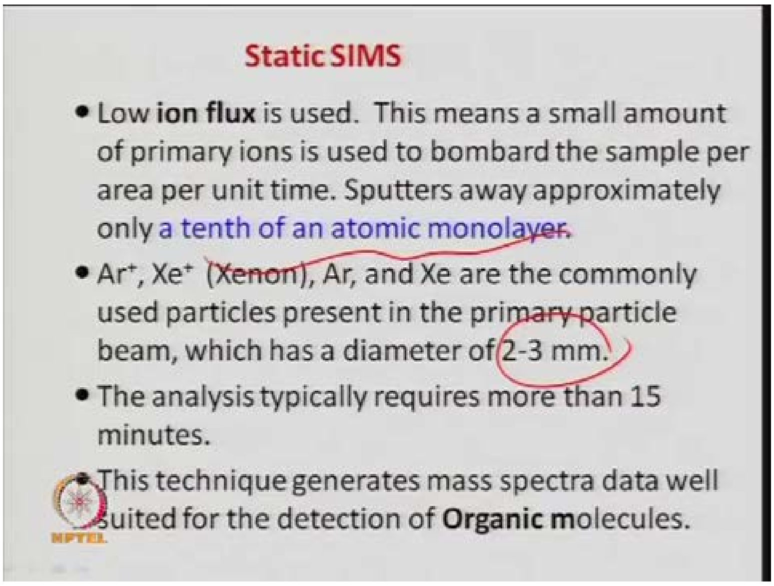

Static SIMS

- Low **ion flux** is used. This means a small amount of primary ions is used to bombard the sample per area per unit time. Sputters away approximately only a tenth of an atomic monolayer.
- Ar^+, Xe^+ (Xenon), Ar, and Xe are the commonly used particles present in the primary particle beam, which has a diameter of 2-3 mm.
- The analysis typically requires more than 15 minutes.
- This technique generates mass spectra data well suited for the detection of **Organic m**olecules.

So, in the static SIMS low ion flux is used. So, what is it mean that; small amount of primary ions is used to bombard these sample per area per unit time. That is what is call ion flux, to bombard the sample per unit area per unit time is known as ion flux; sputters away approximately only one-tenth of an atomic monolayer. So, the depth will be small here in this case; so, one-tenth of an atomic monolayer information can be obtained; when you have this kind of ion flux, low ion flux. So, argon, xenon, argon in terms of the form of the ions or argon and xenon are commonly used particles; they are present in the primary particle beam; and which has the diameter roughly 2 to 3 millimeter. So, these kinds of sources are used for this ion mass spectroscopy. The analysis typically requires the more than 15 minutes; so not too must time is taken here. And, technique generates mass spectra data well suited for detected for organic molecules. So, this just an information which I am providing that; what methods can be used for characterization of a surface. So, I am not going depth analysis of these methods or I am not going in chemistry or physics of the atoms or the instrument.

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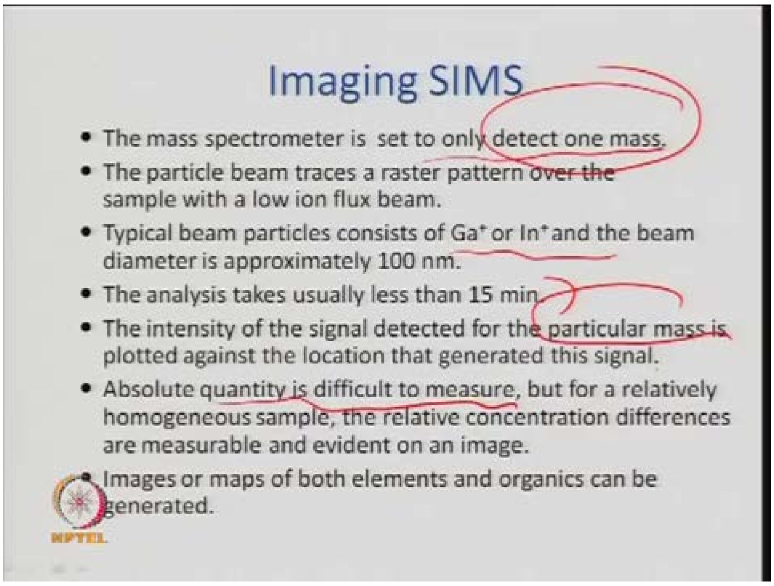

Imaging SIMS

- The mass spectrometer is set to only detect one mass.
- The particle beam traces a raster pattern over the sample with a low ion flux beam.
- Typical beam particles consists of Ga^+ or In^+ and the beam diameter is approximately 100 nm.
- The analysis takes usually less than 15 min.
- The intensity of the signal detected for the particular mass is plotted against the location that generated this signal.
- Absolute quantity is difficult to measure, but for a relatively homogeneous sample, the relative concentration differences are measurable and evident on an image.
- Images or maps of both elements and organics can be generated.

So, imaging is another method as I told. So, by using SIMS; so mass spectrometer here is set only to detect one mass; the particle beam traces a raster pattern over the sample with low ion beam as in SIMS. And, typical beam particles here, it consists of gallium or indium ion and the beam diameter is approximately 100 nanometer here. So, you can take the image with that; the order on 100 nanometer. Again, time taken is just 15 minute or even less than 15 minute. The intensity of signal detected for particular mass is plotted against the location that generated in this by this segment. So, basically again just like a transmission electron micrograph; you take the image of scanning electron micrograph. So, here the images are generated rather than the concentration.

So, the intensity of the signal detected of a particular mass is plotted. So, it is based on mass to mass basis. So, particular mass is very important here, that we are talking mass to mass basis; is plotted against the location that generated this signal. So, that is co related with that. And, absolute quantity is difficult to measure but for a relatively homogeneous sample the relative concentration differences are measurable and evident on an image.

So, one can differentiate between the 2 soft phases very easily; with one surface you cannot get the idea about the composition just from the image. So, if you have 2 before reaction, after reaction or catalyst A; with A type of composition behind catalyst view different composition with slight modification. So, you can have the image just like a new transmission electron micrography of SIM. But this one can give you some in depth analysis also; unlike, NA transmission micrograph.

