Heterogeneous Catalysis and Catalytic Processes
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Module - 05
Lecture – 15

Good morning, last time we were talking about x-ray photo spectroscopy method for characterization of the catalyst. So, XPS is what I was talking, it provides a wide information about the chemical structure of the catalyst composition, even you can find dispersion also because, you say just like in terms of the bond or energy which is required the kinetic energy of the electron. It measures that and related to the binding energy and electrons which are the core electrons.

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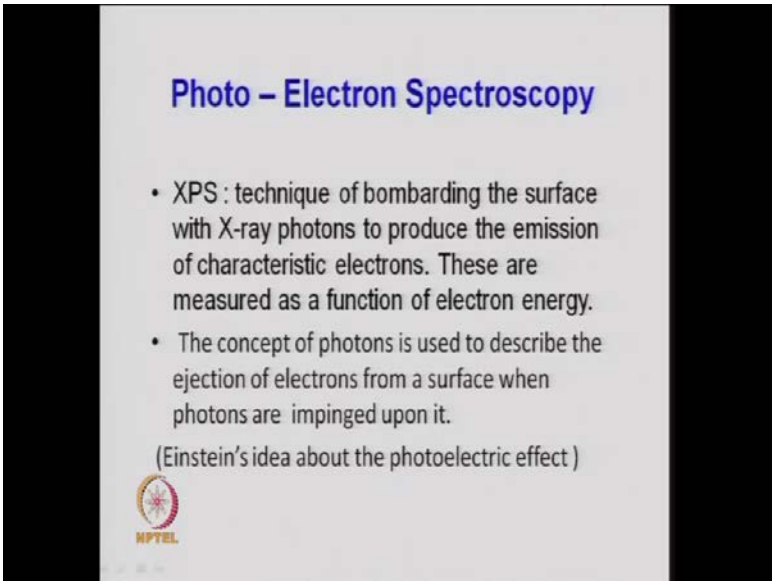

What we are talking last time discussed that the core electrons are more important because, they are attached closer to the nuclei. So, they give you better information about a metal. So, different metals will have different property, about in terms of the binding energy and that is related to the chemical composition. So, the XPS technique as I said before also that bombarding the surface with some kind of energy, being x-ray photons to produce.

The emission of characteristic electrons so, you measure the response of that these measured function, these are measured as a function of electron energy. So, you calculate

the energy of that electron so, the concept of photon is used to discuss the ejection of the electrons from a surface when photons are impinged upon it.

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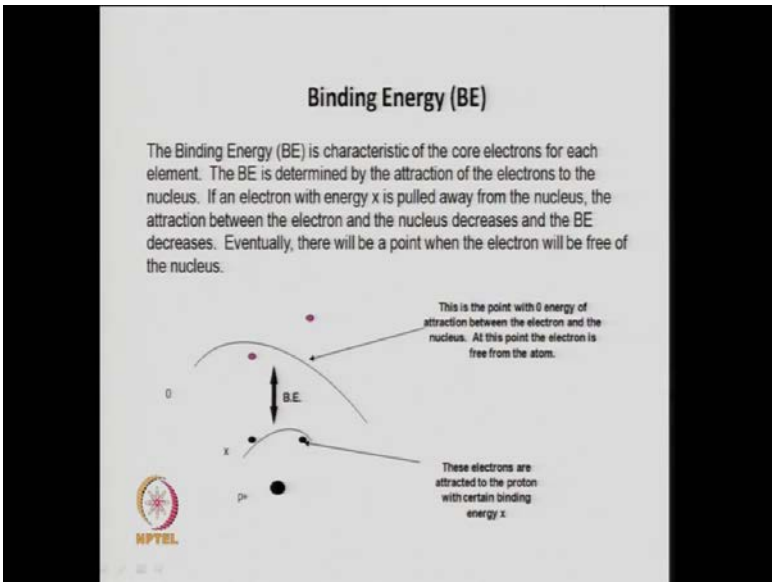

So, basically it is based on the Einstein's idea about the photo electric effect which you must have read before. So, what is binding energy? I have discussed it last time just quickly to talk that this is the nuclei and the core electrons are somewhere here and the electron or the energy required to release the electron from here and take it to the outermost that is related to the material property that is the chemical composition of the metal electron.

So, d band models what I was talking last time. So, binding energy is the characteristic of the core electrons and for each element it will be different. So, the binding energy is determined by the attraction of the electrons, to the nuclei so, you can just look at that how the electrons are attached to this proton, here and there is a kind of force and you need some kind of energy to release the electron from that. So, this can be used to determine the total chemical composition or structure property of a metal.

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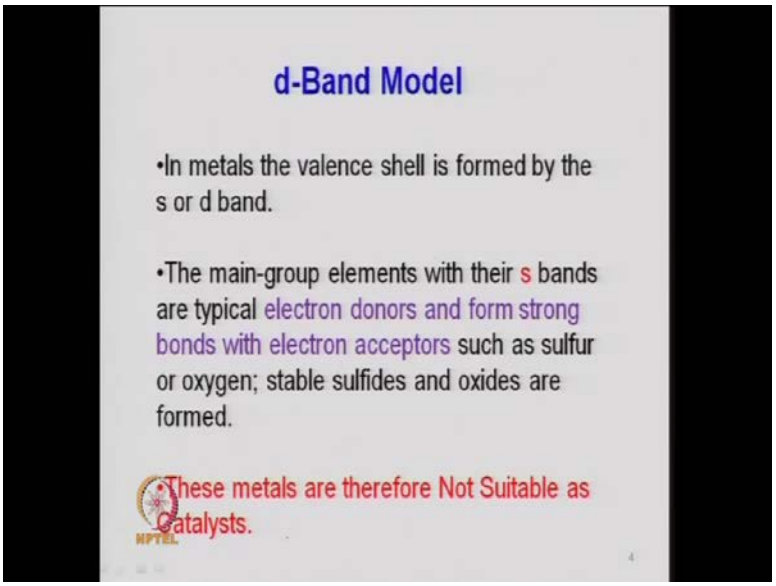

So, d band model because, that is the most important property of a catalytic material as I said that the p g m group metals may be active group one b second b metal transition metals element , they are active because, they have the d electrons unpaired electrons. So, and if you look at the left side of your periodic table, there may be s or p bands but, they may not be very effective as a catalytic activity. So that, is the theory of the band which simply says that in all the metals a valence shell be formed either by s or d band. The main group elements with their s bands are typical electron donors. So, they can easily donate the electron and once they donate the electron they can easily form the strong bond with the electron x factor, such as sulfur or oxygen. So, they oxidized faster the sulfide faster.

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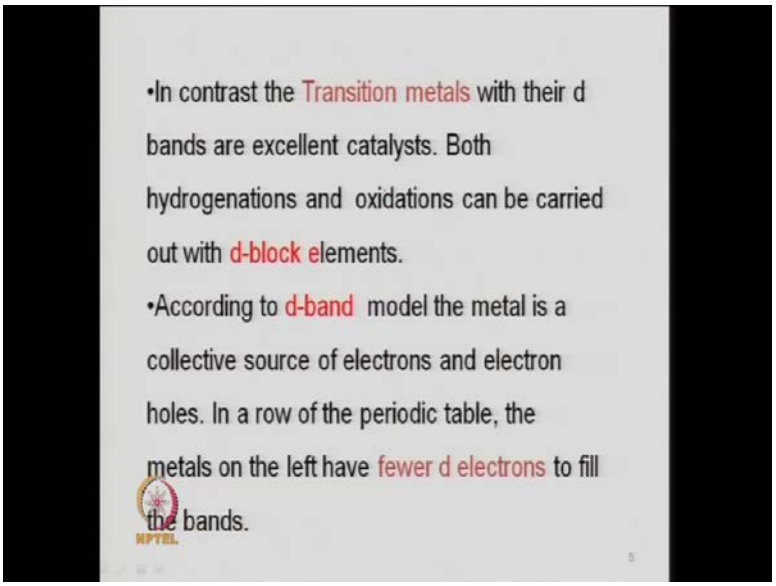

So, they are stable molecules cannot provide you the catalytic activity so, these metals may not be good for the catalytic activity, if you look at the transition metal they have very good catalytic property and hydrogenation, de-hydrogenation, oxidation, that can be carried out with these d-block elements. So, according to the d-bond model the metal is the collective source of electron and electron holes, these are the just electrons which are moving around the nuclei, k shells as and that is l shell.

So, different shells they are moving and the binding is related to the how many protons are on the nuclei and the how many electrons are in core and then outermost. So, this is what the periodic table, if you look at the metals the d which is fewer d electrons, they have a kind of catalytic activity electron holes. So, when the number of unpaired d electrons is very high, they will easily bind to the surface and they will remain there they will not leave the surface.

So, they have strong chemisorptions property, they may not be good so but, they have sufficient number, some kind of sufficient number of unpaired d electron they have good catalytic activity. So, as I said that no d electron unpaired d electron that is also not good but, if you have large number of d electron, then also it is not good because, it has much more or strong affinity for surface. So that is the theory and volcano plot but, you are talking earlier that is related to these theory electrons.

So, this is known as the electronic theory for the catalytic activity d-bands. So, in a row of periodic table the metals on the left side have fewer electrons to fill the bands, so that, is the one which is important point here; So, transition metals are most active catalyst in that base equation, this was discussed last time, that a kinetic energy is related to h n which is the energy of the photon minus the binding energy and minus the work function or work potential. So, this will depend on the type of instrument.

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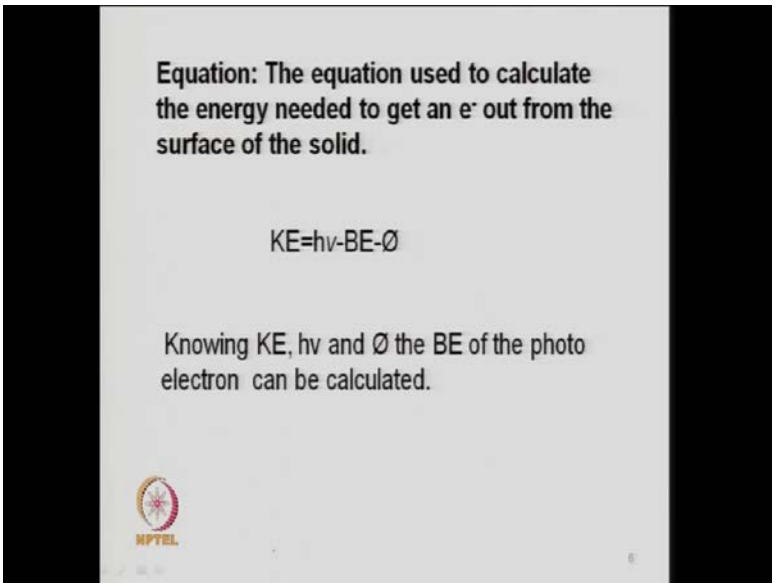

So, this equation can be used to correlate the energy which is needed to remove an electron from the surface of the solid and that is the property of a metal. So, kinetic energy if you know that that can be measured and you can find out the binding energy of the photo electron. So, this has been discussed.

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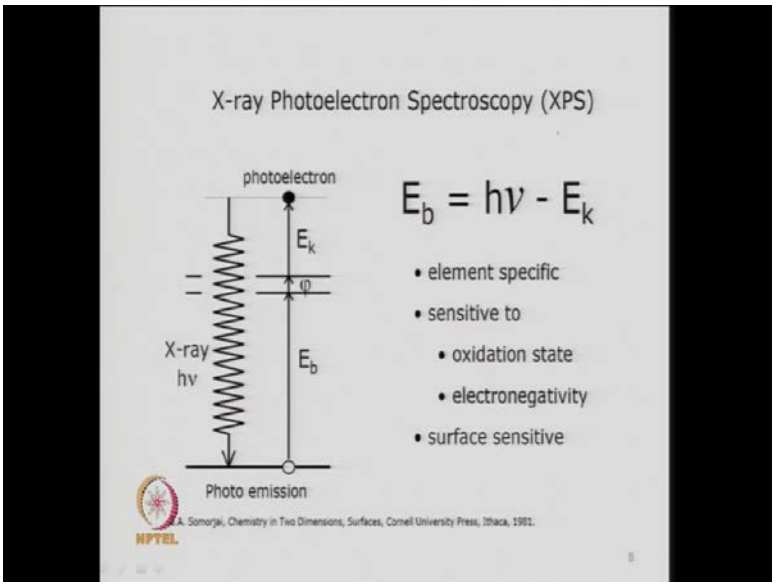

So, this is the what you are talking that the kind of biding energy, which is specific to the metal and by knowing this E k because, the electron release and its energy is known so, this can be a secondary electron or back scattered electron also. As I discussed last time, that it can be when it is the secondary electron or back scattered electron, you call it auger electron spectroscopy a e s. So, that is a lower energy basically, because these are nothing but, the electrons which have been released from the other hold or the not from the core. But, they have transferred their energy some electrons are transferred their energy and there by the less energy, now is being released. So, that is known as back scattered electron.

So, that time the principle relate or similar to your electron. So, there also by using if you know the energy of the secondary electrons, what you call auger electrons and that their energy is also related to the property of the metal. So, the same fundamental principle is used for auger electron spectroscopy also. So, binding energy is related to the energy of the photon minus the kinetic energy work function is roughly observed of core electron volt a low number. So, high electron been considered here but, it can be taken minus the work potential phi.

So, this is the elementary translation that is binding energy. So, it states to the oxidation state so, energy shift that is when the a metal which has 0 valance and it goes to positive side or negative side. So, accordingly this value will change. So, you can have the

composition as well as oxidation state idea or the what you call from the energy shift which is nothing but, change in the binding energy when say 2 plus position or just 0 position or a negative position.

