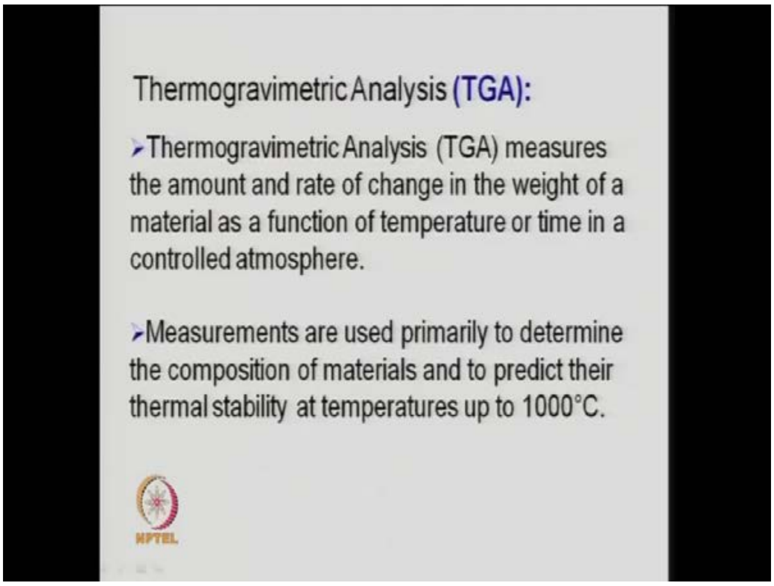
Heterogeneous Catalysis and Catalytic Processes

Prof. K. K. Pant
Department of Chemical Engineering
Indian Institute of Technology, Delhi

Module - 04
Lecture – 14

Good morning, in the last lecture I was talking about catalyst characterization methods and we were talking the heat method. So, I said that you can have some ions you can have some x-rays photons and you see the response of the refracting beam diffracting beam. So, different methods can be used to characterize the catalyst or to identify the surface methodology. So, we were talking about APR that was the one method and the second one is TGA thermo gravimetric analysis.

(Refer Slide Time: 00:55)



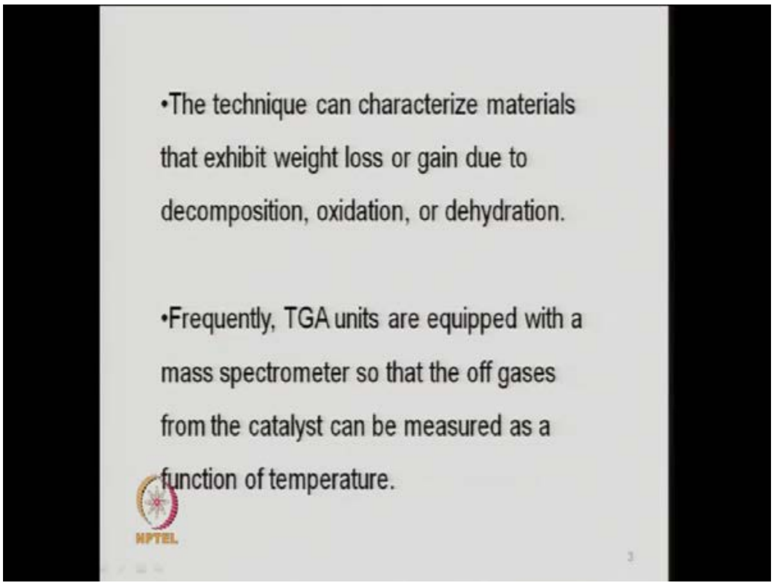
Thermogravimetric Analysis (TGA):

- Thermogravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere.
- Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C.

So, we have talked about this yesterday also, the thermo gravimetric analysis if you look at it measures the amount and rate of change something with respect to temperature and time if you have some data and how weight changes with either temperature or time. So, you can find out very easily the kinetics, also by using this operator but, in the case of catalysis this can used to determine the temperature required for oxidation. The moisture present if you want to remove the coke from the catalyst then, you can again have the heating in the stream of oxygen you can get the different information.

So, basically you can get weight of a material as a function of temperature or time in a controlled atmosphere. So, measurements are used primarily to determine the composition of material and to predict their thermal stability may be at temperature range up to 1000 degree, 1225 and so on. The unit or furnaces, which have been, which has been used for the operation.

(Refer Slide Time: 02:06)

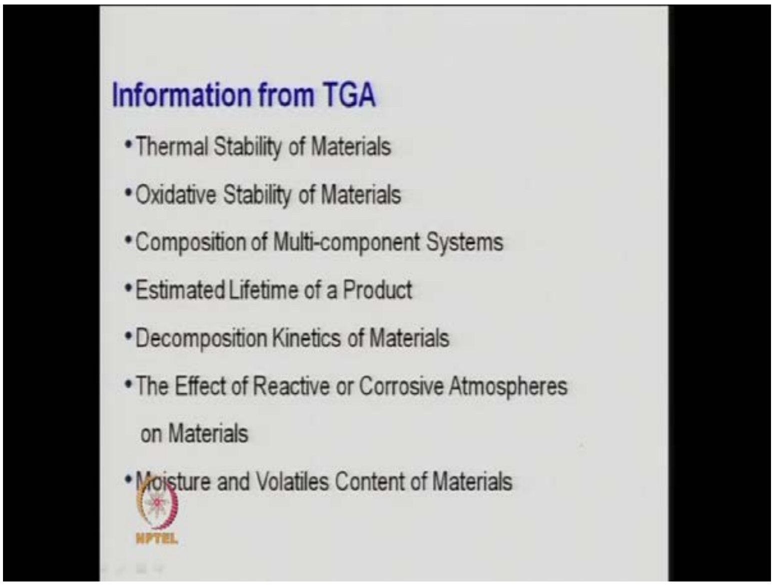


- The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration.
- Frequently, TGA units are equipped with a mass spectrometer so that the off gases from the catalyst can be measured as a function of temperature.