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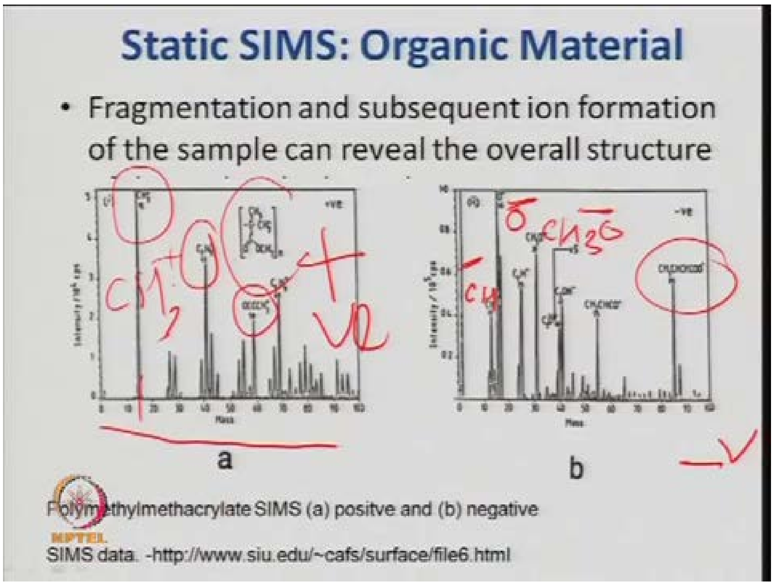

Static SIMS: Organic Material

- Fragmentation and subsequent ion formation of the sample can reveal the overall structure

Polymethylmethacrylate SIMS (a) positve and (b) negative

SIMS data. -http://www.siu.edu/~cafs/surface/file6.html

It is just a picture for statics SIMS. So, in statics SIMS you just get the; just a different mass, atomic mass units and versus the intensity. So, one can just like an gas crude grapy and mass spectrometry one can co relate these with their corresponding; say positive ions or either the negative also. This is for positive and this is for negative and same compound polyethylene, methacrylate, SIMS.

So, structure can be determined by understanding these because at different mass, you are getting the composition which may not be visible right now but this is just like O negative here. This is your C H negative, this is your C H 3 O negative. Here, if you look at here this is your C H 3 plus. So, one can co relate this positive and negative; and then can co relate it with the composition. So, this just a one chemical composition and same thing can be done; when you have a catalyst material. So, these kind of peak can be co related with the composition of the metal.

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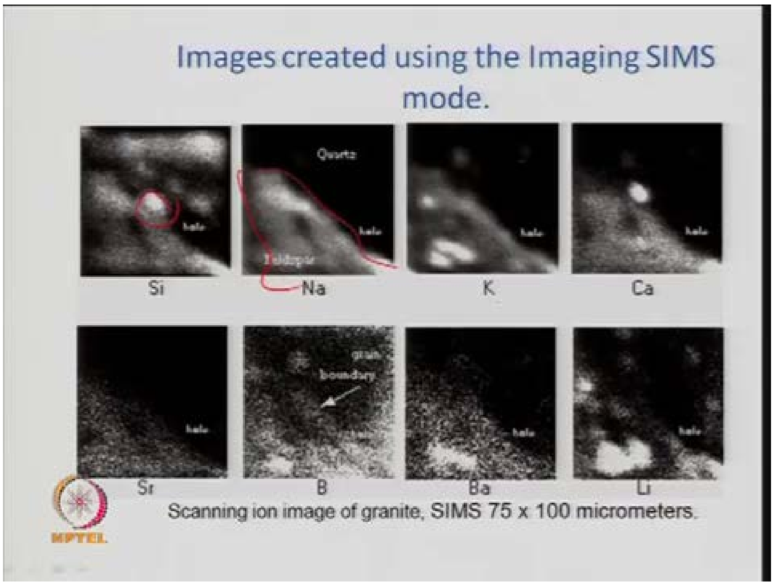

Images created using the Imaging SIMS mode.

Scanning ion image of granite, SIMS 75 x 100 micrometers.

And, when you look at the image; you can get the image something like this. So, this is just for a quartz material, feldspar; you can see the image like this, white spots like this. So, you can compare for sodium this, silicon this, potassium this, and this will come appear at different for a particular say I told mass unit. So, at different location you have this kind and that is related to the mass of that sample. So, these images can be co related when you have A and B. So, I can very easily distinguish between sodium and potassium because appear a different mass. So, one get this information which is similar to transmission electron micron but here it can be in depth also. So, you can get the idea about the composition of the or surface structure or morphology of the surface and in depth up to certain depth.

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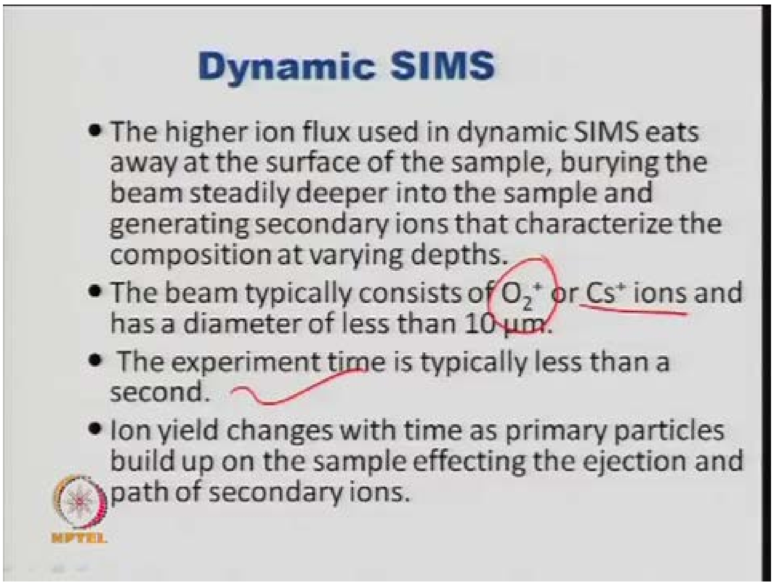

Dynamic SIMS

- The higher ion flux used in dynamic SIMS eats away at the surface of the sample, burying the beam steadily deeper into the sample and generating secondary ions that characterize the composition at varying depths.
- The beam typically consists of O_2^+ or Cs^+ ions and has a diameter of less than 10 µm.
- The experiment time is typically less than a second.
- Ion yield changes with time as primary particles build up on the sample effecting the ejection and path of secondary ions.