So, the valency state, oxidation state change and that that say c o 3 c o 4 or some other any metal species, which have the different oxidation state. So, there will be shift of energy. So, just like in your x-ray diffraction, here the information may not be sufficient but, here you can get the oxidation sate information which may not be very clear from your t p r study or temperature program desorption or reduction study. But, from x p s you can have much more valuable information on the surface.

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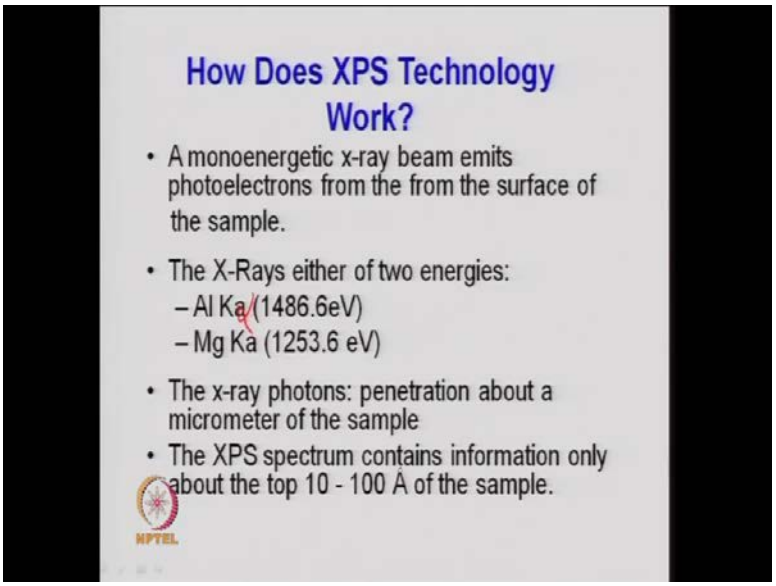

So, how does XPS work? There is a monochromatic energy been, of different energy that depends on the source. So, like Aluminum Alfa radiation or magnesium Alfa radiation. So, these kinds of radiations may be that is the primary beam of the energy. So, which are monochromatic or mono-energetic x-ray beam and that emits the photo electron from the surface of the sample. So, roughly 1.4 it is a 486 kilo electron volt or Alfa potassium Aluminum potassium Alfa and for magnesium potassium Alfa, this value is 1.2583 kilo electron volt.

So, these kinds of energy beams are generally used for x-ray photo spectroscopy and these things are done under high vacuum. So, the x-ray photons they penetrate about a micro meter of the sample. So, they can penetrate because, of these high energy beams

they can penetrate up to a certain depth of the sample. So, depending upon this energy you can get the in depth analysis also. But, I was talking multi layer core formation whether it is mono layer multilayer.

So, different kind of a spectra's when the hard coke forms or graphitic in nature amorphous in nature. So, all these information can be obtained from the x-ray photo spectroscopy. So, the XPS spectrum contains the information about the top of 10 to 100 angstrom of the sample. So that, is the in depth analysis when you can go up to 100 angstrom or even more when the energy of the beam is high.

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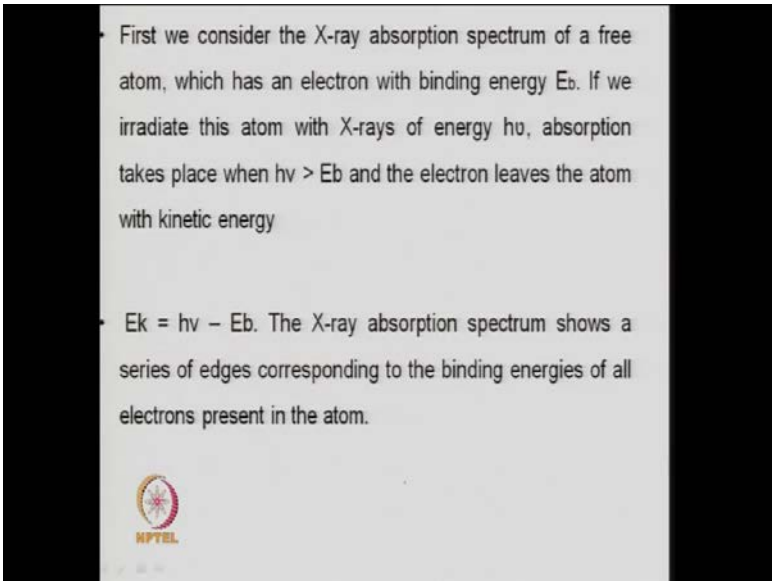

So, when you do that you first the x-ray adsorb adsorption spectrum of a free atom, which has an electron with binding energy E b. As I said the electron has binding energy E b and some energy beams has been striked or impinge on that. So, h u, just if you do that then and if h v is greater than E b then electron will come out from the surface because, this is the what the equation you have seen here. So, when the binding energy that is kind of energy which is it should be sufficient to remove the that the force of attraction like that is between the nuclei and the electron. So that, is the first thing and that the hv should be larger than the binding energy so, then the electron will leave the surface.

So, kinetic energy can be measured, that the surface which has been electron which has come out its kinetic energy is measured by the measuring element. So, there are sources

or method by which the kinetic energy can be measured and then you can see the series of edges corresponding to the binding energy of the entire electron present in the atom. So, all kind of electrons if you look at the surface x-ray adsorption spectroscopy depending upon the oxidation state, it can give you the all information about the surface structure that will see little later.

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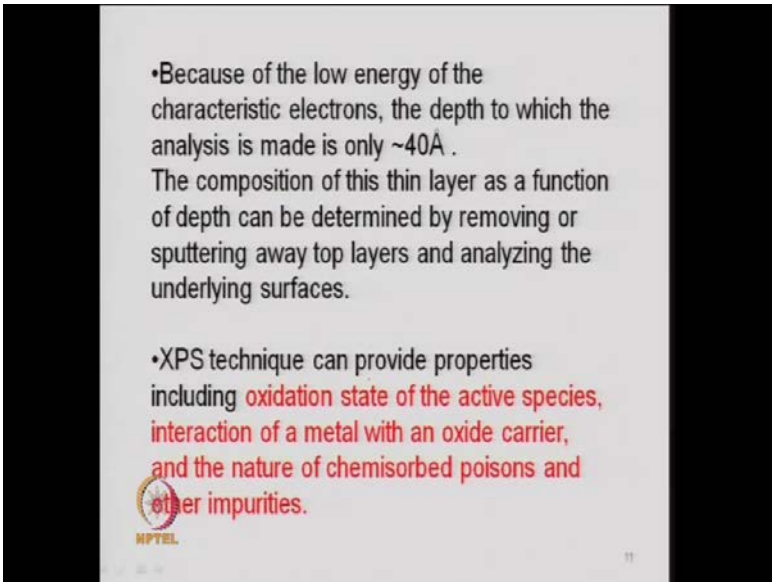

So, since as I said the characteristic of the electron, it can be a back scattered electron also it can be just the electron, which is released and directly coming out from the surface because, in the last lecture I was just saying that it goes to the in depth depending upon the energy. So that, last time what we are showing that multi atoms here like this so, the in a strike it can strike at in catinary electron, it can come to here then it can collide here and like this and release comes out. So, depending upon this kind that is the surface or the in depth analysis or depending upon the energy of the beam main beam, primary beam the electron which release the surface or release from the surface, the energy will be different.

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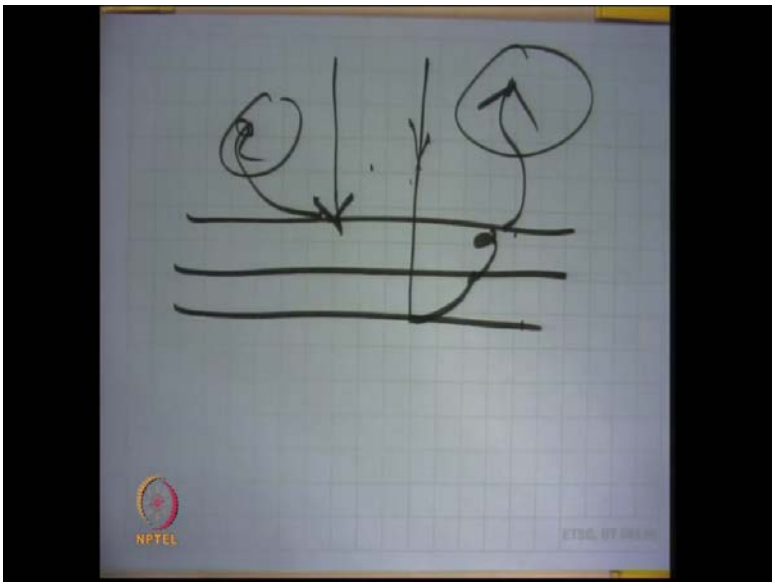

Now, generally this over electron will have low energy and the primary energy also because, it has striked on the surface and then electron leaves and comes out of the surface. So, depending upon the type of the metal or the composition oxidation state the energy level is low the output energy. So, that is the characteristic of the electron. So, the depth to be analysis is made is roughly about order of 40 Angstrom. So, 10 to 100 Angstrom is the 1 but, in general to you need a high energy beam, if you want to go for the in depth analysis a different kind of operators may required to have this kind of analysis in that case. So, composition of this thin layer as a function of depth can be determined by removing or sputtering away top layers and analyzing the underlined surface.

So, this is what I was talking that you will get electrons of the different energy, the kinetic energy which you are getting at the exit will be different and that can be correlated with the in depth analysis at to what depth they have been released, if they are which has not the back scattered electron. So, XPS technique in that way can provide you the oxidation state of the active species, so this is very important you see the oxidation space states from TPR but, sometime it may not be the correct information but, here you can have it.

Interaction of metal with an oxide carrier, if there is a strong metal support interaction then XPS can give you the information, if there are 2 metals bi-metallic and there is

some kind of interaction between these 2 metals. Then our XPS can provide you the information because, the energy is related to that every metal has this property and nature of the chemisorbed poison as I said just for coke.

But, depending upon the poison precursor and how this poison precursor chemisorbed during the reaction, during the course of reaction so, if you have a deactivated catalyst or spent catalyst, you can do the x-ray photo spectroscopy of that and you can get the type of poison precursor. So, you can find a remedy for that when you look at the new catalyst or novel catalyst for the process. So, the XPS can provide you the wide information, wide sort of information in terms of the catalytic composition or catalyst composition.

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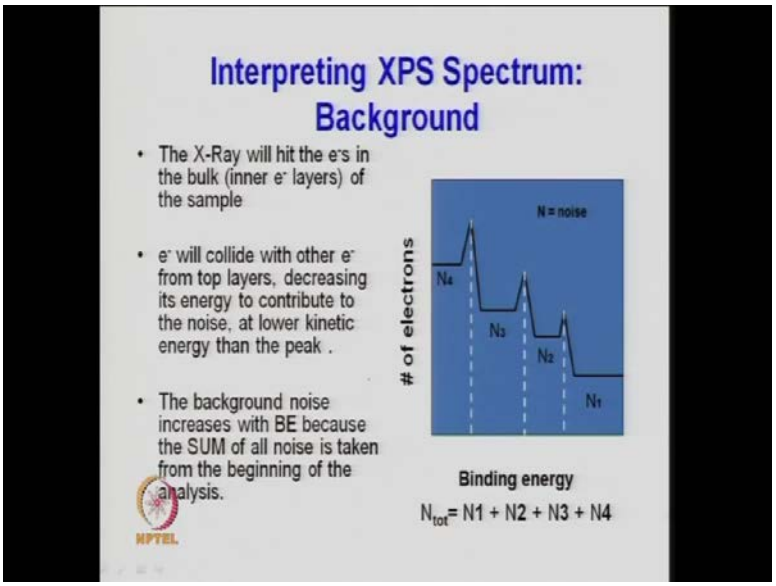

So, the kind of structure if you look when the x-ray hits. So, x-ray will hit the electrons in the bulk inner electrons layers which I said core layers of the sample. So, you will get a response the electron will collide with other electron on the top layer which I have just talking that the down bottom layer the electron release but, it strikes again with the other layers and come out and the energy to contribute to the noise so, you will get a kind of noise here just like a response at different layers so, total noise you have to just we are looking the total number of energy of the electron. So, kind of it is a kind of detector which gives you the signal and which is related to the numbers of electrons which have come out from the surface. So, that is a kind of the indication that number of electron as a function of binding energy.

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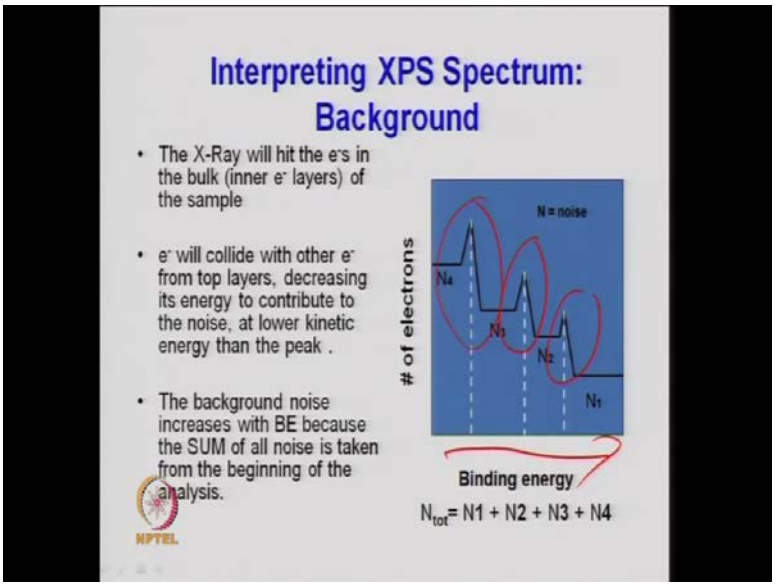

So, in the surface the different binding energy you will have at different binding energy, Eb you will have different number of electrons which have come out and their property can be examined. So, the background noise increase with the binding energy because, the sum of all the noise is taken from the beginning of the analysis. So, sigma of all that is nothing but, the that if you have the noise increased. So, number more number of electrons are coming and that will be function of binding energy. So, that is very important in terms of the metal property. The same is this, what is discussed here that binding energy increased from to left. So, this is the increase in binding energy.