So, the technique, this can characterize materials, which is weight loss or gain, because sometime if you have a recursal of the metal and then, you have the oxidation or oxidizing environment, it may oxidize also, during heat treatment, you can have the weight gain also. So, weight gain. So, depending upon, that you can find out that delta H, which is related to temperature for a given weight gain. So, you can find out the enthalpy of the reaction also.

Oxidation dehydration. So, all these kinds of information, the temperature required for oxidation temperature required for dehydration decomposition of a material. So, this are information can be obtained from thermo gravimetric analysis, sometimes if you connect it with the mass spectrometer unit then, you can have the composition also of the products. So, what is the product? So, especially when you have bio mass type material and if you want to paralyze, it and to look at different conditions of temperature and even this can be done at pressure also. So, you can get the information about the product gases and you can have the catalyst also in the unit. So, kind of reactor you have a bed of catalyst and then, do the thermo gravimetric analysis. So, it is a kind of micro reactor you can have a different type of tubes with different catalyst and give the same stream of the reactant gas and then, look at the product composition through the GCMS.

(Refer Slide Time: 03:36)

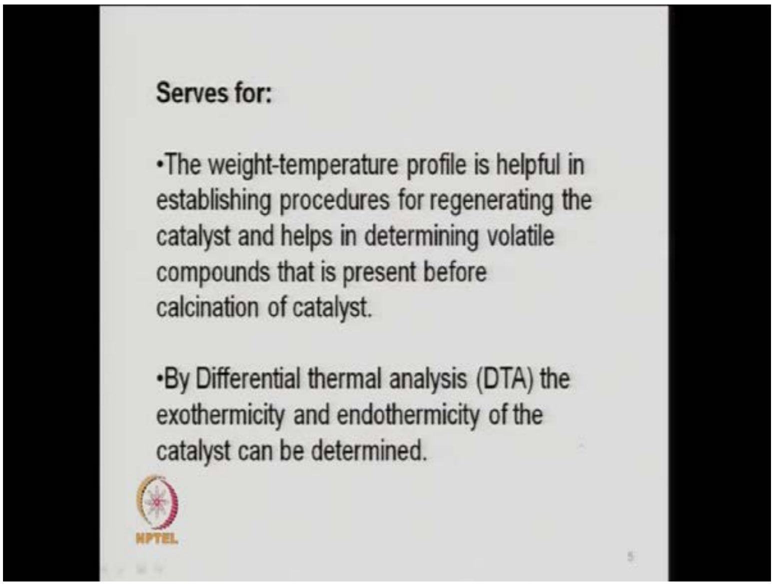


Information from TGA

- Thermal Stability of Materials
- Oxidative Stability of Materials
- Composition of Multi-component Systems
- Estimated Lifetime of a Product
- Decomposition Kinetics of Materials
- The Effect of Reactive or Corrosive Atmospheres on Materials
- Moisture and Volatiles Content of Materials

So, the information from the TGA, it can be of variety thermal stability of the material oxidative stability of the material composition of multi-component systems then, estimated lifetime of a product that is the decomposition if you look at the upper product decomposition kinetics of the material. So, TGA can be used for that bio mass coal conversion, non catalytic type reactions, you can have kinetics as a function of temperature and time correlation effect of reactive or corrosive atmospheres or on different kind of material. So, that corrosion studies can also be done with that moisture and volatile content. So, this can also be used estimated from the TGA analysis.

(Refer Slide Time: 03:36)



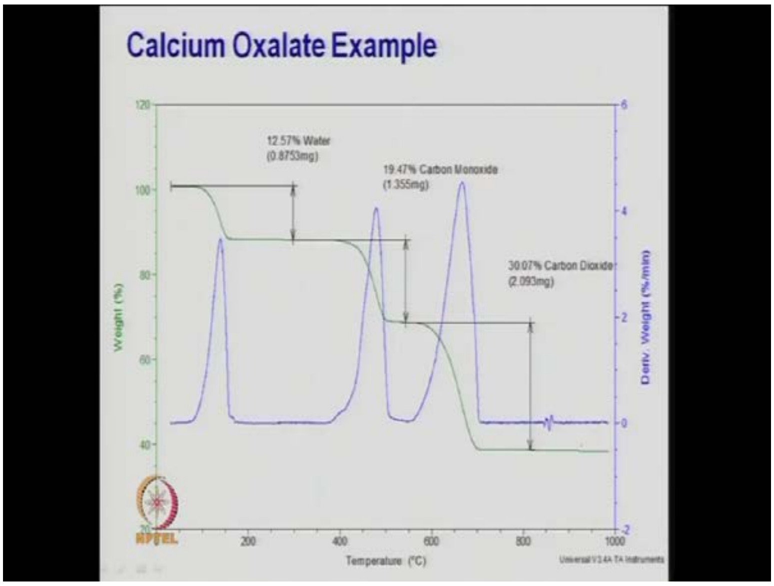
Serves for:

- The weight-temperature profile is helpful in establishing procedures for regenerating the catalyst and helps in determining volatile compounds that is present before calcination of catalyst.
- By Differential thermal analysis (DTA) the exothermicity and endothermicity of the catalyst can be determined.