Same thing for dynamic also; when you have dynamic SIMS the higher flux ion is used compared to the static or image SIMS. So, here it is high flux; and this eats away at the surface of the sample, burying the beam, steadily deeper into the sample and generating secondary ion that characterize the composition at varying depth. So, this is much more appropriate or much more in depth analysis. But you need a high energy beam for this kind. So, here the beam typically, consists of oxygen plus or cesium plus ions which has a diameter of less than 10 micron.

So, these are related to the diameter of this primary beam ions the earlier case it was the order of millimeter, nanometer like that. So, different beam diameter. So, and then you can get the analysis of the surface. So, the experiment time here it is less than a second; so, very quick response you get from this dynamic method. And, ion yield changes with time as primary particles build up on the sample effecting the ejection and path of the secondary ions. So, this can be used to get the complete composition of the surface. So, I am not going in details of this but these methods can be used for characterization of the sample.

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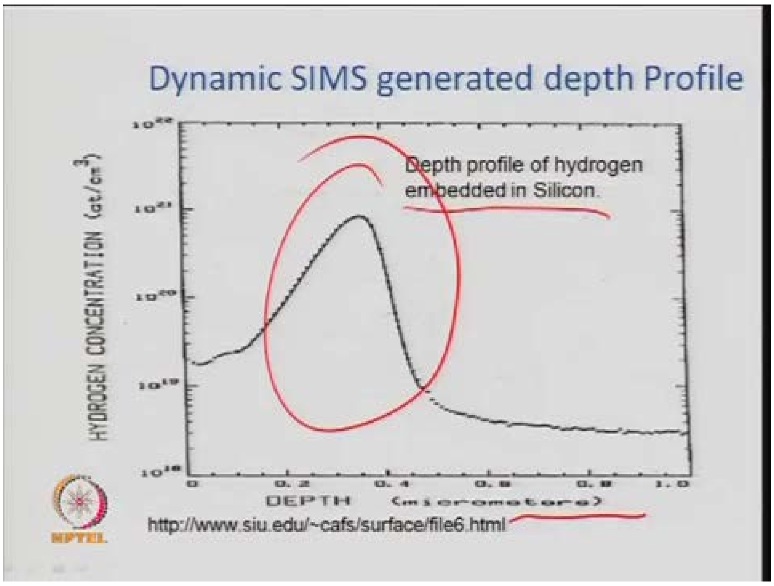

Dynamic SIMS generated depth Profile

Depth profile of hydrogen embedded in Silicon.

http://www.siu.edu/~cafs/surface/file6.html

So, this is what the response you get, in terms of the depth in micro meters here, 0.2, 2.4; so this is depth profile of hydrogen embedded in silicon. So, you can get the information in terms of the at what depth the hydrogen has penetrated on the surface. So, just like in chemisorptions you get so once you have done chemisorption you can do this; and then you can get the idea about the metal support interaction also.

These information useful; when you look at your hydrogen fill over on the catalyst or the metal support interaction, when we say there strong metal support interaction and the different gases. So, information can be can be obtained; so, this is just a hydrogen concentration on the depth of the surface of a solid. So, dynamic SIMS can be used for this purpose.

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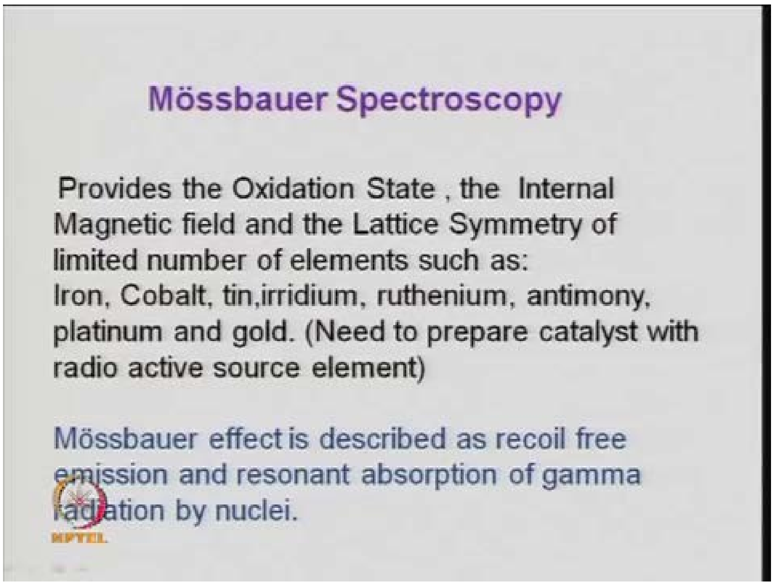

Mössbauer Spectroscopy

Provides the Oxidation State , the Internal Magnetic field and the Lattice Symmetry of limited number of elements such as:
Iron, Cobalt, tin,irridium, ruthenium, antimony, platinum and gold. (Need to prepare catalyst with radio active source element)

Mössbauer effect is described as recoil free emission and resonant absorption of gamma radiation by nuclei.

The another characterization technique is known as Mossbauer spectroscopy, M S. So, this can give you the oxidation state but only for the selected metals which have magnetic property. So, for iron if it is on a catalyst then this is more prominent, more effective method. So, this proves the oxidation state, the internal magnetic field and lattice symmetry of limited number of elements. So, these elements can be like iron, cobalt, tin, iridium, ruthenium, antimony, platinum and gold; so that is it means you need to prepare the catalyst with some radioactive source element.