And kinetic energy increased from left to this sort, that is what the kinetic energy of the electron, that is the equation which I have discussed here the binding energy is hv minus Ek the kinetic energy or kinetic energy nothing but, the hv minus Eb. So, 1 increase other decrease. So, this is the 0 electron volt to suppose you have a 1000 electron volt in terms of the change in the energy of the source light beam source. So, your binding energy values goes like this.

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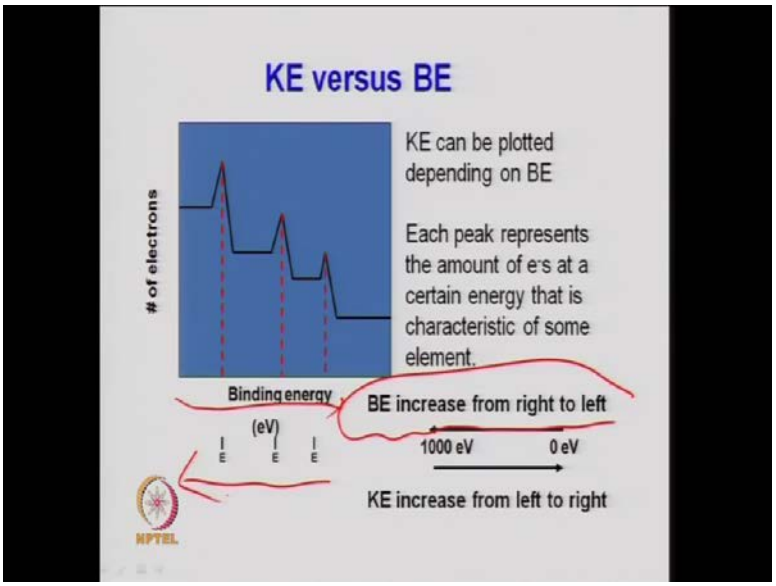

So, this is just the highest binding energy here and then this is somewhere here 0 when it comes to that, binding energy increased from right to left. So, this side to this side binding energy increased here this side and kinetic energy is this, the kinetic energy which Increase from this side to this side. So, both are interrelated that when the kinetic energy increase binding energy decrease or in other words. So, basically binding energy is the property of the metal.

So, higher amount of hv the same source is applied and if the electron comes at a faster that same because, the binding energy is high so, it means the electron is are tightly Binding towards the nucleus, they have more so, you need a higher energy either it would or that or the same energy hv is applied, then your kinetic energy of that electron will be low energy electrons will come out and that is related to different metals. So, number of electrons emitted that is also known as noise here we call noise.

So, kinetic energy can be plotted depending upon the binding energy. So, you can have equation the number of electron versus binding energy or number of electrons versus kinetic energy either which you can have the information because, hv is fixed in kinetic energy.

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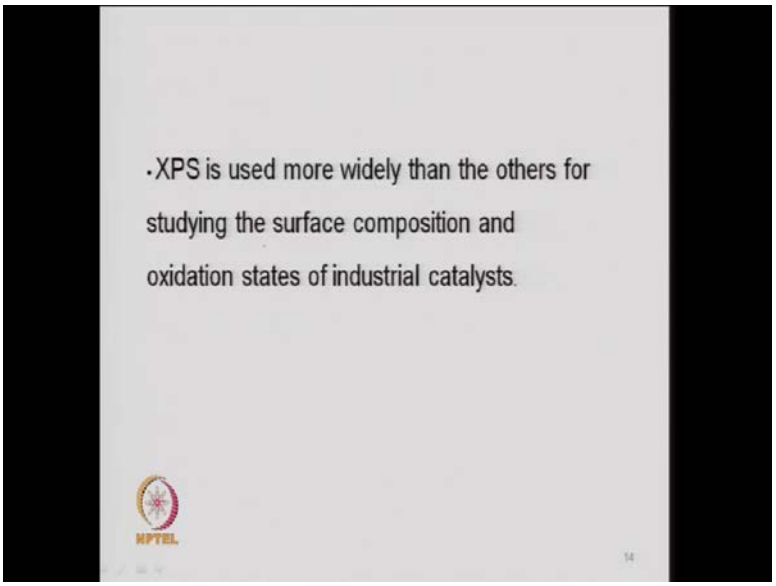

So, XPS is used more widely than others for studying the surface composition and oxidation state of a many industrialists because, this you see that exact metallic composition or how metal have been or metals have been deposited on the surface of the solid. And if there is a strong metal support interaction you can get the information on that so that, is why the XPS is one of the most important tool now a days for characterizing, the catalyst. So, this provides you the in depth analysis

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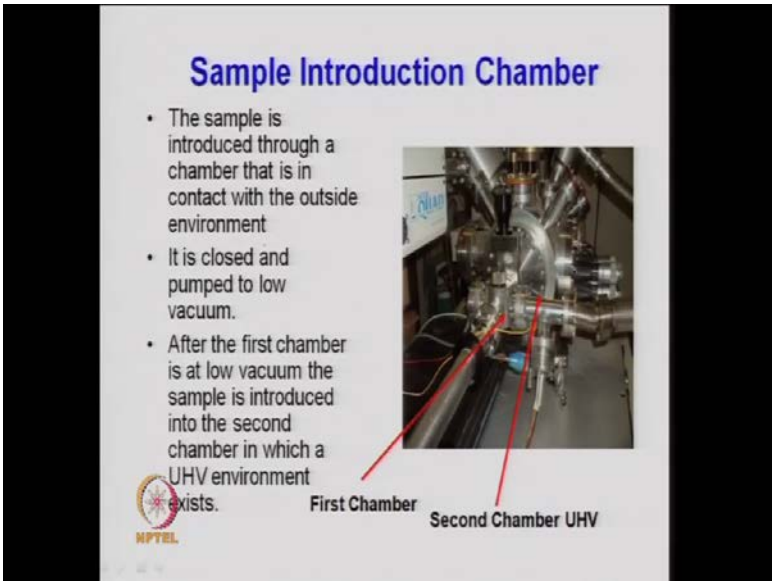

So, this is just a kind of induction chamber if you look at here the actual picture of XPS so, that what the how the samples are introduced, the sample is introduced.

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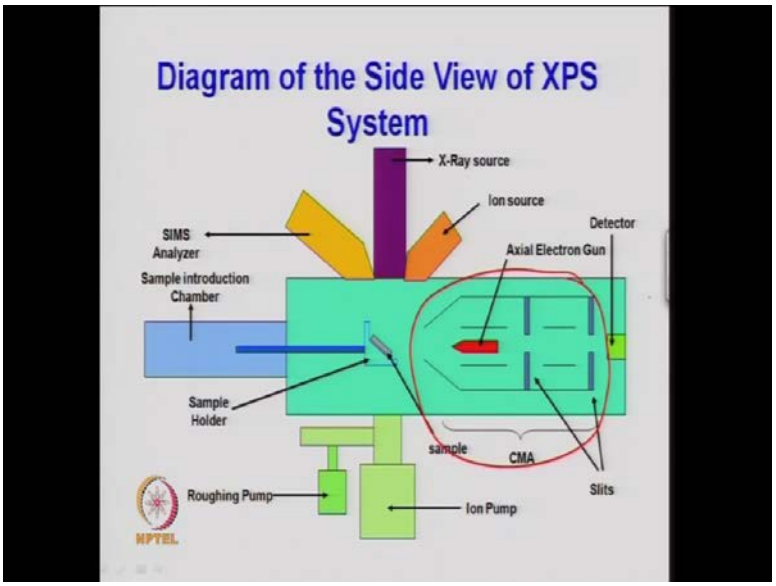

So, before that just I will show you the actual this diagram which just show the schematic of that XPS. So, this is the important here, where this is the electron Gun which gives you the energy source hv this one and this is the detector circulator. Detector which observes the kinetic energy of the electron set actual. So, this totally is your cylindrical mirror, what is the kind of assembly if you look at here in this. So, the electron beams the sample is placed here and you have to pump to create the vacuum because, this works under a vacuum.

So, sample holder where is this is the secondary mass spectrometer can analyze the ions, this is a x-ray source this is ion source. So, you can have a variety of information from the depending upon the binding energy required or hv required source you can use different kind of energy sources and then this is the detector. So, you can measure the kinetic energy of that. So, this is what they actually if you look at the sample is placed to one side here so it is a closed pump to low vacuum.

So, you have to put the vacuum which I have shown here so, it works under high vacuum extremely high vacuum, of the order of to minus 10 to power minus 4 to even lower vacuum. So, the sample is introduced to a chamber, that is in contact with the outside environment, just a have to slide it inside it is closed and pumped to a low vacuum. So,

create the vacuum in the system. So, the pump should have a high rating that the vacuum should come immediately because, it requires a very high vacuum ultra high vacuum also be required.

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So, after the first chamber it is at low vacuum, the sample is introduced into the second chamber in which in ultra high vacuum environment exists. So, very high vacuum is required for this. So, which is actually here the system do ion pump roughing pump so, that creates the vacuum in the system and then there electrons we get the kinetic energy of that electrons after getting the beam this axial electron Gun, hv energy and then the electron will come out from the sample and its kinetic energy is measured by the detector.

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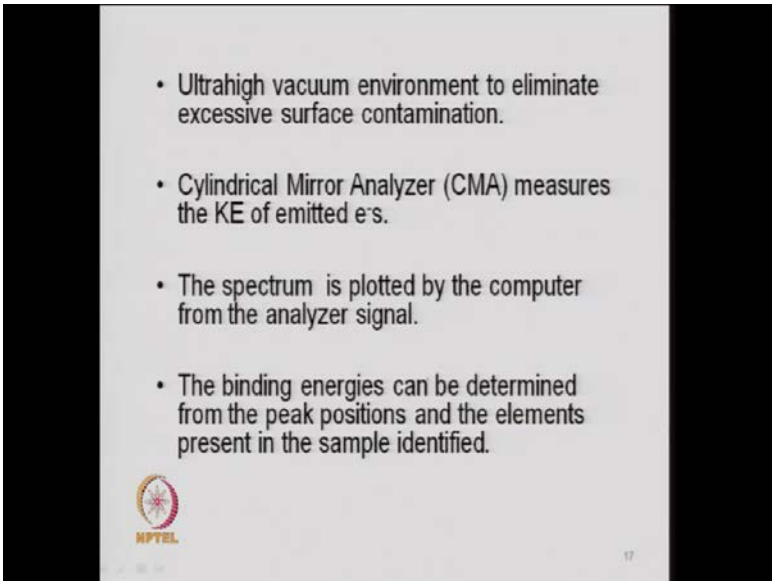

So, ultra high vacuum environment to eliminate the excessive surface contamination because, it is very suspicious technique cylindrical mirror Analyzer CMA, that measures the kinetic energy of the emitted electron. So, this is the system which is known as cylindrical mirror Analyzer. The spectrum is plotted by software from the Analyzer signal. So, you can get the kinetic energy and electron number of electrons versus kinetic energy, we can plot the binding energy can be determined from the peak position.

And the elements present in the sample identified so, once you the kinetic energy are known you calculate the binding energy and binding energy then again just like a software tools. The binding energy are specific to the metal com metal just like in x-ray diffraction I told the phase d value is important and knowing that d value from you can just calculate the phase identify the phases and that again I the miller indices Bessel phases 1 1 1 0 0 1. What the different phase is present and at different the indices that can be determined, when you do the action similar information you get in terms of the s p d f characteristic that is k shell, when you say l m n whatever the different Quantum's.

In that you can get the signal here and that again in terms of the s p d f like that in that numbers the different location, the number of electrons can be calculated or in terms of the oxidation state of the metal can be obtained from this information, once you know the binding energy this is the actual picture.

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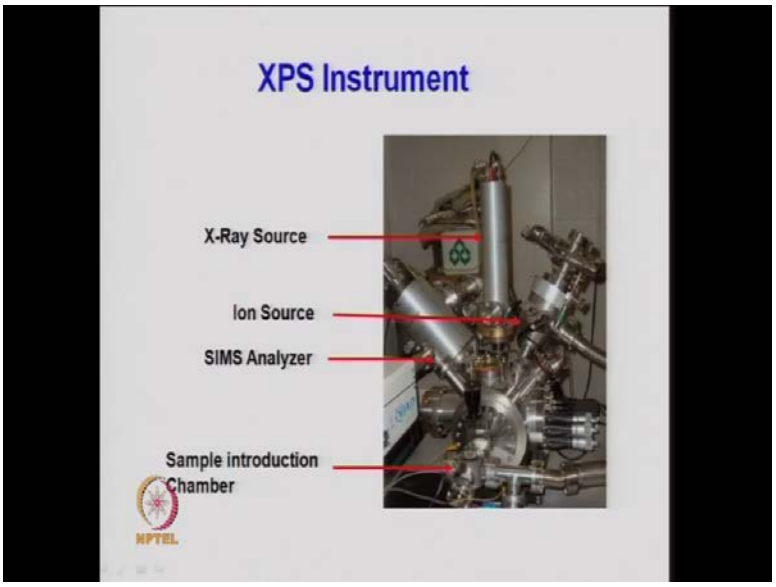

So, of a unit and 1 of the units so, x-ray source the ion source then secondary and mass spectrometer Analyzer then sample introduction chamber and then the other side detector source.