So, in general when we look at a catalytic activity, we are interested in determining the weight loss as a function of temperature or time on a stream. So, then you can have the idea about the calcinations temperature if you have the hydrogen stream, you can get the idea about the reduction and that will be similar to your TPR study if the coke is deposited on the catalyst and you want to study the kinetics of the coke removal by gasification. So, you can do the kinetics and the TGA operators. So, weight temperature profile, which is helpful in establishing the procedure for regenerating the catalyst and helps in determine the volatile components that is present before calcinations of the catalyst.

So, this is kinetics of the coke removal. So, what temperature is required for regeneration of catalyst especially, when you have epsisy type or fidish stock is hydrocarbon then, large amount of coke deposits on the catalyst? So, you may need a fix men reactor that may have a larger life if the catalyst may last for 6 months or a year or 3 years or if it is deactivating much faster, you can have a fluidized bed reactor. So, how the coke can be removed or what is the nature of that coke precursor, because when you have a temperature time profile, the different coke species will come or just gasify at different temperature. So, you can have the graphic nature, amorphous nature or type of carbon, which is deposited on the catalyst, you can have that information also and if you take the DT that is the differential weight loss as a function of temperature or time then, you can also have the information on the endothermicity or exothermicity whether, heat is generating during the reaction when you call it exothermic reaction and when heat is required for decomposition, it is known as endothermic. So, when, there is the reaction is endothermic then, there will be a drop in temperature in the system, because it takes the heat to have some reaction and when, the heat is generating. So, you will find a rise in temperature. So, by looking that profiles you can get the idea about the endothermicity and exothermicity of the reaction.

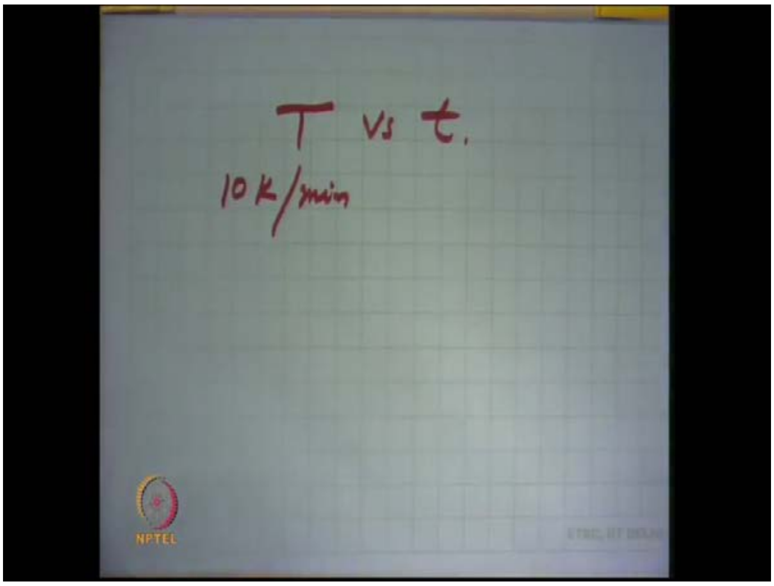
(Refer Slide Time: 06:38)



Calcium Oxalate Example

So, just as an example, what TGA can do or what information you can get from TGA is it calcium oxilates. So, this is just like calcium carbonate or any calcium nitrate just to look at the decomposition profile. So, calcium oxalates. So, if you do the TGA. So, there are three zones. So, one zone, first zone, second zone and third zone here. So, this is the actual profile, which you will get from TGA. So, that is the weight loss as a function of temperature and this temperature, you know, what is the rate of change of temperature with time? So, d t by d t.

(Refer Slide Time: 06:38)



T vs t.

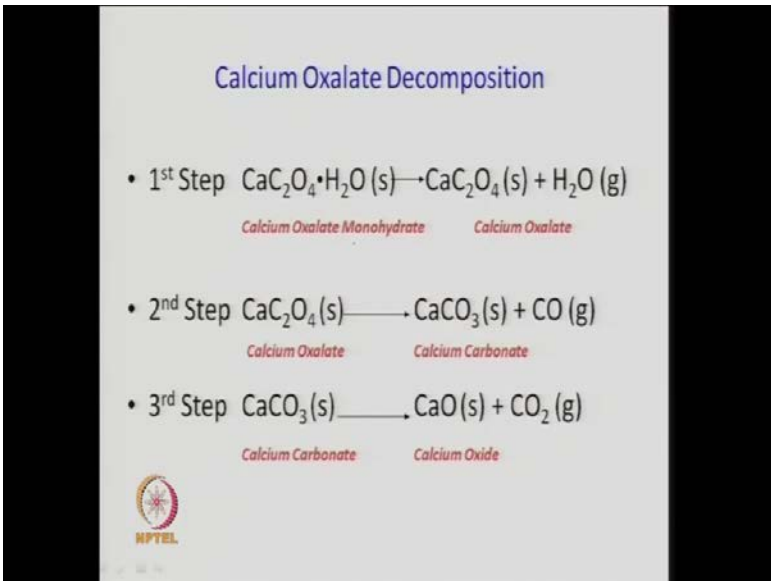
10 k/min

So, basically we have two information temperatures versus time on a stream. So, which are generally, you give the profile something like 10 degree Kelvin, what I was talking per minute something like this. So, d t by d t linear profile something, some kind of, if you just take d t by d t times. So, it is something like alpha t plus some constant something like that a constant would be j.