So, very selected metals but the analysis is more accurate when you have the Mossbauer spectroscopy for these kinds; the effect is described as a recoil free emission and resonant absorption of gamma radiation by the nuclei. So, these are kind of neutral the what we say methods; where you can have the I R spectroscopy is one where you look at the vibrational energy and in can you characterize the catalyst using the bounding or between the metal support after reaction the composition can be analyzed. Same thing here, in Mossbauer for the magnetized material it can be determined.

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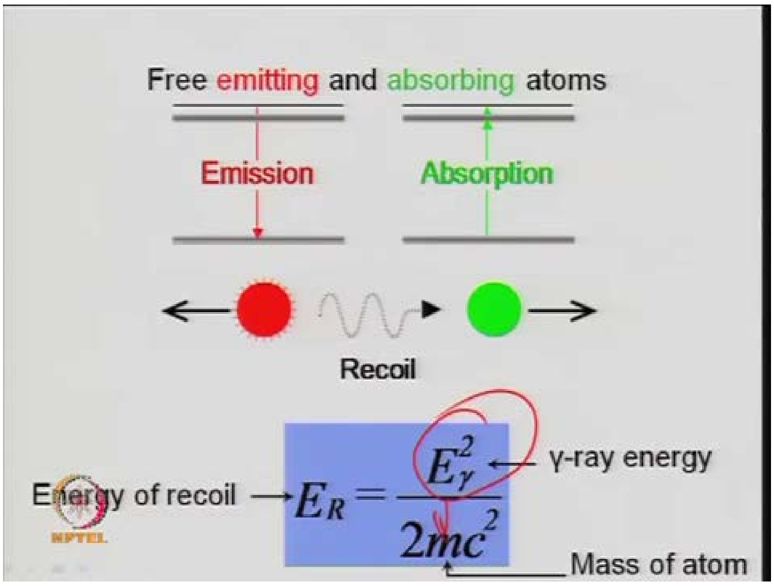
Free emitting and absorbing atoms

$$E_R = \frac{E_\gamma^2}{2mc^2}$$

So, the principle is something like this; that we measured this gamma energy, energy of that is what the recoil what you call; so you are free emitting and absorbing atoms; emits radiation and absorbs it. So, this what the recoil we call the this recoil that is based on this Mossbauer spectroscopy; based on this principle.

So, that will not happen for all kind of metal, it will happen only for the radioactive metals or which have the magnetic property. So, energy of recoil can be calculated and co related with the gamma ray energy and m is the mass of the atom. So, this energy of recoil or gamma energy is function of this mass of the atom. So, different metals will have different mass, atomic mass; so, this can be co related with the property of that metal.

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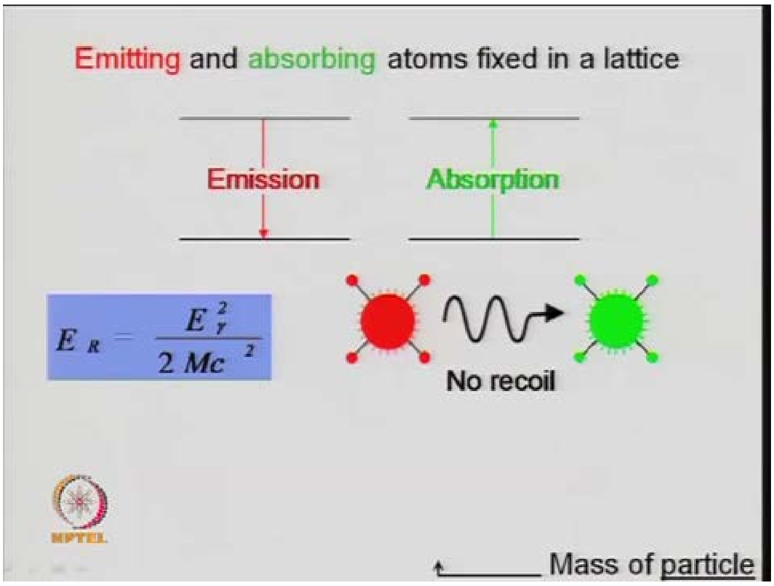

Emitting and absorbing atoms fixed in a lattice

Emission

Absorption

$$E_R = \frac{E_\gamma^2}{2Mc^2}$$

No recoil

Mass of particle

So, this is what when there is no recoil. So, that is what your no recoil here; so, you will not get any kind of diffraction or any kind of intensity radiation. So, it will not have any gamma radiation in one way.

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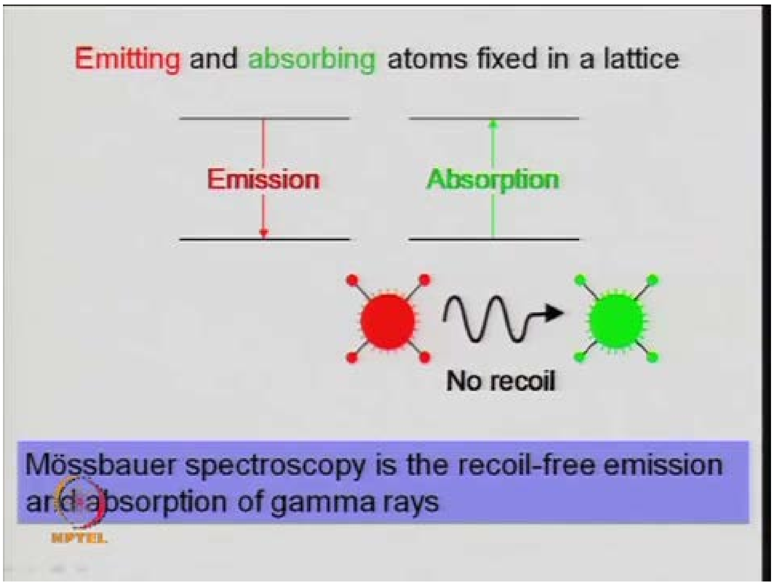

Emitting and absorbing atoms fixed in a lattice

Emission

Absorption

No recoil

Mössbauer spectroscopy is the recoil-free emission and absorption of gamma rays

So, Mossbauer spectroscopy is the recoil free emission and absorption of the gamma rays. So, that is the Mossbauer spectroscopy.