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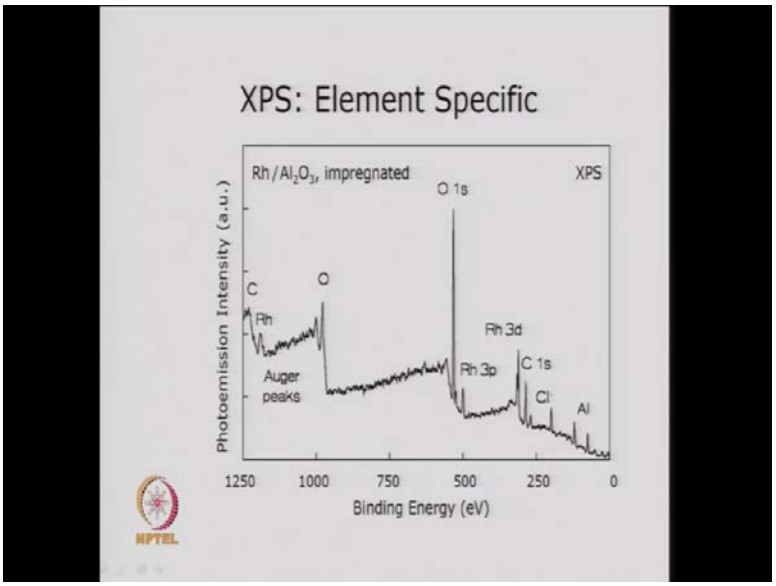

So that, is the picture of the XPS unit the results may be in the form of this signal. So, photo emission intensity which is some orbital unit versus the binding energy you can see here, the difference makes like this will get which are a specific to the structure or the composition of the metal Aluminum radium. So, it is a radium alumina in a catalyst so, you can see the radium you can see aluminum you can see oxygen oxide. So, you can get their positions also minus 3 d 3 p like that.

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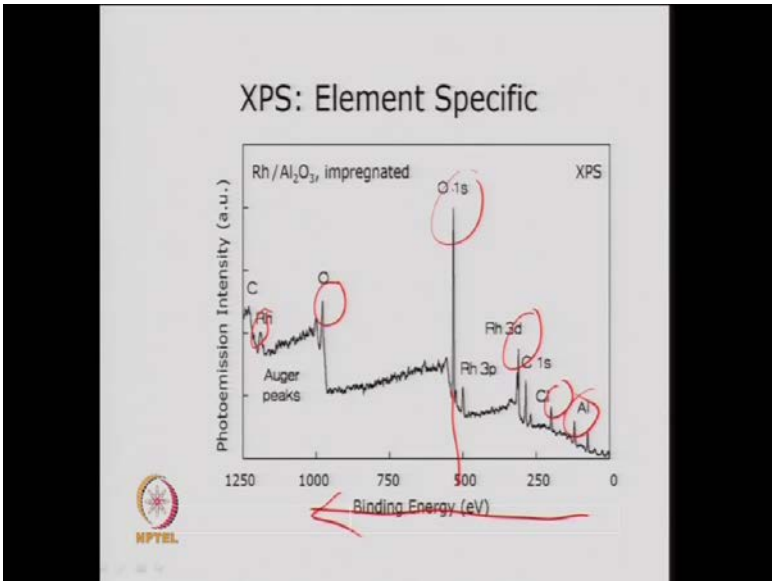

Because, they are very specific in terms of the binding energy. So, binding energy is increasing in this side so, you can get the information about the composition of the metal because; these binding energies are very specific. So, at this binding energy if I am saying this from information which is available in terms of the software, you can have the idea that this binding energy because, of this you know the initial metal composition.

So, you know what is the metal loaded there you can have the idea that what is the position is or quantum or what number what is the oxidation state of that metal. So, XPS provides you wide information about the chemical compositions. The every element specific so, notations you have seen here I have just given in terms of 3 d 1 s like that.

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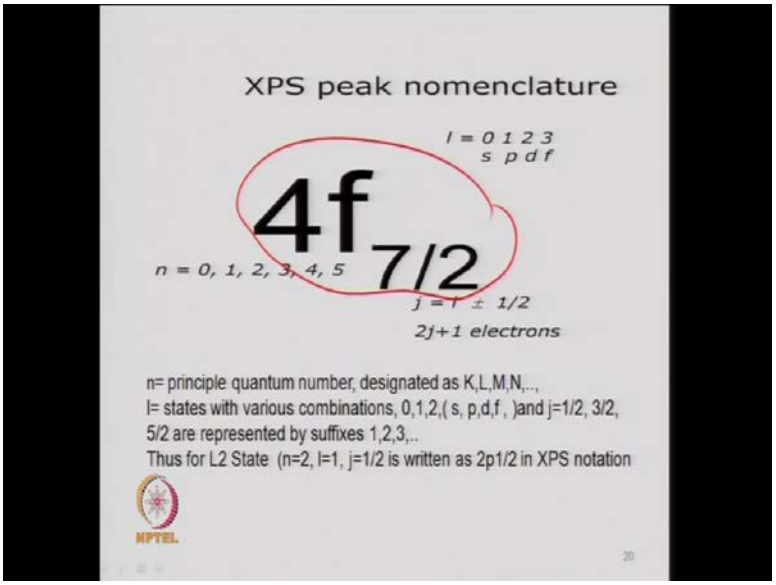

The notation may come like this also 4 f 7 by 2 something like that so, most of the time and we report it like this also which is just you can see here for the platinum 4 f 5 by 2, 4 f 7 by 2 platinum 0 platinum 2 plus platinum four plus.

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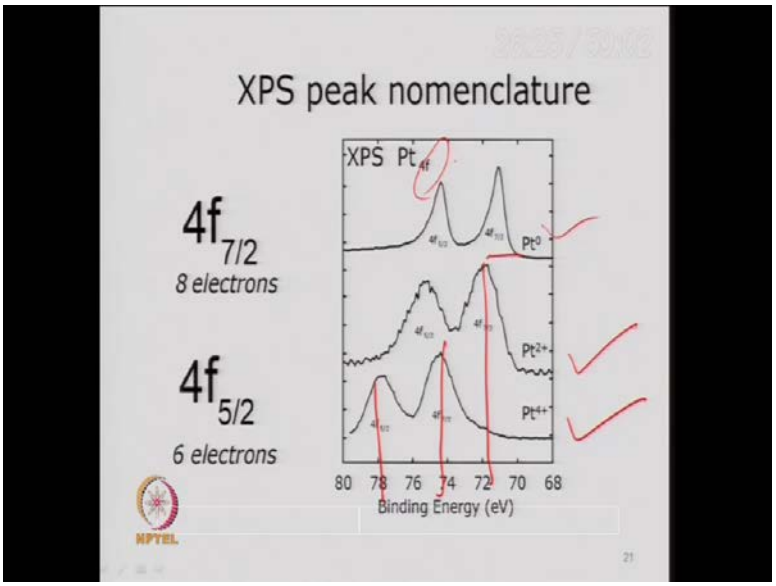

So, a different oxidation and the binding energy which is something like 78 74 like this 73 or somewhere 72. So, you have the different information in terms of this which we write 4 f or a slash 7 by 2 5 by 2. So, what does this number mean? It is something like this so, n which we write a principle number here, the first number is your n which is quantum number which represents your K, L, M, N like that instead of writing when you write auger electron you write it like that sometime we write it say 4 so, 4 means n.

So, this can be written like that also n so, this is representing the quantum principle quantum number, which is designated as K, L, M, N so, 4 mean this is n, 1 term. l is states the various combination of 0, 1, 2. So, generally these are indicatives of s, p, d, f. So, this either you write in form of l or you write here f. So, f means this is something like 1, 2, 0, s 1 p, 2 d, so 3.

So that, now this talks about the state of combination, various combinations. That may be possible and j is generally abbreviated like this 1 by 2, 3 by 2, 5 by 2 which is represented by suffix 1, 2, 3. So, basically this is representing the number of electron will be which when I write j is equal to some l plus minus half, so that, is talking in terms of energy shift which I am talking earlier so, negative means it is on the negative side from the reference 0 metal oxidation state positive side means on the positive side. That will depend on the binding Eb energy.

So, what I mean to say here is that once you know this 7 means 7 plus 1 because, j is equal to l plus minus half. So, it can be a positive or negative 2 j plus 1 is representing the number of electrons. So, if I just write directly because, j is plus minus then this l plus minus half so, basically this plus 1 will be your number of electrons. So, this is the just as an example here that for l 2 state suppose the state is l 2, so n is 2 so, your this l 2 state means n is 2 second quantum is k, l.

And suppose small l is state of that is 1. So that, 1 means it is p so, if state is 1 it is s p d f like s is 0 p is 1 d is 2 f is 3 like that. So, for l is equal to 1 it will be written p and j is half suppose so, the notation will come like this 2 p half where 2 is representing the quantum p is either you write 1 or it is the s p d f. The electrons from the s cell p cell d cell like that and l is j is representing the basically j plus 1 which is written here it representing the number of electrons.

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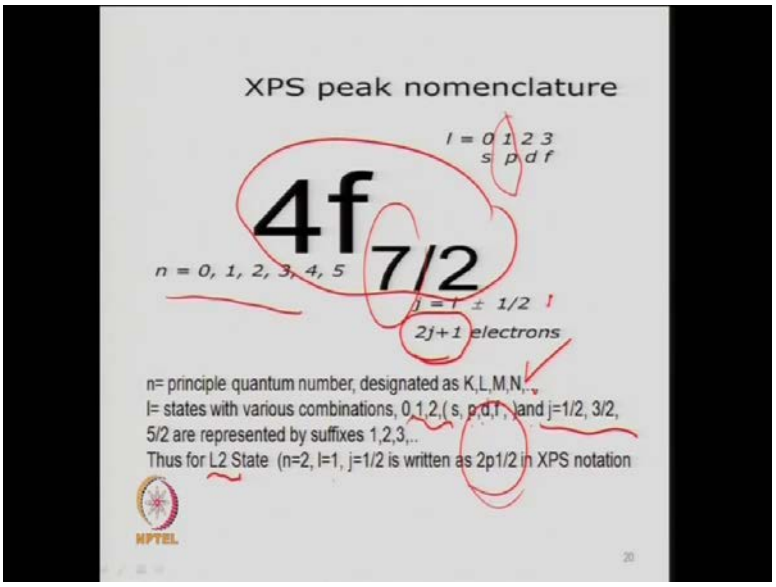

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So, this is just if you look at here the 4 f 7 by 2. So, k is 4 this is f which is now s p d f. So, 0 1 2 3 so, this is 3 and 7 by 2 is your the value of j which is as I said 2 l plus half plus minus half rather so, it can be energy shift from the metal site. So, this 7 plus 1 means 8 electron you can very easily now directly add here also or you do what about 2 and2 times whatever this number plus half 1. So, here 5 means its 1 6 electron.

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So that, is what written here 2 j plus 1. So, 2 time j plus 1 so, you can have the information about the state so, platinum 0 which comes at this binding energy and position is 4 f 7 by 2, it means 8 electrons here 4 f by 2 6 electrons in that cell or quantum. So, this gives you a valuable information about the oxidation state of these metals or reduction state of that metals also beside that it can talk about the dispersion also because, it is a metal and the support.

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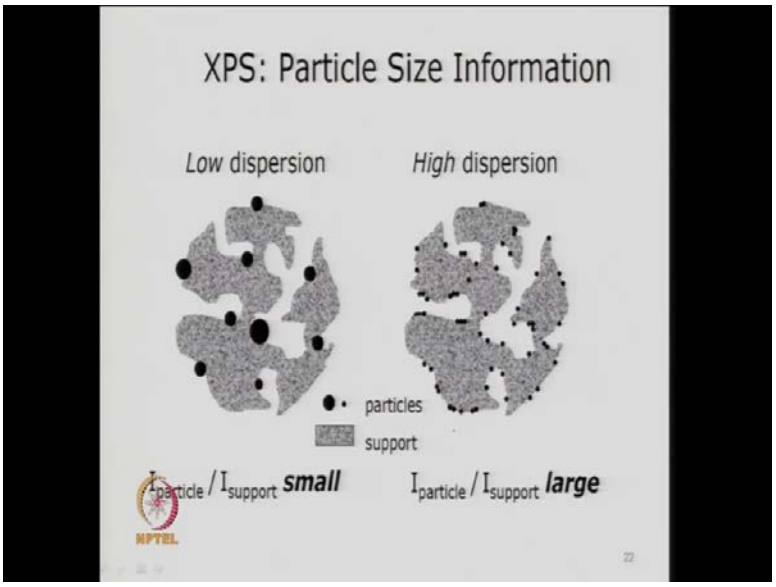

So, intensity of the metal will be different intensity of the support will be different. So, we just measure here I particle intensity of the particle divide by the intensity of the support. So, the intensity this number is low it means the particle size may be larger because, they are cluster is the or the support is dominating in one way it is less dispersed, where as in the other case you can see here the fine crystallites are sphere. So, for them I particle over I support will be large.