So, this information you weight loss as a function of temperature where, temperature may change with time, if you are not maintained this is thermal condition. So, the first zone is here, which is around say up to 200 degree centigrade then, second zone, another weight loss which is 400 between 400 and 550 degree and then, after 580 or 590 that is another decomposition and that last up to this and after that, there is no weight loss. So, a constant triangular line and this is simply nothing but, the weight or if you have a derivative of that is which is here in terms of the percentage per minute that is d w by d time.

So, that can give you the idea about that, at what time there is a maximum decrease in the weight or change in weight, which is nothing but, rate of change of mass per unit time and if you just take it per divide by per unit mass of this solid, you are getting something like rate, which is related to the kinetics example, just what I said earlier also that d w by d t is equal to k times, 1 minus alpha which is the fraction left to the power n simple kinetics power of kinetics. So, this is the derivative of weight, that is using this, you have to you are just take the slopes the temperature is related to time. So, I can take the tangent at different points and you can get the information on this weight loss. So, why should it take law? So, you can analyze the data.

(Refer Slide Time: 09:21)



Calcium Oxalate Decomposition

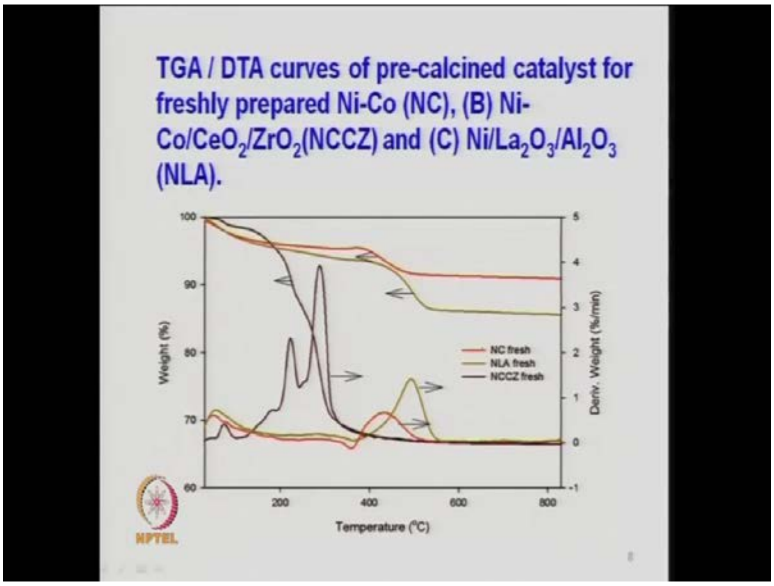
- 1st Step $CaC_2O_4{\cdot}H_2O\,(s) \rightarrow CaC_2O_4\,(s) + H_2O\,(g)$
  Calcium Oxalate Monohydrate — Calcium Oxalate
- 2nd Step $CaC_2O_4\,(s) \rightarrow CaCO_3\,(s) + CO\,(g)$
  Calcium Oxalate — Calcium Carbonate
- 3rd Step $CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$
  Calcium Carbonate — Calcium Oxide

So, just if you look at here, the first step if you have the calcium oxalate. So, that just release it is a hydrated 1 monohydrate. So, the water is removed in the first step. So, the rate of removal of water from the solid can be calculated kinetics of that and in the second step, which is somewhere near 400 centigrade or after that, the calcium oxalate decompose and gives calcium carbonate and carbon monoxide.

So, this is what, the gain weight of carbon monoxide in one way, which forms if you have a mass spectrometer or if you have a detector, you can measure that carbon monoxide concentration and that can be related with the decrease in mass of this calcium oxalate, because ultimately the sample has now, calcium carbonate the kinetics of this reaction can be obtained and third one then, further that is above 580, 590 degree centigrade and calcium carbonate decompose and you get calcium oxide plus carbon dioxide. So, you will get carbon dioxide gas through the detector and you can measure that concentration.

So, this is what here, the weight loss is related to the mass of the gasses product, because of it is material balance. So, that is what, you can write from that either the rate of formation of carbon monoxide rate of formation of carbon dioxide or rate of decomposition of calcium oxalate or decomposition of calcium carbonate. So, the information the variety of information can be obtained if you look at just a non catalytic type of reaction or decomposition of the material from catalytic point of view, again we get similar information, that is you have a catalyst, which is pre-calcined something like a calcium carbonate itself may be a pre cursor for catalyst support material calcium nitrate.

(Refer Slide Time: 11:07)



TGA / DTA curves of pre-calcined catalyst for freshly prepared Ni-Co (NC), (B) Ni-Co/CeO_2/ZrO_2(NCCZ) and (C) Ni/La_2O_3/Al_2O_3 (NLA).