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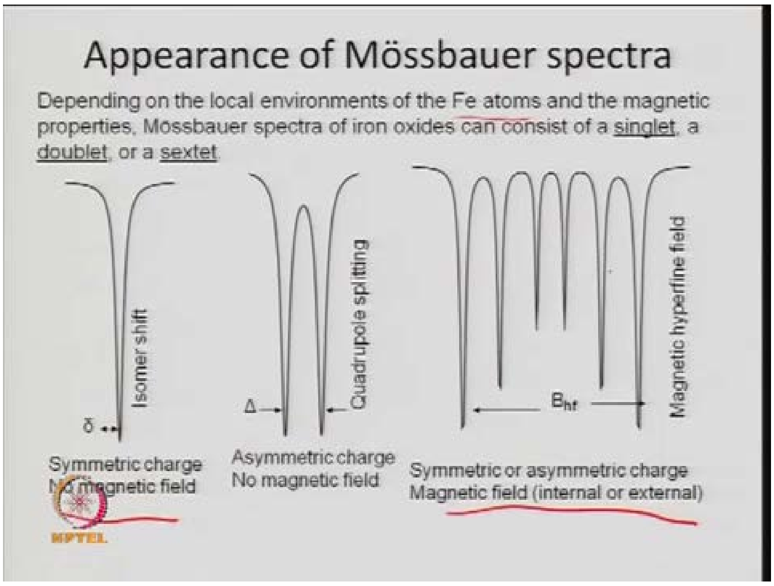

Appearance of Mössbauer spectra

Depending on the local environments of the Fe atoms and the magnetic properties, Mossbauer spectra of iron oxides can consist of a singlet, a doublet, or a sextet

Symmetric charge
No magnetic field

Asymmetric charge
No magnetic field

Symmetric or asymmetric charge
Magnetic field (internal or external)

So, just quickly I will show you that what kind of structure you can get here you can compare; because it is a kind of swift now, in terms of energy swift; what you call when some absorption is taking place. So, depending upon the local environments just for iron atoms of the iron atom and the magnetic property the Mossbauer spectra of iron oxide can consist of singlet, a doublet or a sextet. So, it depends on the atomic mass; and the magnetic property of the metal. Because the coil what I said recoil that analysis or gamma energy that generated will be of the property of the metal or the atom atomic mass of that metal.

So, the symmetric charge with no magnetic field; so, there is shift no shift in energy. So, you will have just one peak here. When asymmetric charge with no magnetic field again there is a splitting but the effect is not measured. But in the case of when the asymmetric charge and magnetic field then you have internal and external. So, you get 6 peak here something like this. So, one can compare the oxidation states of the iron; which is present on the catalyst by using this.

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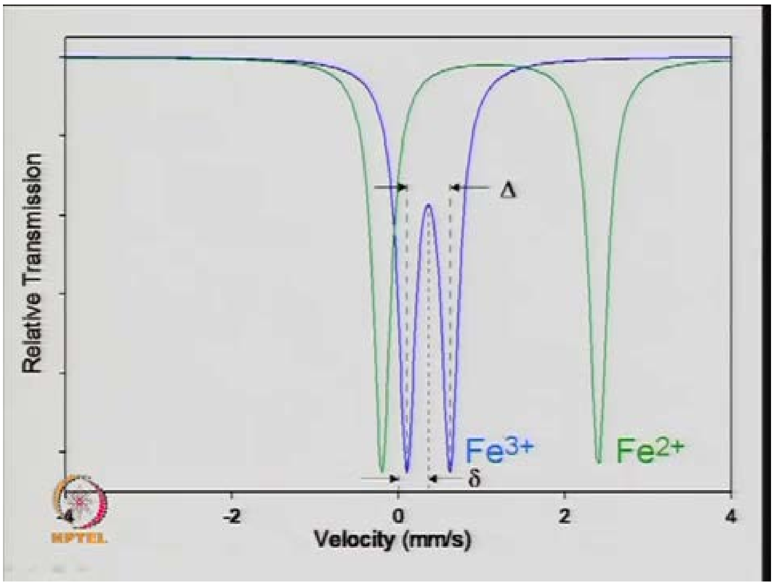

So, this is just collated here again in this form Fe 3 plus. So, if you just relative transmission versus velocity you have the shift in that. So, this shift is related to the property of the atom. So, oxidation state of the matter atom; so, iron 2, iron 3; so, this can be distinguished which is shown here like this. So, iron 2 has a shift like this, iron 3 has this; so, you can measure that shift at different velocity.

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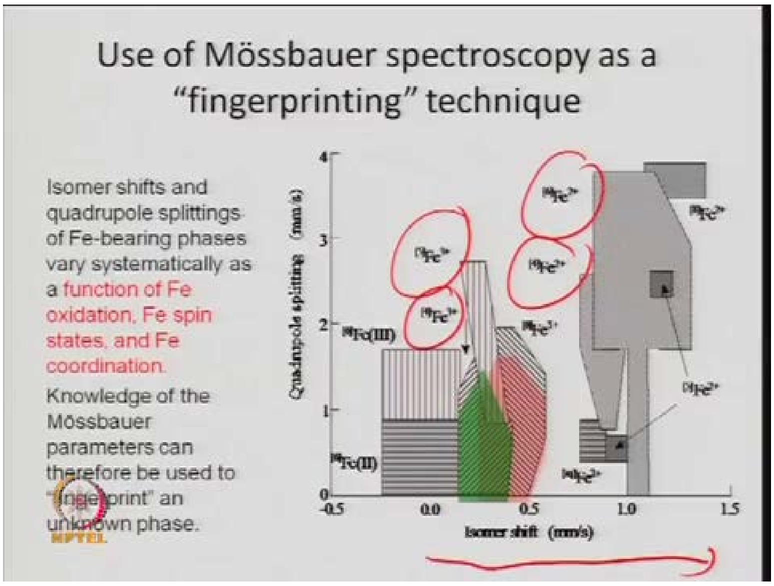

Use of Mössbauer spectroscopy as a "fingerprinting" technique

Isomer shifts and quadrupole splittings of Fe-bearing phases vary systematically as a function of Fe oxidation, Fe spin states, and Fe coordination.