And which is related to again intensity of the energy that is kinetic energy which you have measured for the different electron or again the binding energy because, you are looking in terms of the metal and support the both properties are being measured metal as well as support as I said. Aluminum is there oxygen is there platinum is there. So, it will measure everything so that, information so, by knowing this spectra you can also see whether it is highly dispersed or poorly dispersed.

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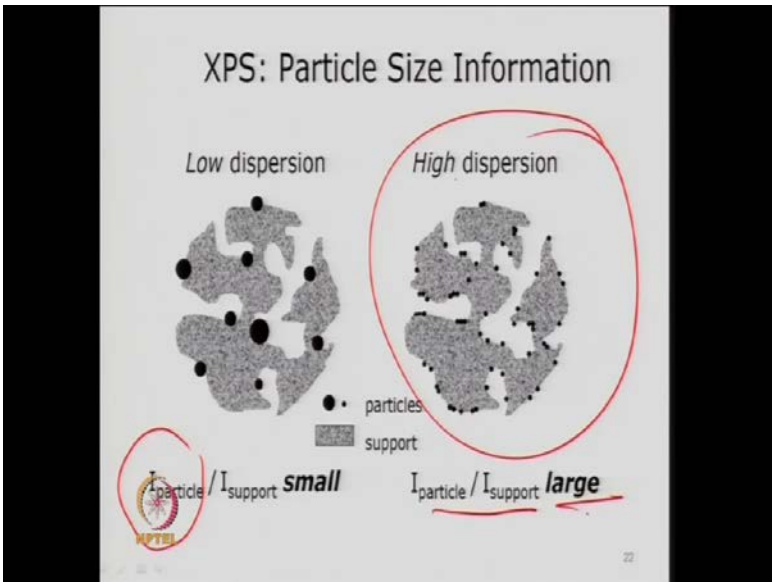

So, these are the particles which can be seen here. So, larger particle these are the smaller particles well dispersed on to the support so, there I particle over I support will be larger.

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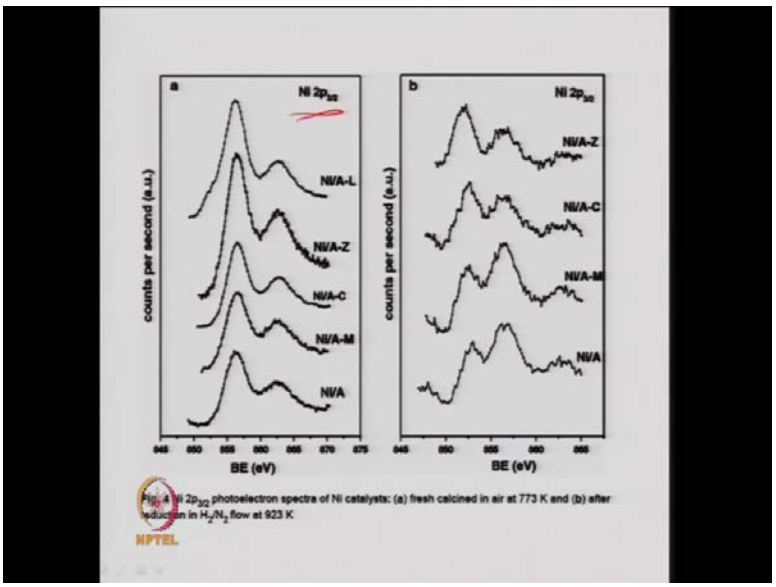

This is again some information or a nickel based catalyst on different support. So, the information again can be used for the first catalyst this is the fresh 1 and this is the catalyst which is after reduction in hydrogen, nitrogen. So, there is some difference here if you look at the spectra here. So, nickel and a 2 p 3 by 2000 that is 1 here and for all cases us are just measuring this at this binding energy which is roughly 855 electron volt.

So that, is the nickel specie and if you just analyze them in terms of the spectra because, the spectra which you see after so

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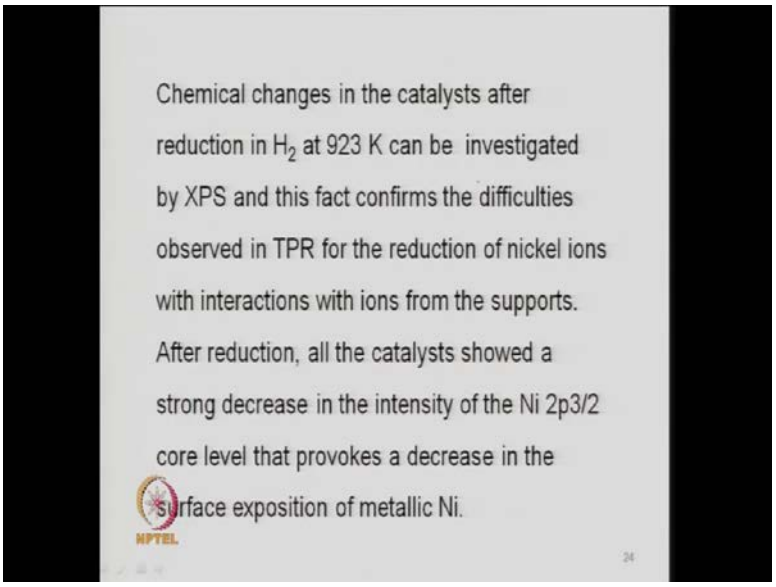

I will just discuss here that, the chemical changes in the catalyst after reduction in hydrogen at 923 Kelvin can be obtained from XPS. So, this can give you the information which may not have been obtain or observed from your temperature program reduction, the similar information. It is a basically it is a information which can also be observed from the temperature program reduction because, you have heated it in the presence of hydrogen and TPR also gives you the similar information but, sometimes either the metal support interaction may be an issue very strong so, spillover may be a problem hydrogen may have given you h positive.

H t plus different oxide deduction states different state so the this may be a spillover of the hydrogen so, TPR may not give you the adjective information of the metal after reduction. But, here with team XPS you can get much more information so, nickel ions which are interacted with the support. So, TRP may fail in that metal support interaction so, here in this case the after reduction the all the catalysts showed a strong decrease in the intensity of the nickel 2 p 3 by 2 core level.

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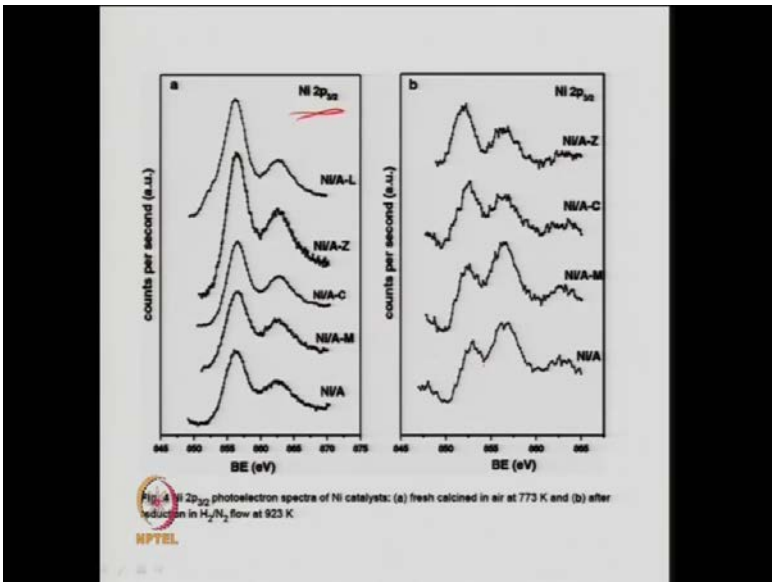

So, you can see here the intensity of the peak here is lower now. The peak if I just look at in terms of the height from the base. So, in all catalyst after the reduction the peak intensity is poor. So, this is because, the interaction now you can correlated that when you reduced it there may be some kind of nickel Aluminates something like a different metal nickel has reacted with the aluminum oxide and found that ways and because, of that when the reduction is taken these are difficult to reduce. So that, Aluminates fails some interaction you can or some observation is that all the catalyst showed a strong decrease in the intensity of nickel which is in the formula 2 p 3 by 2. So, 4 electrons here core level that provokes a decrease in the surface exposition of metallic nickel.

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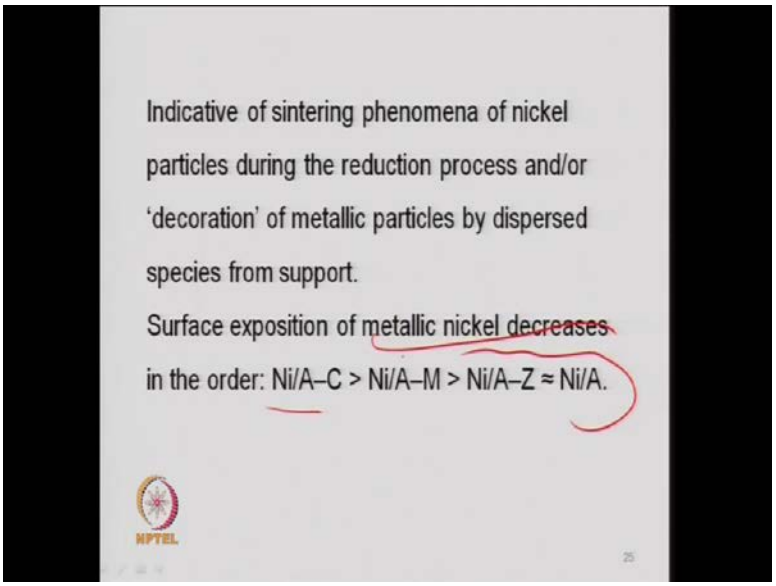

So, this can be indicative of the sintering phenomena during calcinations so, calcinations because, of sintering of the nickel particle during reduction process and it may be a decoration of metallic particle. That because, sometime when the structure change or the shape change so, we call it decoration. So, decoration of metallic particle by dispersed specie from the support so that, can be another reason the surface exposition of the metallic nickel. In this case decrease in order of a c nickel a m nickel so, this is sometimes order of magnitude by which the surface property has change so if you look at here(Refer Slide Time: 34:12) in the graph. So, you can see the structure wise and the intensity wise so, there is slight shift also in that.

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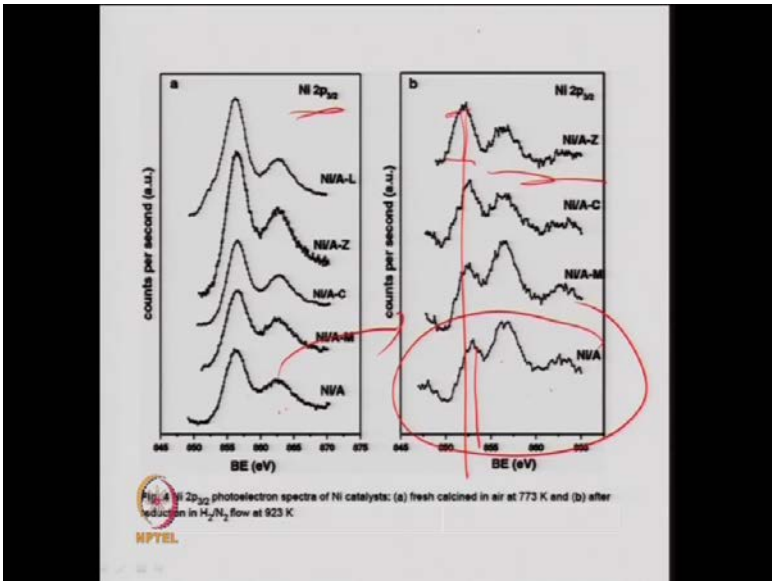

So, here it is slightly at this here it is slightly if you just look at here it comes here same thing here so this is better in that way reduction of this catalyst compared to this one here you see here. So, that is the that from XPS you can get the information if you compare these two this and this so in this case it is better compared to rest of the catalyst so XPS if you just have a definite info analysis or a thorough study of these peaks you can get much more information from the XPS which may not have been observed from the TPR.

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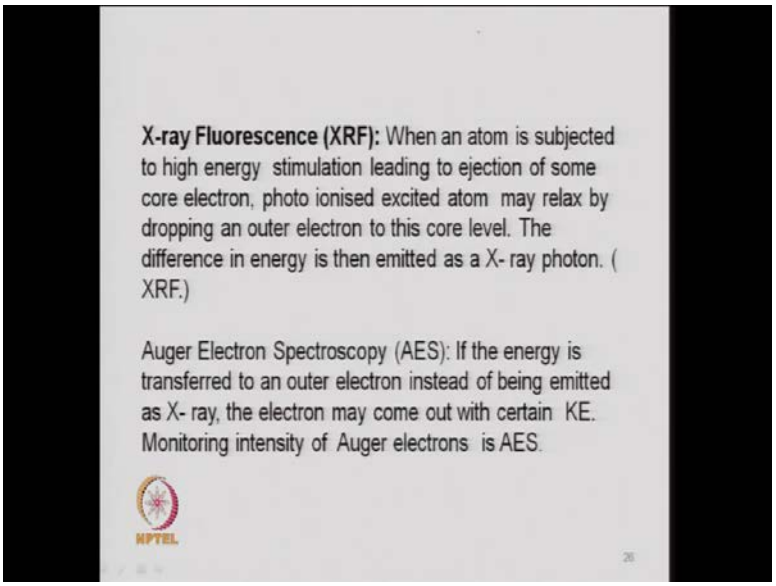

So that, in that way the XPS becomes a very important tool for characterization another one which is x ray fluorescence, the again it can be used because, the based on the principle same principle of the energy of the photon. So, you can use it for determination

of sulfur compounds also at low level. So, becomes a very important tool the principle is that when atom is subjected to a high energy stimulation leading to an ejection of some core electron this like an XPS.