It can be also a support material same thing for other like nickel nitrate if you have in your catalyst precursor. So, after when you have done the initial preparation part but, you say the co-precipitation method, solder method, what method and you have done the drying or ageing for 24 hours. Now, we say that calcinate where, you get the definite phases. So, that is one thing.

Simultaneously, during that step this the salt decomposes and you get the oxide precursor. So, that is known as pre calcinations. So, what is the temperature required as I said that, calcinations temperature is very important, because it gives you the phases during calcinations you get different phases on the catalyst and excessive calcinations is not desired, because it is a kind of reaction solid reaction and that may happen that, there may be at different kind of phase form, because of the solid reaction or because of the interaction between the metals. So, the crystal size increases grow in size. So, your dispersion and which we talked yesterday increase.

So, in order to avoid those situations, you have to look at the optimum condition required for calcinations and higher than the temperature, another thing that beyond calcinations. you are giving more energy to the system. So, energy consumption point of view also, you have to check these things. So, this is the TGA operators or TGA by doing TGA of the pre calcined samples, we can find out the calcination temperature.

So, here if you look at, just you have taken nickel cobolt, nickel cobolt on seria zirconia. So, basically used for forming of the bio oil components or methanol ethanol. So, these kind of materials can be used for forming reaction another is on nickel lanthanum oxide aluminium oxide, which is again a composite support here and nickel.

So these are but, pre calcined catalyst. So, this will be in the form of nitrate components. So, if you look at the graphs. So, this is the NC, which is your nickel cobolt. So, a first one, this is first one. So, this is a TGA line, this one the orange color line is the TGA of that nickel first catalyst if you have something, the second one which is Anla type lanthanum, aluminium oxide the TGA obtained is something like this 1. So, this is weight loss I am talking. So, this is site.

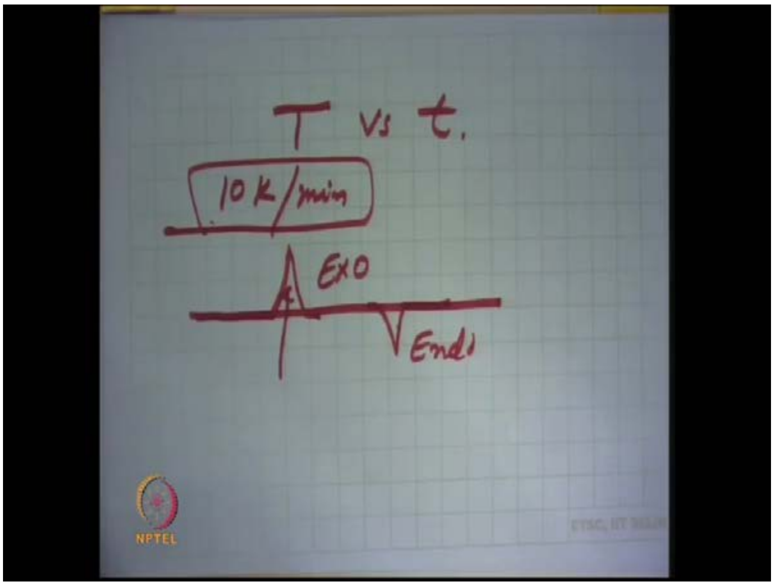
So, weight versus temperature and these 2 graphs are something like this and for third 1, which is again for first catalyst the TGA line is this, it decrease in the weight, which is much more compared to these two if you look at this point if you have the weight loss is very high. So, this third one, which is your catalyst related which is given here and c c z nickel cobolt seria exponent reason is the weight loss is that, because nickel nitrate may be there cobolt nitrate is there both are decomposing and the temperature for nickel nitrate may be different cobolt nitrate may be different but, there may be a kind of overlap. So, if you look at this the peak changes here in terms of shape. So, you can have 1 cobolt nitrate separately, you can have nickel nitrate separately and then, you check at what temperature nickel nitrate decompose what temperature this and this should give you the combined weight loss of nickel nitrate and calcium cobolt nitrate.

So a combined temperature, which is required for these two matter precursors or calcinations, you can identify from this. So, at this temperature you see that, all this material have both materials have a composed. So, it means around 350 or 380 may be the suitable temperature for calcinations. So, you can go around 400 degree centigrade and also what is the time required for complete decomposition that information also you can get from this a 5, 4, 3 hour, because depending upon your material amount of material you can just do that also. So, that is the information which you get from the weight loss as a function of temperature and if you do the further analysis that is the derivative of this can give you the information about the change in weight as a function of time kinetic information kinetic allow for the calcinations, you are not much interested in getting those information but, if you need for some kinetic reaction, you can calculate this derivative also but, from this you can find out also the exothermicity or endothermicity nature of the reaction. So, here it is decomposition.

So, which is requires the temperature for decomposition. So, temperature required. So, it means, there will be a variation if you look at the temperature will fall down at certain if you take the derivative of temperature and weight loss. So, drop will come if this is something like, if you have the isothermal system, the system will go like this but, in between when, there is heat is generating. So, it will go like this, because temperature has raised certain under the mass of the material is of the order of micro gram.