Knowledge of the Mössbauer parameters can therefore be used to "fingerprint" an unknown phase.

So, it is a kind of finger printing also because once you know the oxidation state you can just talk about these different oxidation states here like this FE 2 plus, Fe 3 plus and which is just in terms of isomer shift or velocity. So, that is the energy shift what we talk when you have kind of radiation. So, it is the; when for radioactive material, we are just calculating that for different radioactive material depending upon their gamma energy and related with the energy of the source the Mossbauer; what we are talking in this equation. So, just this equation which we were talking here. So, these two recoil energy and this surface energy or the gamma radiation is function of mass. So, depending upon these two you will have different kind of shift here; in terms of energy shift. And, that shift is related to the oxidation state of these metals.

So, that is what and once you know those information; then you can just look in types of the splitting of these atoms or the mass. So, isomer shifts, quadruple splitting of iron bearing phases vary systematically as a function of oxidation state; the metal oxidation state, metal spin; so iron spin states and iron coordination. How these are coordinated? So, the knowledge of the Mossbauer spectra’s parameters or can therefore be used to finger print an unknown phase. So, you can identify the phases by using this Mossbauer spectroscopy but only thing is that it is only magnetic materials like iron one not for all kind of metals. So, for selected metal but this provides a very useful information; that time may not be effective but this can be effective.

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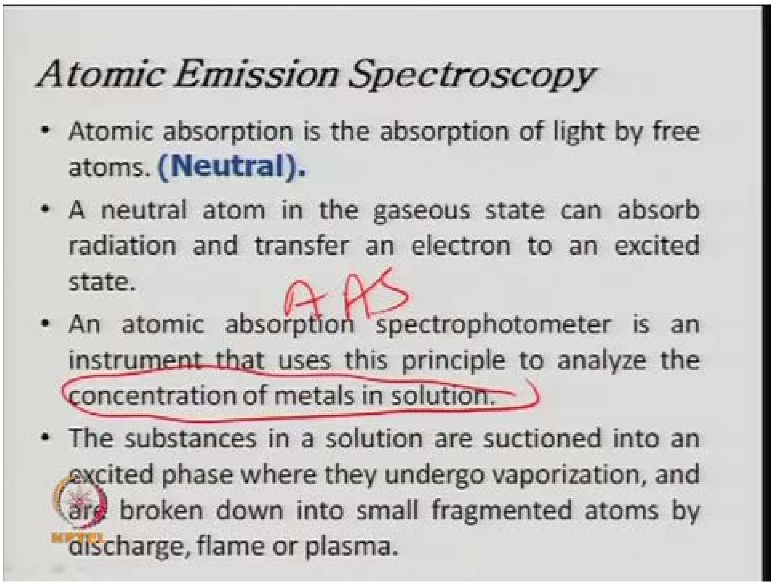

Atomic Emission Spectroscopy

- Atomic absorption is the absorption of light by free atoms. **(Neutral).**
- A neutral atom in the gaseous state can absorb radiation and transfer an electron to an excited state.
- An atomic absorption spectrophotometer is an instrument that uses this principle to analyze the concentration of metals in solution.
- The substances in a solution are suctioned into an excited phase where they undergo vaporization, and are broken down into small fragmented atoms by discharge, flame or plasma.

The another, which is based on neutral technique, is atomic emission spectroscopy. So I R spectroscopy; all of you know ultra violet UV spectrophotometer you know; this can be used to determine the composition, chemical composition. So, and can provide you the total concentration of the metal inside the catalyst. So, once you extract the metal from the catalyst and then you do the UV at a particular wavelength. And, then you can find out the total concentration by measuring the absorbance as a function of concentration, calibrated and you can find out total concentration. I R spectroscopy can give you the chemical composition; once after reaction or absorption; so, you can just talk at different wave numbers and then, see the absorption.

So, you can identify the composition. I R, F T I R a chemical bounding can be used by using for your spectroscopy. So, before reaction or after reaction and you can have the structure or composition. But there are some other techniques like atomic absorption spectroscopy; I C P, inductive coupled plasma, these are based on neutral techniques. And, they are versatile in terms of determining the total concentration of the solid catalyst; that is metal concentration in the final catalyst.

Initial loading is one thing; you have done the calcinations, you have done the reduction. And, based on those calcination reductions; then finally after that you need to find out the final composition. Because during the heat treatment; they there may be a loss of the metal active metal. So, in that case it becomes important that you co relate the catalytic property or your turn over number; dispersion which you define based on this actual composition of the metal on the catalyst. So, that is important in that case this atomic absorption which is the absorption of light by free atom. So, here we are not talking any ions, we are not talking any electron, not talking any photon or X ray neutral technique.

So, neutral atom in the gaseous state can absorb radiation and transfer an electron to an exited state; that will depend on the type of metal. You need different type of lamps to measure their absorption; because there will be for a particular wavelength, absorption will be. So, an atomic absorption spectrometer; if you just look at is a instrument that use, this principle to analyze the concentration of metal in solution; which is very important for the catalyst; when you prepare the catalyst for the final concentration of the metal is to be determined. So, this can be used which is known as A A S also, atomic absorption spectrometer. The substance in the solution is suctioned into an exited phase where they undergo vaporization and are broken down into small fragmented atom by discharge, flame or plasma.

So, there can be a flame; so, flame detector flame ionization method, there can be a plasma method which is requires very high temperature. So, depending upon the type you can determine the absorption. So, the ions will generate or the metal comes in the ionic state. And, you measure the concentration of those ions it can come in the vapor state, gas phase, you measure the concentration. So, in U V, it is just in the solution and you are making some complex and which comes at a particular absorbance, wavelength, particular wavelength; and then you co relate with the original concentration. So, that can be you need to do certain kind initial calibration or titration in order to confirm them.