So, you have the energy beam and then you get some electron which leaves a surface and comes out from the surface the core electron photo ionized excited atom may relax by dropping an outer electron to this core level. So this is something where you have given some energy and that stimulate some electron so, which comes out core electron same thing which is a closer to the nuclei photo ionize it can be ionized, excited atom that may relax by dropping an outer electron to this core level.

So, whatever the electron which is in outer level that may also get excited because, of the energy which has been given so that, is the fund of the outer electron also in outer electron spectroscopy also it is a back scattered electron. So, here it is the attack on the core electron but, because of that the outer electron is also getting excited so, what the outer electron to this core level the difference energy is then emitted as an x- ray photon so, when you have the energy of this core electron and energy of its outer core electron then that is related to the some energy which can be measured between them and that is again because, every metal has the atom and these have the specific s p d shell.

So, energy levels are different of these so that, is metals specific so, you can find out the information from that so, this is known as x- ray photon or x ray fluorescence x-ray fluorescence, that method can be used for determination of the composition. So, sulfur compounds can be determined by using x- ray fluorescence based on this principle another thing auger electron again as I said if the energy is transferred to an outer electron instead of being emitted as x-ray the electron may come out with certain kinetic energy.

So, now it is not that the core electron is coming out rather it has transferred the energy to outer electron and that may relive that is after back scattering secondary electron which may have lower energy but, its kinetic energy can be measured the electron may come out with certain kinetic energy and monitoring intensity of these electron and these are known as auger electron, which have relatively lower kinetic energy so, principle is same I am not going in details of that so, this some auger electrons if you look at here just to explain that the electron released.

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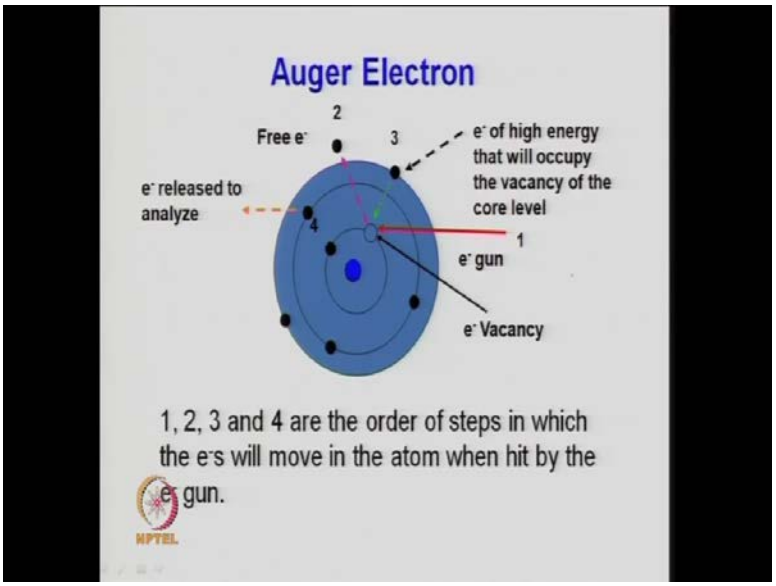

So this is your core, so electron gun comes to the core here and then the vacancy comes from here and since so, this is your step number 1 this electron will go out because, energy try to go out rather and once this goes the form here, the electron of high energy that will occupy the vacancy of core level because, this is now vacant. So, electron will come out from here and then since there again the electron from this outer one will again release and this will go out.

So, you can measure the energy of these electrons these are secondary electrons this is your primary which, where this information is basically for XPS but, this is a weaker electron secondary electron or a back scatter electron. So, this energy released is analyzed now rather this one which was directly coming from the free electron. So, energy of the secondary electron can also provide you the information in terms of surface composition.

So, which is just here electron of high energy that will occupy the vacancy of the core level, once the some h new source has been impinged on it so that, is what the here the when the core electron leaves a vacancy an electron of higher energy will move down to occupy. The vacancy while releasing energy by photons or auger electrons each auger electron carries a characteristic energy that can be measured. So that, is the fundamental of the auger electron spectroscopy similar to the experience.

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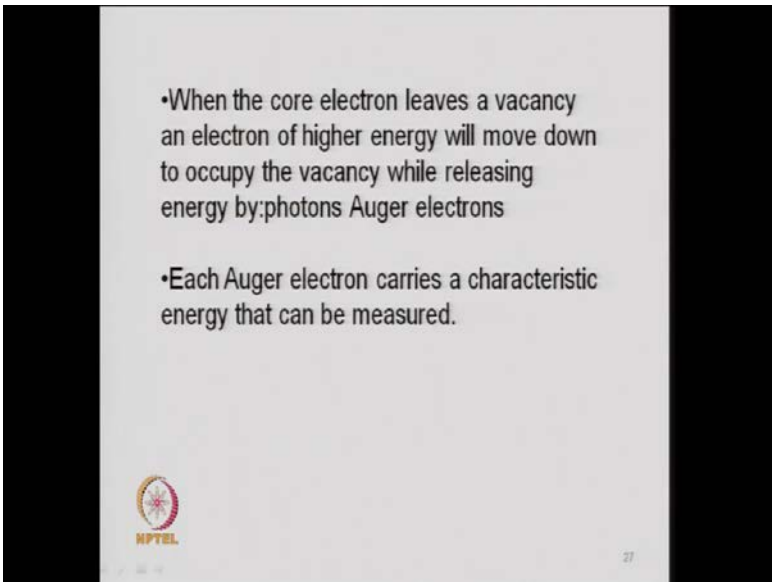

But now, it is not the primary core electron but, a secondary electron so, this is what the structure here it is shown that the electron release from the top layer. So, this is the top layer this is your inner surface and electron beam which is here and you can measure the energy of these secondary electrons now not the core electron. So, the electron which is released from the top layers so, their energy can be measured.

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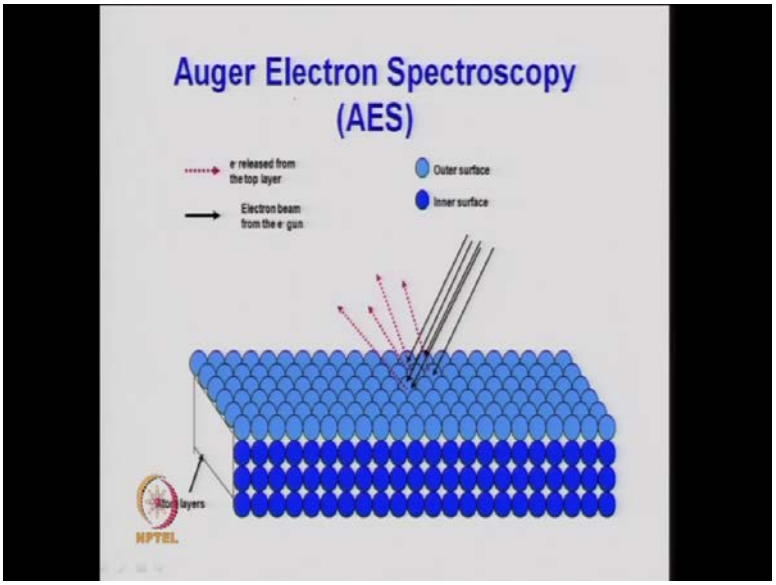

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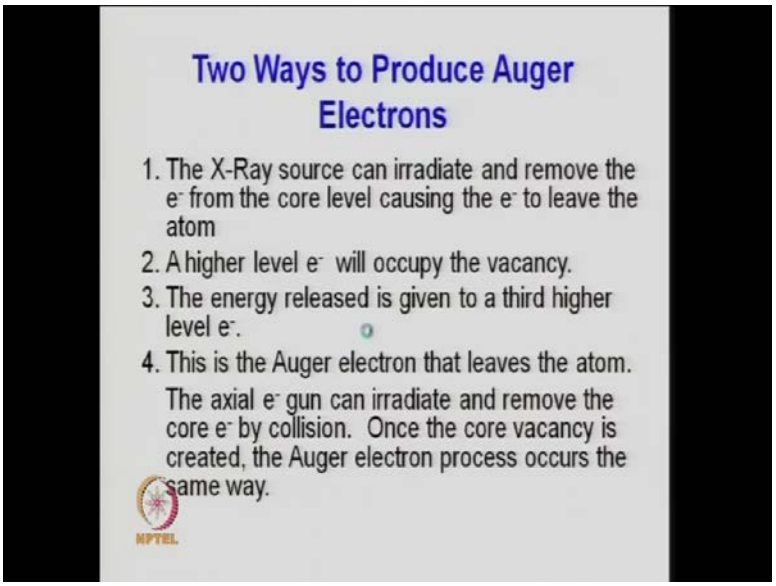

Auger electrons can be produced there are different ways. So, there are basically 2 ways which have been discussed here in this, is that the x ray source as usual you do for the XPS h new energy. So, x-ray source can irradiate and remove the electron from the core level causing the electron to leave the atom, that is the first step which is in has been discussed earlier also in x-ray photo spectroscopy. So, at higher level electron will occupy the vacancy because, the core electron has lost the energy released is given to a third higher level electron that is what is discussed in this figure.

So, core and then this is what the step the energy will transfer the core electron transfers to the outer core comes to the inner core. This is the auger electron, that leaves the atom the axial electron gun can irradiate and remove the core electron by collision so, there so that is the in-depth analysis you look the electrons are colliding with subsequently layer and the electron comes out from that.

So, these are back scattered electron also once the core vacancy is created the auger electron process occurs in a similar way. So, the process continues. So, you can measure the energy of these secondary electron and the basic for catalytic composition is that we are measuring the kinetic energy of the secondary electron and that is related to the property of the metal. So, composition can be determined.

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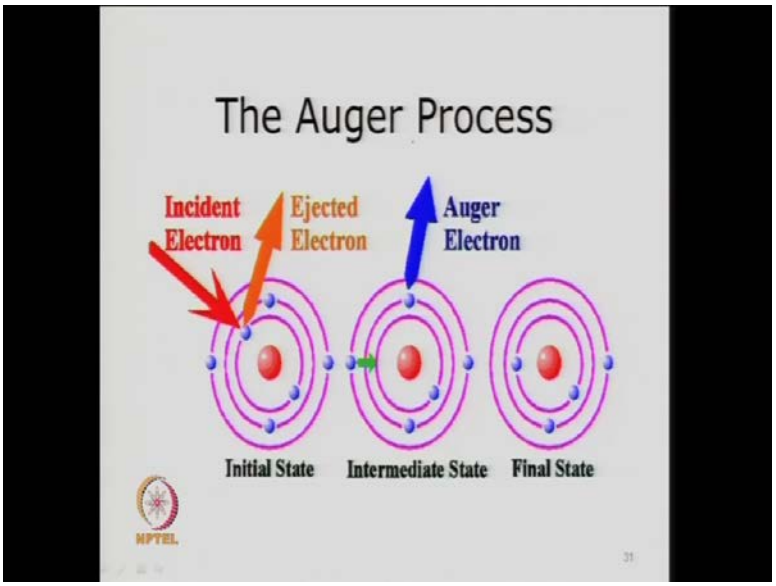

So that, is what the auger process we have discussed is that the auger electron this is what the core electron something like here. So, the incident electron ejected this is the secondary electron so and the vacancy creates this going into the inner core. So that, is the final state now when the electron has left the process. So, you can get the information in the similar way you can get the intensity as a function of kinetic energy.

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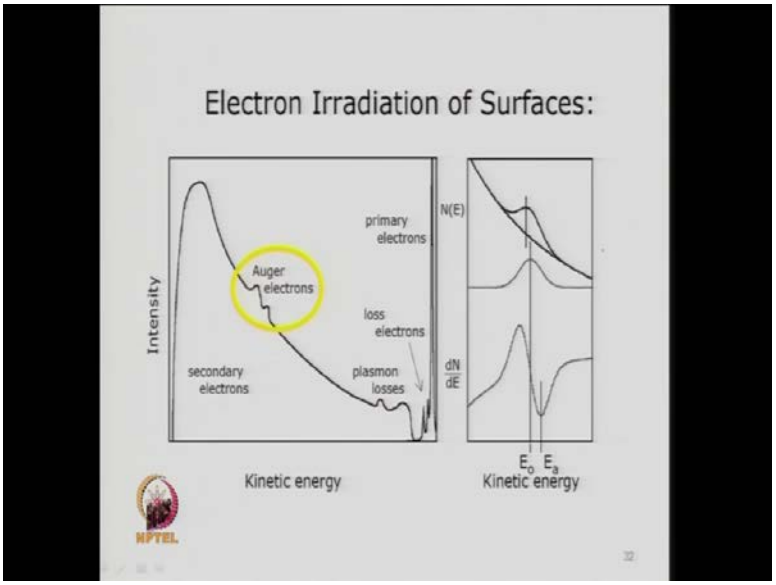

So during XPS process also you can have the auger electrons which is shown here because, XPS is similar they are the core electron energy you are measuring but, if you

measure the energy of the back scattered electron or secondary electron, then you will see those also the low binding energy so, they have low kinetic energy in one way something like here which is shown here auger electron or secondary electrons. So, primary electrons are they have like this intensity if you look at ionic electrons plasma everything this is the second you can measure them.