So, that delta T will be just of the order of 1 degree or 2 degree depends what is the delta is for that. So, but, you will see some kind of deflection if you have temperature profile as a function of time here. So, actually what you have given is T say 10 degree ram. So, you could have gotten from a linear profile. So, but, if you write look at that profile then, there will be something, when there is a decomposition weight loss or weight gain. So, you will have something like this, which talks that, it is exothermic in nature and if there is something which profile, which goes down like this it means, this is endothermic, because there is a drop in temperature. So, when you see that, there is a drop in temperature.

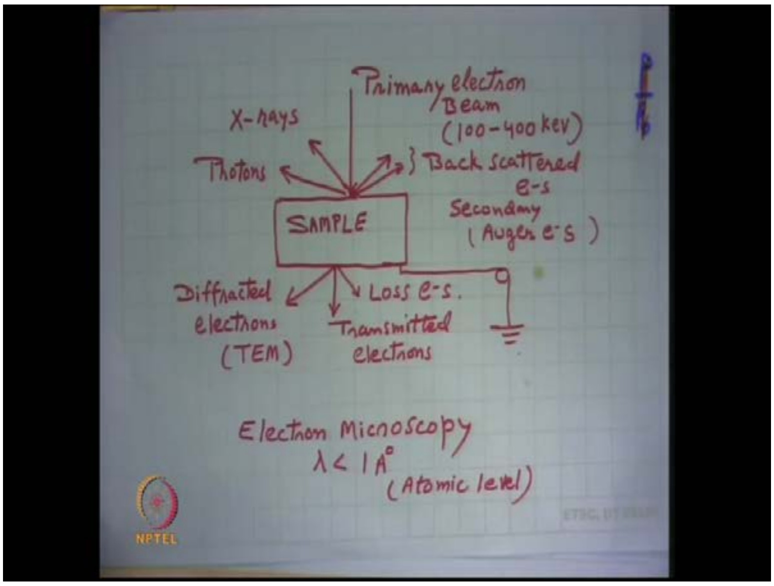
(Refer Slide Time: 17:33)



So, this is simply gives the idea about the endothermic, because the system takes heat during the however heat for the composition. So, temperature will fall down these information’s can be obtained, whether endothermic or exothermic nature of decomposition you can get. So, combustion when you have coal combustion or where you have the regeneration of the carbon from the catalyst. So, that time you will find that there is a heat generation, because the combustion reaction is exothermic.

So, this is what the information you get from TPR, TPD and then, TGA. So, I told that heat based system then, for you heat the sample and you get the information the another term which we are talking about photons or some energy source, which may be your primary energy beam and then, you look at the diffraction. So, last time I was talking about that, the information what you can get from the different catalyst system if you just look at I can just have the slide something like this.

(Refer Slide Time: 17:33)



So, this is I will take little later not for this but, generally for a primary electron beam or x rays, the principle is similar the x ray has the wavelength of 100 angstrom of the order of that. So, it means, it will cover a wider surface something like that but, when the electron beam if you see, it has the wavelength, which is less than one angstrom. So, it can give you the atomic information.

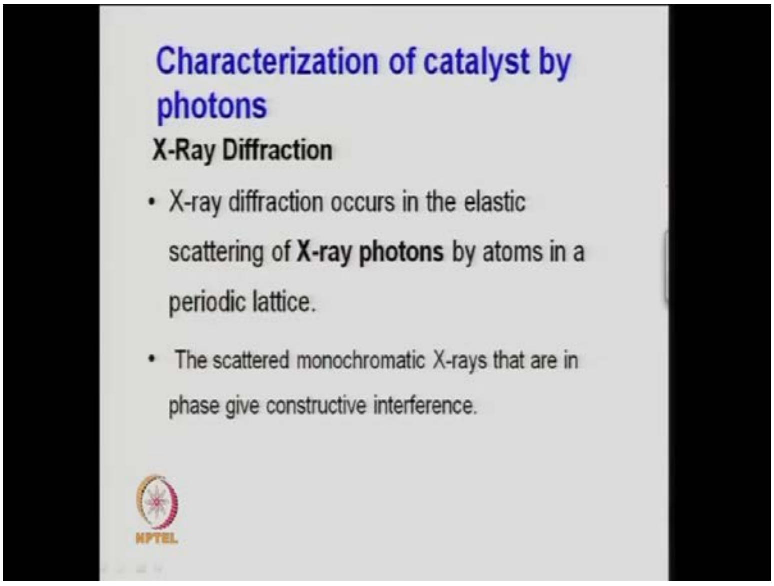
So, now what I want to inform that whenever, there is a primary beam which is strikes the solid surface then, there will be some kind of diffraction, because it will depend on the nature of the solid soft material hard material. So, that is material science here the platinum hard material but, if you have alumina soft material. So, but, in any kind of when, depending upon this energy whether it may be of the order of 100 kilo electron volt or it may be of the order of 400 it requires a vacuum also.

The only thing that you may not get the information at actual reaction condition, that is the only drawback of these methods, because actually your reaction may be at say 500 degree centigrade and 20 atmospheres but, these system generally work at high vacuum. But, to have the information about the surface not at the actual reaction condition or how does the electron emits the surface of a catalyst from a catalyst of a catalyst then, you have the different information which can be correlated to the actual reaction condition. So, that is the idea in the catalytic activity that we were talking that transition metals are good why they are good. So, just I want to look at give you the certain information on that which is based on your electrons choice atomic atoms, how they are on a metal electrons and when, you have the bombardment then how these electrons emit.