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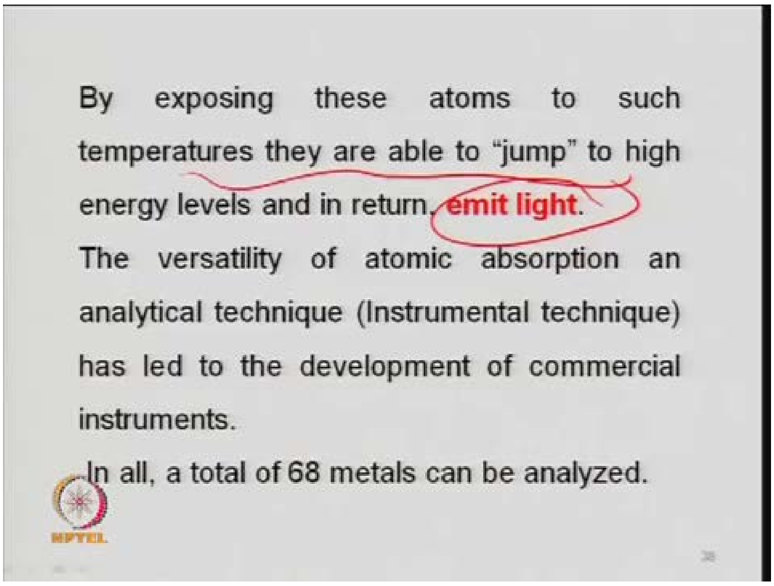

By exposing these atoms to such temperatures they are able to "jump" to high energy levels and in return, **emit light**.

The versatility of atomic absorption an analytical technique (Instrumental technique) has led to the development of commercial instruments.

In all, a total of 68 metals can be analyzed.

So, by exposing these atoms to such temperature that they are able to jump to high energy levels and in return they emit light. So, what happens when you have given these kind of the some high voltage or high a furnace, high temperature furnace which is used furnace can be used or plasma. So, under these conditions these are broken down all the solution suctioned in the exited phase where they undergo vaporization; and broken down into small fragmented atoms by discharged flame or plasma. And, these atoms at such a high temperature they just able to jump and reach to higher energy level; and in return they just emit light.

And, the versatility of the atomic absorption which is an analytic technique, instrumental method it has led to the development of commercial instrument. So, this the one of the important tool in terms of characterization of the catalyst in also other just a in other inorganic chemistry just to find out the composition of the metals, purity of the metals all these can be done by using this here. So, whatever light emitted that is measured by that lamp; a specific lamp is required when you have atomic absorption spectrometer. So, more than 68 metals can be analyzed by that wave important tool.

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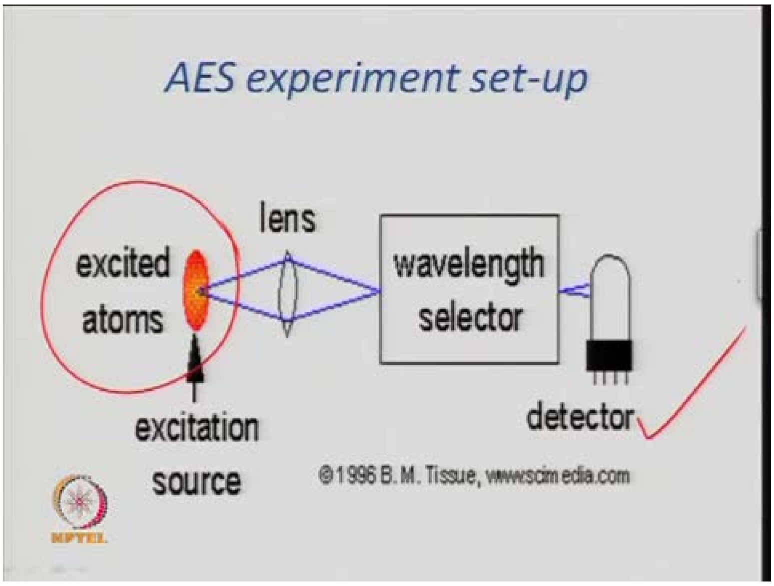
AES experiment set-up

So, this just a simple if you look at the principle is very simple you have some excitation source. And, so once you have that this; you get exited items which is connected which is passed through a some lens. And, you have a lamp here which is a definite wavelength selector; you have to select that wavelength for absorption of that particular metal. Because a particular metal will emit the light at a particular wavelength which can be absorbed. So, that is here and you pass through a detector and you get the concentration.

Because the absorbed lens versus concentration can be calibrated. And, for any unknown sample; once you know its absorption you can collated with the concentration and data base are available now a days.

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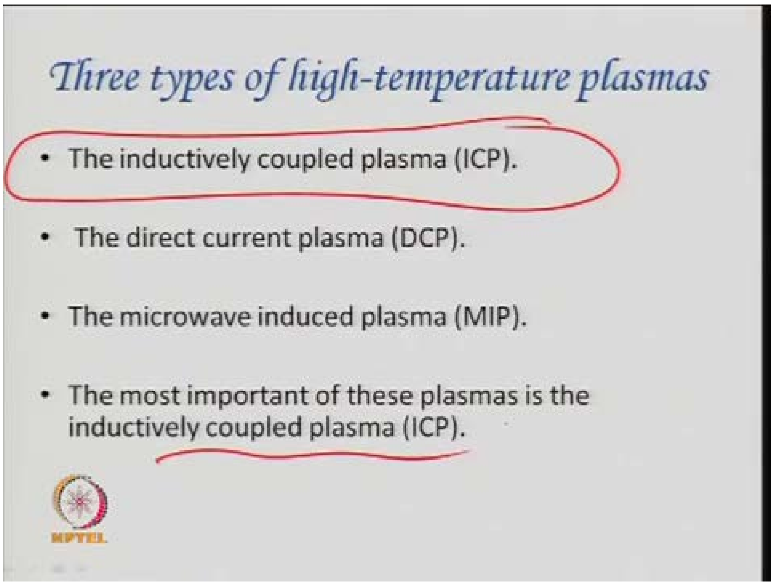

Three types of high-temperature plasmas

- The inductively coupled plasma (ICP).
- The direct current plasma (DCP).
- The microwave induced plasma (MIP).
- The most important of these plasmas is the inductively coupled plasma (ICP).