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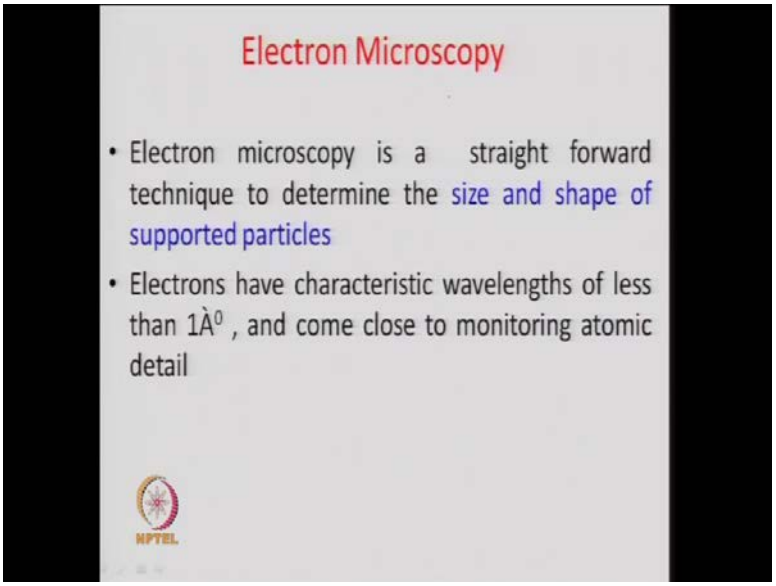

This is what the technique based on photons. The third which were talking for characterization the b electrons, the atoms when you are talking now electron bombard will not the photons x-rays the this earlier was based on the photons x-ray photons so, here the electron microscopy is one. Which is the straight forward technique to determine the size and shape of the supported particles very important tool to determine the size shape and even you can measure the dispersion also from that so that, is so here the electron guns the electron bombardment because, the electrons have a characteristic wavelength of less than 1 angstrom where as the x-ray what I was talking wavelength is roughly 100 angstrom or like that so, they come close to monitoring the atomic detail.

So, you can have the information of the atoms even you can have the pores pore structures and through that the electron can penetrate to that pore and then it just look at the metal property so, you can have the information on the pore also you can have the information of the metal particles their crystallite. So, this is a very important tool in

terms of the catalyst characterization or topology of the surface morphology crystalline size shape.

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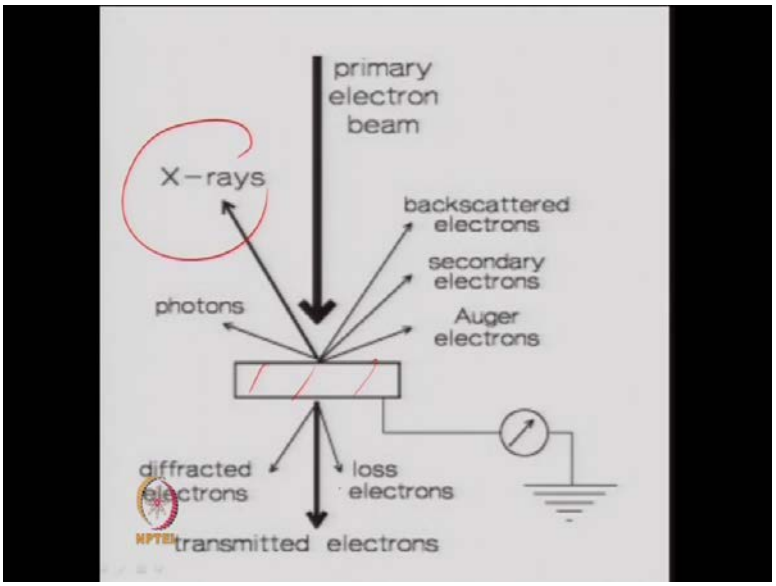

So, the principle if you look at here what I was talking last time also that a primary electron beams again. And you have the x-ray you measure what we have seen in x or photons so, x ray photo spectroscopy auger electron they are based on these technique back scattered electron again the same secondary electron auger electron so, these are the electrons when the primary electron beam strikes on the solid substrate, that is the catalyst or which contains the metal there are the diffracted electrons there are loss electron and transmitted.

Now we are looking here the transmitted electron or the back scattered electron. So, they strikes the metal so, whether a metal is hard or soft so, this or there is a core or hole so, the beam can transfer easily through that. So that, what the scanning electron microscope or transmission electron microscope these are based on 2 principles.

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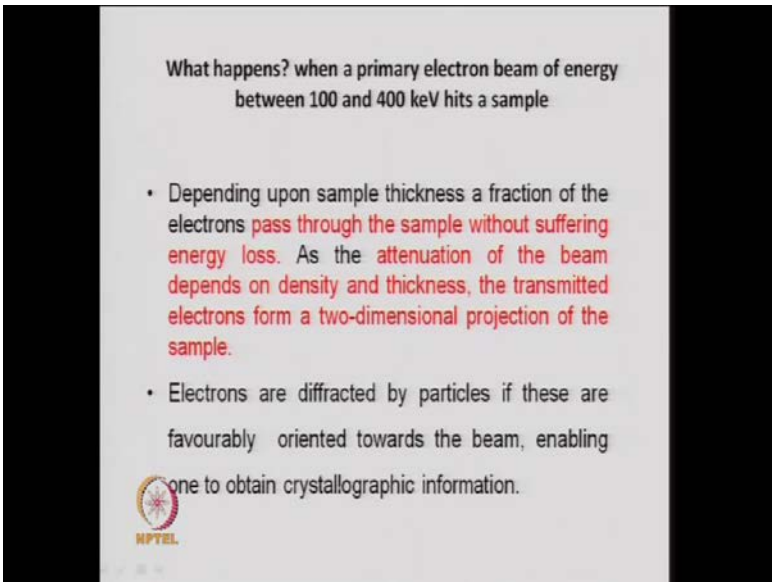

What happens when a primary electron beam of energy which has roughly the energy level of 100 kilo electron volt or which can have a up to 400 electron volt also they hit the sample. So, depending upon the sample thickness a fraction of the electron pass through the sample without suffering any energy loss, that is just to transmits to that as the attenuation of the beam depends on the density and the thickness of the transmitted electron form a 2 dimensional projection of the sample. So, know you can have from that the how the beam has diffracted or striked has been transmitted through that sample, it can give you a 2 d image of that. So, whether it is solid, it is a hole there cracks there.

So, depending upon that the beam this energy beam will transmit through that and it will give you some a kind of 2 dimension emulsion of that so, electrons are diffracted by the particle where as some particle the and hard materials so, depending the electron will diffract if these are favorably oriented towards the beam. This can provide you the crystallographic information.

So, you can get the information or shape of the crystal so, that is because the edges are there. So, there will be a more and more diffraction so, by knowing that you can create a surface basically, how the surface is created you can just look at the energy of that surface and then you can have the idea about that. So, electron can collide with the atom in the sample and it can be a back scattered back, what we talked back scattered electron.

So, back scattering will be more effective, if the mass of atom is high like platinum, if you have rhodium, ruthenium you have.

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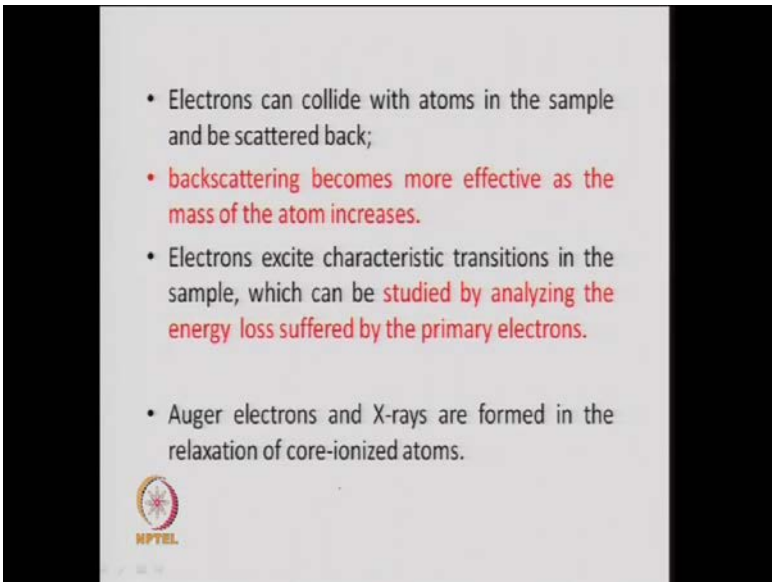

Rhodium ruthenium hard metals so, it will be more electron excite characteristic transitions in the sample which can be studied by analyzing the electron loss suffered from the primary electron. So, principle is same again the how much energy is lost that is your principle of your auger electron or your x-ray photo spectroscopy. So that is what the electronic property that's what the energy change or energy loss is and that was measured. So, auger electron and x-rays are formed and that is what the core ionized.

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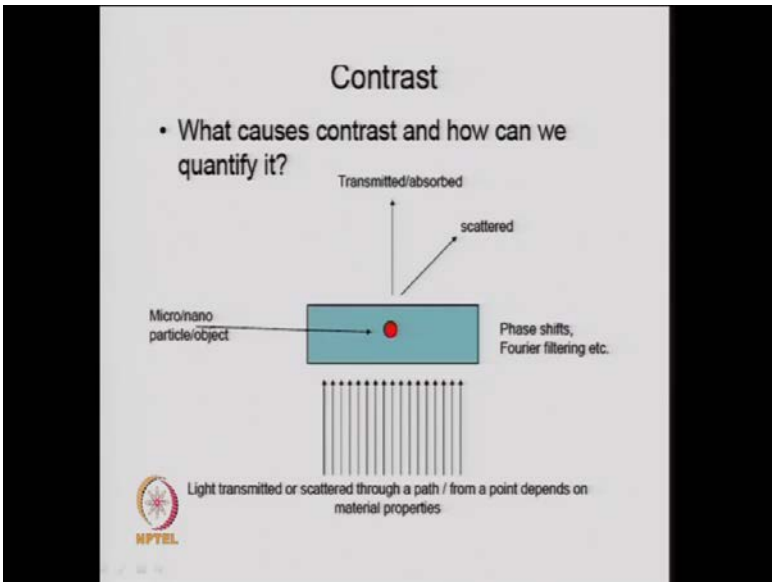

So that, we have already said so, we are not talking this when we talk about the scanning electron or the transmission electron but, the basic is same so, what cause contrast when you look at the transmission electrons microscopy or scanning electron microscopy you look some kind of difference a solid is there when the metal comes out that or different metals are there so, the diffraction is different and that is what is the contrast using and can we quantify it you can quantify.

So that, is what the transmitted or adsorbed beam. So, you have given some primary electrons here light transmitted or scattered through the path from your point it depends on property of the material. So, it is scattered say transmits and phase shifts whatever the Fourier filtering so, many things micro nano particles object. Whatever so, you can have the information by measuring these things, the fraction patterns. So, this is what the transmission electron microscope.

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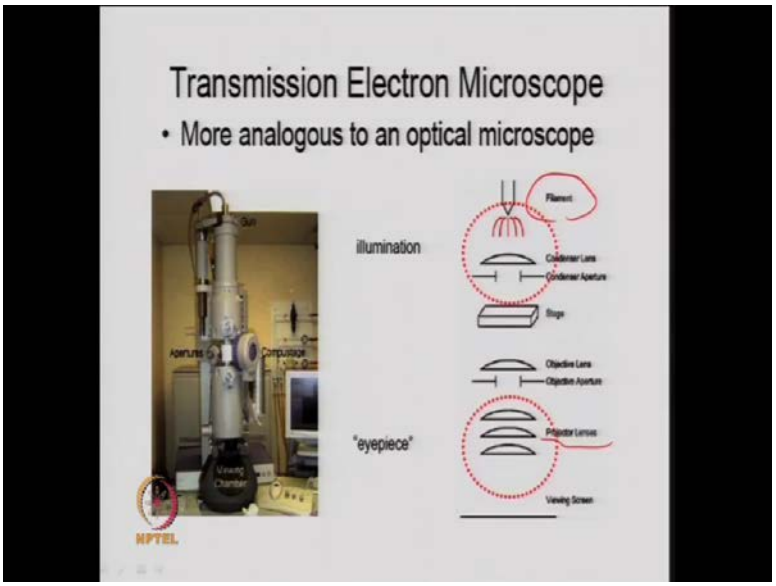

So, the idea is again that it is a high energy beam a kind of energy beam basically but, high energy electrons in one electron and so, you have a filament a if you take this is a filament here and just these are the condenser lens to have the monochromatic relights. So, energy source so and this is your objective lens here objective aperture and this is your viewing screen.

So, you have the protector lenses here so, there are series also, this is just like an optical microscope if you look at the only thing that instead of having optical microscope here you have electron microscope. The otherwise it is a just you are taking a picture of that but, optical microscope cannot give you the image of say 1 angstrom 10 angstrom 100 angstrom 500 angstrom. But, this can give you because, electron has the wavelength of less than 1 angstrom. So, it can detect that so, this is the kind of instrument.