So, this primary electron beam it strikes the surface. So, there can be some back scattered electrons, this back scattered electron what you call secondary electron and also known as auger electron. So, they are slightly weaker in energy but, the information from this is also very useful information, you can get that is known as auger electron microscopy, we will talk on that later and the same there may be different kind of x-rays, which reflects on the surface, there may be photons and the material is soft then, there is a kind of diffraction also. So, it is depending upon the beam energy. So, it can be a diffracted electron so that is atmospherically used for transmission in electron micrograph. So, you measure the property of the diffracted electron it. It can be some kind of loss electrons, which have just from here, the metal have, because it is a kind atom layers. So, from which layer of the surface top layer, middle layer so that will depend on the beam energy and it goes in depth when, we talk x p s x-ray photo spectroscopy that. So, it is depending upon the energy of that beam in the x-ray photo spectroscopy that goes up to the in depth. So, you can have in depth analysis of the spectra like say carbon, when deposits whether it is only on the top layer or in a different layers same thing electronic. Now, metal composition can be determined size of the crystal can be determined, because these information's are at atomic level.

So, that is why this is for electron microscopy not for the x-ray basically, because the electrons they have the wavelength of the order of less than 1 angstrom. So, you can get the information about the atomic level. So, I will come back to this again later but, now just my idea here is that when, some energy source strike the surface that there will be a refraction, there will be some transmission and we are interested in looking at properties of those reflected transmitted energy, secondary electrons and that is correlated with the property, because something in a atom you have the s p banks and you have a d orbital's d d bank. So, based on those s p d bank you get a certain kind of electronic property and that is related to your catalytic activity because you are talking in terms of chemisorptions we need a kind of chemisorptions between a gas molecule and the atom and that will depend on the actual property that, when the gas molecule, what is the electronic configuration of this metal and then, how do they contact. So, orientation also becomes very important in terms of having a certain catalytic activity.

(Refer Slide Time: 23:30)



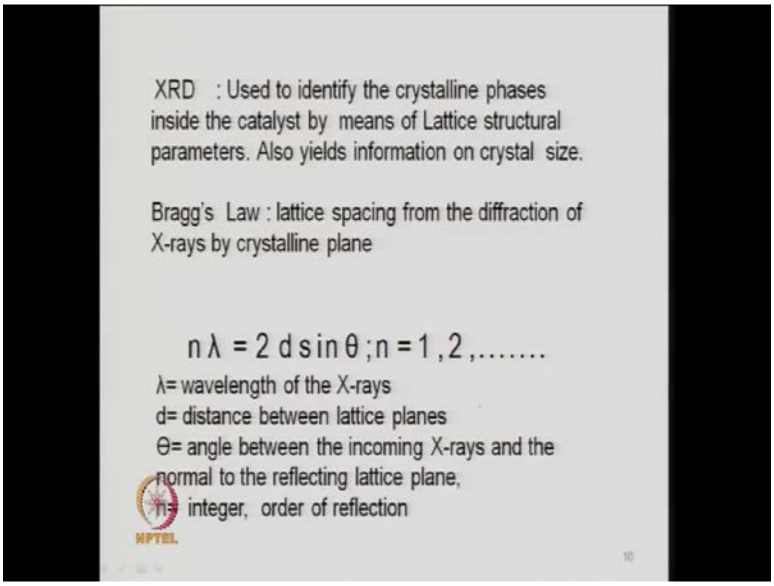
Characterization of catalyst by photons

X-Ray Diffraction

- X-ray diffraction occurs in the elastic scattering of **X-ray photons** by atoms in a periodic lattice.
- The scattered monochromatic X-rays that are in phase give constructive interference.

So, in this case of x-ray the diffraction occurs in the elastic scattering of x-ray photons by the atoms in a periodic lattice. So, it is a nothing but, structural surface on which atoms are arranged and some x-ray beam, which has a roughly wavelength 100 angstrom and starts and starts from the surface. So, the monochromatic x-ray, that is in a phase gives the constructive interference infer. So, this is what, the information you get from the x-ray is nothing but, beam strikes and then, diffraction is there reflection is there. So, we are just measuring, it based on the bragg's law. That is just basically, n lambda you know the lambda is equal to 2 d sine of theta, that is the bragg's law.

(Refer Slide Time: 23:30)



XRD : Used to identify the crystalline phases inside the catalyst by means of Lattice structural parameters. Also yields information on crystal size.

Bragg's Law : lattice spacing from the diffraction of X-rays by crystalline plane

$$n\lambda = 2d\sin\theta ; n = 1, 2, \ldots\ldots$$

λ= wavelength of the X-rays
d= distance between lattice planes
θ= angle between the incoming X-rays and the normal to the reflecting lattice plane,
n= integer, order of reflection