So, that there can be the different types of high temperature plasma; so one is the inductive coupled plasma there is widely used method for the characterization, this is finished; but we have talked or discussed. Then, second one is a direct current plasma then, microwave induced plasma and most important of this is what the I C P method. Sometimes, I C P, A E S also atomic emission spectrometer. So, there can be a variety to get the complete composition of the metal. So, I C P is a tool by which you can find out the composition of the catalyst; complete composition which may not be correct from the SEM E D X but this is much more versatile compared to SEM E D X.

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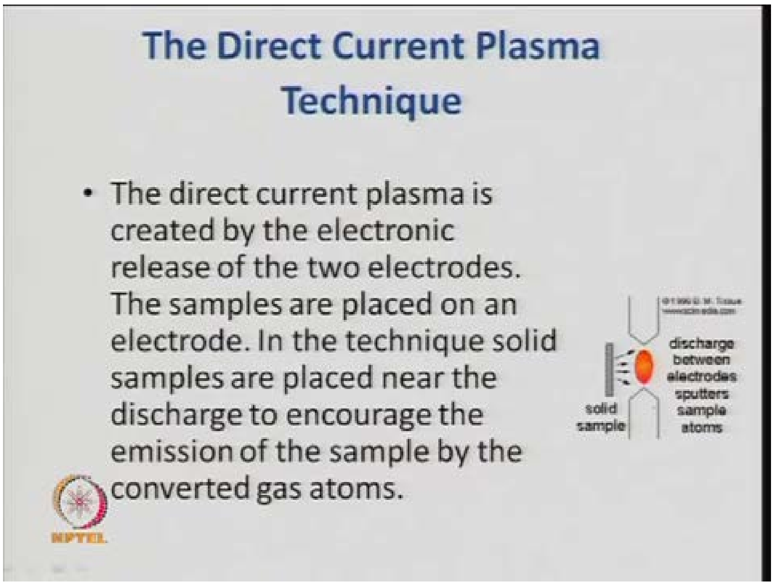

The Direct Current Plasma Technique

- The direct current plasma is created by the electronic release of the two electrodes. The samples are placed on an electrode. In the technique solid samples are placed near the discharge to encourage the emission of the sample by the converted gas atoms.

So, direct current plasma technique; so, just a principle I am talking not in detail. So, you have the direct current plasma and which is created by the electronic release of the 2 electrodes. So very high voltage electrode are used. The samples are placed on an electrode; in the technique the solid samples are placed near the discharge to encourage the emission of the sample by converted gas item. So, very versatile technique. So, you have just the electrode here, and you have solid sample here; so, discharge between electrode splatted sample item and that pass through the detector and you absorb that absorbance. So, can easily related to the concentration of that metal.

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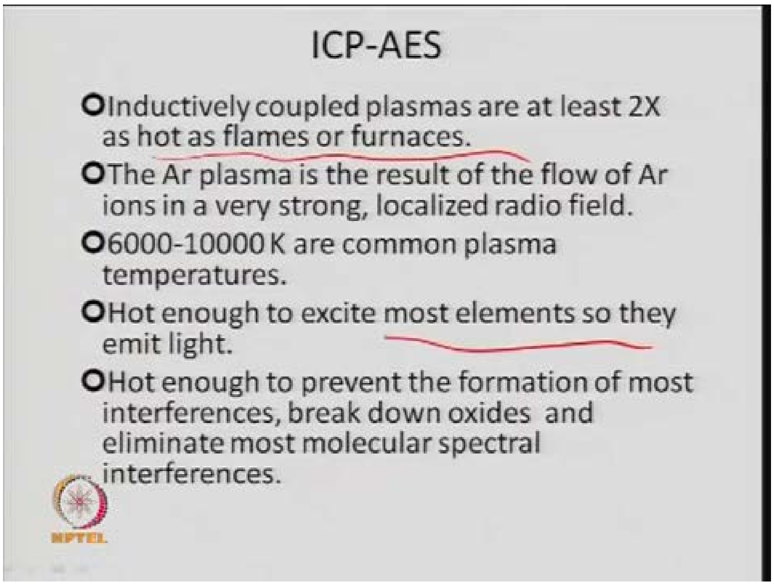

ICP-AES

- Inductively coupled plasmas are at least 2X as hot as flames or furnaces.
- The Ar plasma is the result of the flow of Ar ions in a very strong, localized radio field.
- 6000-10000 K are common plasma temperatures.
- Hot enough to excite most elements so they emit light.
- Hot enough to prevent the formation of most interferences, break down oxides and eliminate most molecular spectral interferences.

I C P A E S, as I said inducting coupled plasma; this is connected with atomic emission spectra. So, inductively coupled plasma are at least 2 times as hot as the flames or furnace. So, very high temperature is generally used as I mentioned here that common plasma temperatures are 6000 to 10000 Kelvin; very high temperature. So, atomic absorption, you use the graphite furnace, you use the astatine lamp, astatine flame; one the using the astatine and then generate the temperature. So, you need a cylinder to burn that and generate the temperature of that order. So, you need a high temperature; graphite furnace may be required when you have very high temperature of the order of 1200 degree centigrade.

So, the organ plasma is the result of the flow of organ ions in a very strong localized radio field. So, these kind of lamps are required generally and hot enough to excite to most electrons; so that they can emit the light. So, they are hot enough to prevent the formation of most interferences; breakdown oxides an eliminate most molecular spectral interferences. So, this is your versatile technique in that wave that it can determine you the actual composition of the metal; with this I just close this characterization part; so, next time I will cover the Zeolite.

Thank you.