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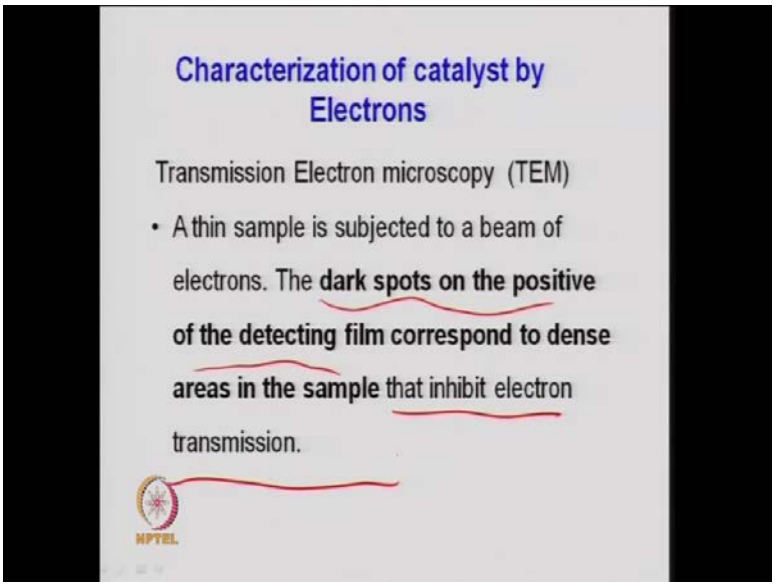

So, characterization if you look at the when the how team works or transmission electron program gives you the result so, a thin sample is subjected to a beam of electrons. And the dark spots on the positive of the detecting film that correspond to the dense area so, wherever the dense area the electron cannot transmit through that so, you will get the dark spot of that. So, this and wherever there is a soft surface the electron can transmit through that so, SEM and TEM the surface will be a darker there or SEM in TEM it is darker in SEM it will be white type. That data will talk so, there is a means transmission is left on micrograph there is 2 d picture basically and it looks the contrast.

So that, the important thing that to how to look at the value when you have the beam of electron. So, the darkest spot which is because, of the hard surface because, the it cannot suppose platinum is hard so, the thing can pass through that so, it will pass through the sites or there are edges it will diffract the light from that. So, that is the different so that inhibit the electron transmission. So, this will give you a dark spot. So, dark spot form the outline of metal particles or crystal or the crystallites.

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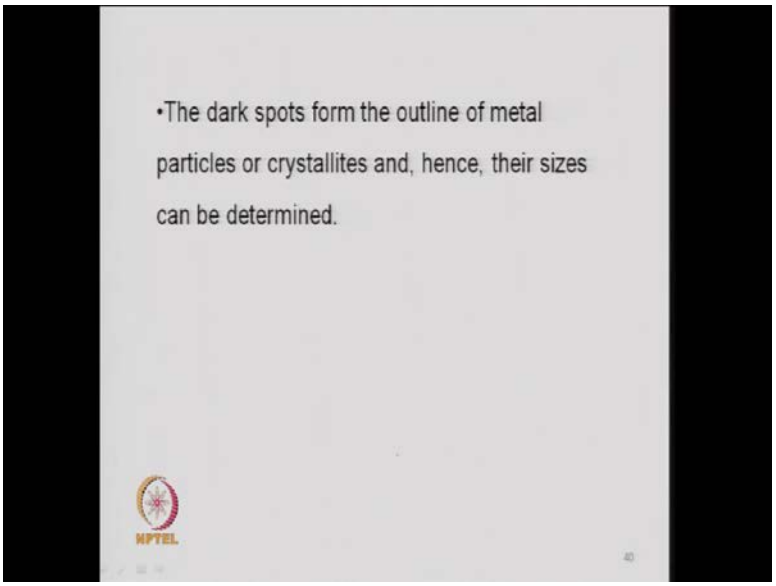

And hence their size can be determined so, wherever you have a metal part so, electron cannot transmit through that so, even if there are edges so, it will show some darkest spot there because, the wavelength is of less than 1 angstrom. So, it can see that up to that level so the even if there is edge. So, it will just detect that edge of that particle. So, even there are multiple edges it can detect that so, that will show because, the light will transmit cannot transmit through that it will defect. So, that Funda is used here to look at the crystallography property of the support or the metal.

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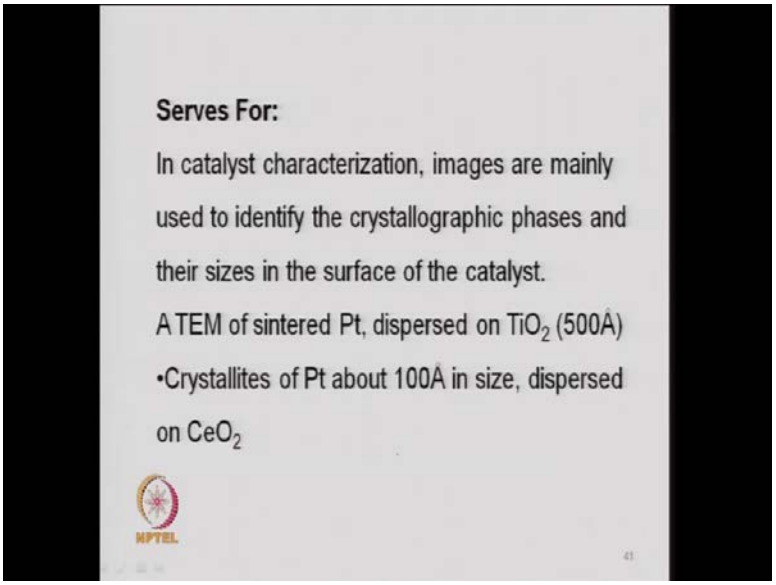

So, in that way the transmission electron micrograph that provides a information and images are mainly used to identify the crystallographic phases, their size and surface of the in the surface of the catalyst. So, whatever the surface of the solid so, how these metals have been distributed even dispersion can be measured agglomeration of the particle can be read from that graph. If the coke is forming that can be sin on the surface of the metal. So, different type of information can be obtained from this transmission electron micrograph. So, just if you look at this a sintered platinum dispersed on titanic which is size of roughly 500 angstrom and crystallites of platinum which is about of 100 angstrom dispersed on ceria.

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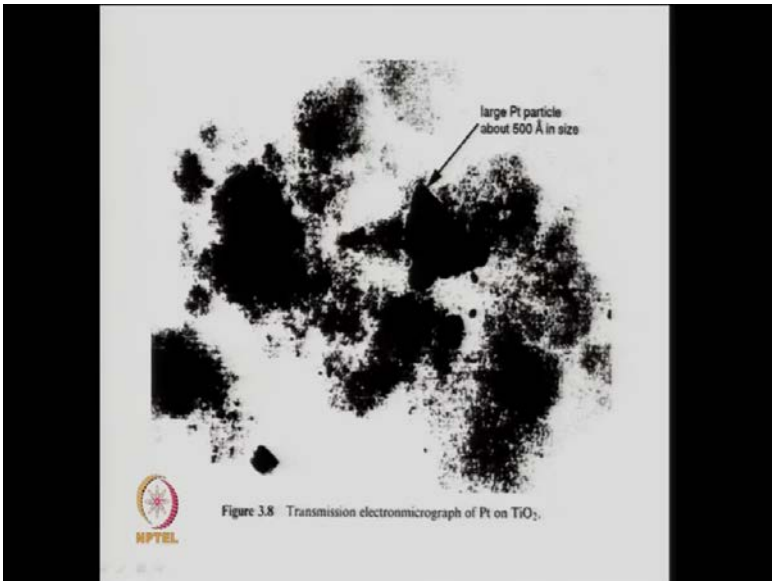

So, that, picture is given here so these are the particles of platinum dark spots the platinum so, large platinum particle about 500 angstrom in size. So, you can see that whatever the different so, they are agglomerated types catalyst site.

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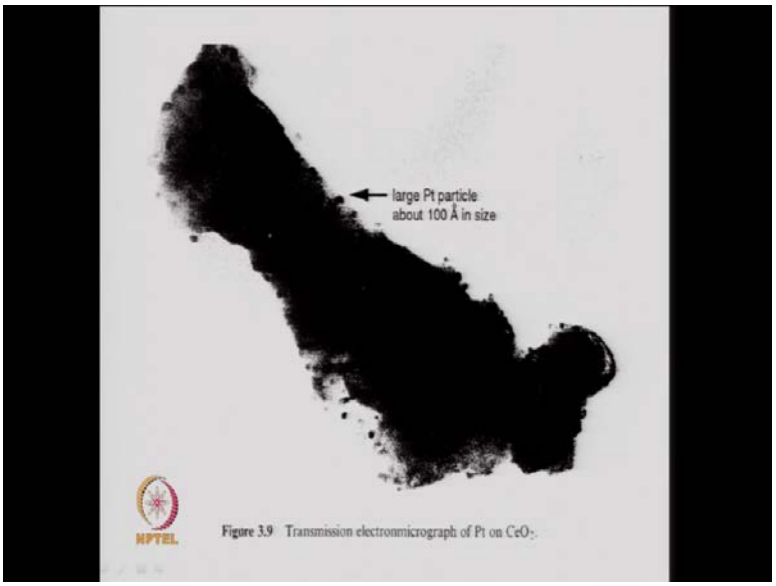

So, particles this is again a crystallography platinum on ceria. So, you can see the large platinum particles, which have roughly 100 angstrom in size. So, this magnification it can be order of the1 lack times. Whatever the actual particles size you can see from the transmission electron. So, you can see the morphology can be determined from a scanning electron micrograph also. But, 10 can give you the you can count the number of particle also they are well dispersed you can count them. And you can define your surface area also crystallite size crystalline surface area so, these information can be provided from this.

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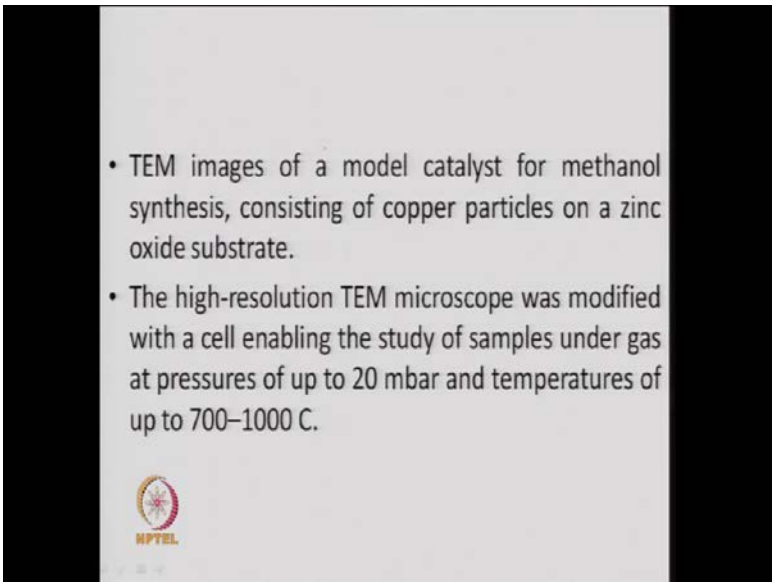

So, just what is here the TEM image of a model catalyst for methanol synthesis consisting of copper particles on a zinc oxide substrate, that another example which are shown taken and high resolution transmission electron microscope was modified with cell enabling. This study of sample under gas at pressure up to 20 million bar and temperature up to 700 and 1000 2000 degree centigrade.

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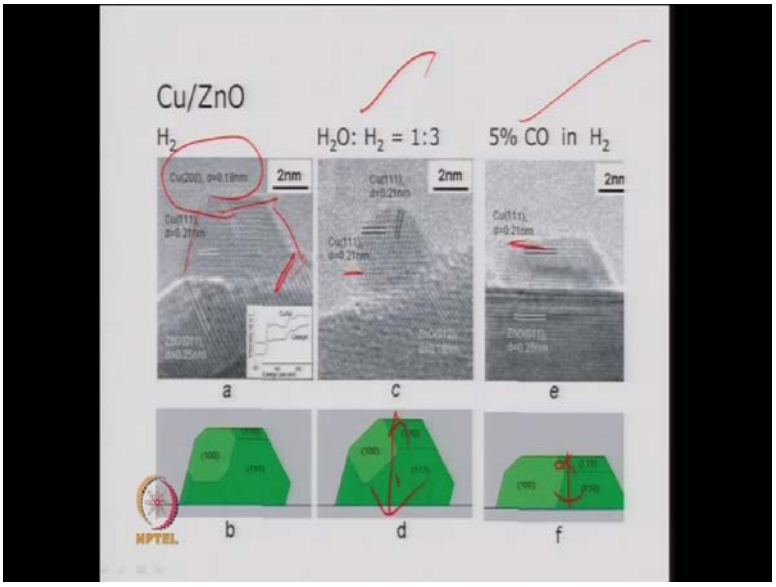

So, this is just a experimental data we just indicate that what information you can get from the transmission electron micrograph. So, you can see here that this because, of the edges the shape can be seen here, this is what the shape of a metal copper on zinc oxide. So, this is what so and that has been pictured here and this way you can see the edges. Now, here because, the different edge there will be diffraction from the edges.

So, the dark spot which is here you can see this like this has been taken picture like this. So, something like this structure this 1 here so, you can see now this size of this metal also because, the particles can be seen here and this scale this is of 2 nano meter this from here to here it is 2 nano meter. So, it means if you can very easily see the points or on a linear length you can measure the length and see the count the number of particles, carefully. So, you can find out that how many particles in that length and then you can find out the size of particle. So that, is what shown here that 0.18 nano meter which is for this copper 2 0 0 that is the position of miller and disease of 2 0 0. So, that information can be obtained from the transmission electron micrograph. So, this is what I mean to say

when you have the treatment with the hydrogen and water when you have treatment with carbon monoxide. The morphology changes you can see the particle size 0.18 here it is 0.21 nano meter here and it is again 0.21 nano meter here but, the structure has changed see here it is different edges and here it is different so, this is the structure is changing basically. So, there TEM can provide you the information about the change in the structure also or crystal size also crystal composition. So, the wide variety of information can be obtained from the or through the transfer transmission electron microscope. So, I will continue it next time I stop here.

Thank you.