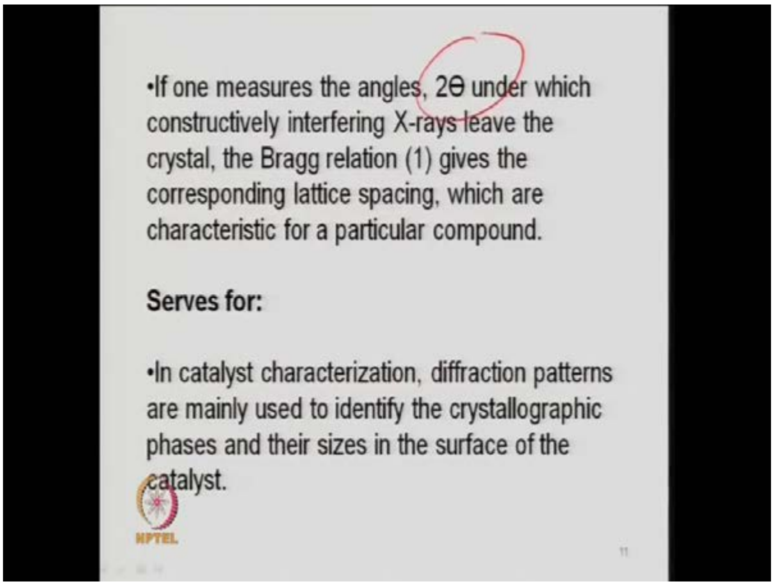
So, this is written here, this x-ray diffraction pattern used to identify the crystalline phases, inside the catalyst by means of lattice structural parameter. So, the arrangement of the atoms on the metals, how they are arranged and when you have the x-ray beam and that reflects. So, there can be different kind of x-ray sources, which of different energy beam energy and then, you see that what angle there is diffraction.

So, it may be up to a certain depth. So, based on the surface, that is depends on the beam energy. So, this is what, we are interested here in lattice structural parameter and if you just go further details then, you can get the crystal size also, because that is also related to a peak width, when you have the x-ray profile then, we talk either in terms of intensity of the peak or we talk the peak width at different diffraction angles.

The different layers this will happen. So, here again the beam diffracts. So, this is what we are talking the angle of diffraction because that may change depending upon the surface and orientation. So, you will have different lattice planes sometime we refer in terms of 111100. So, h k l the planes on which the beam strikes and diffraction in what phase or what plane from which, the diffraction is taking place. So, nickel you may see 111 some and 100 which is just representing the planes x y z planes. So, bragg’s law all of you know.

So, n lambda is 2 d sine of theta where, d is known as interplanar distance that is distance between 2 lattices and this is the property of a phase definite phase. So, this will change from different phase to phase lambda is the wavelength of radiation of the x-ray. So, this is a source beam. So, suppose you have generally most of the time either, you have copper potassium alpha radiation or magnesium potassium alpha. So, this copper potassium has roughly a wavelength of 1.5 angstrom. So, this depending upon the source, you can have this value which is fixed for beam or for a source d is the distance between the lattice planes, that is the property of the crystal and theta is angle between the incoming x-rays and the normal to the reflecting plane. So, that is important, because at different theta value you get the different diffraction and n is an integer for the second third like that.

(Refer Slide Time: 27:27)



- If one measures the angles, 2Θ under which constructively interfering X-rays leave the crystal, the Bragg relation (1) gives the corresponding lattice spacing, which are characteristic for a particular compound.

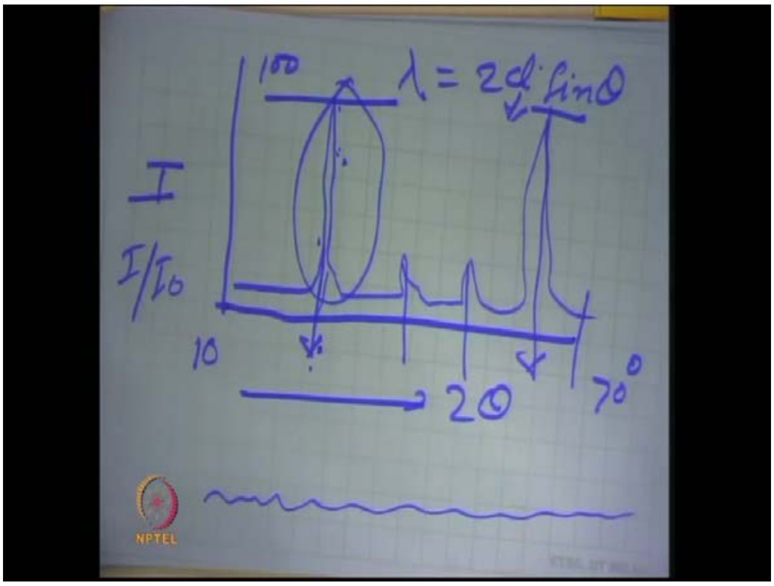
Serves for:

- In catalyst characterization, diffraction patterns are mainly used to identify the crystallographic phases and their sizes in the surface of the catalyst.

dSo, if you know this angle 2 theta, because you have given the beam and you have just measuring the intensity of the different diffracted beams. So, reflected beams, which comes from the surface. So, under which the interfering x-rays leave the crystal the bragg's equation gives the corresponding lattice spacing, which are characteristic of a particular compound. So, that is the discussion if you know this lambda, if you know this theta then, you can find out the d value and d value is related to the material and which are now a day's available in the software j c p d s software is one where, you can have the information that this d value, which is of the order of angstrom is for which kind of phase.

So, x-ray diffraction pattern is this is very useful information in one way you can characterize the catalyst then, diffraction patterns are mainly used to identify the crystallographic phase and their size in the surface of the catalyst. So, generally the crystal size, what you get in XRD.

(Refer Slide Time: 30:38)



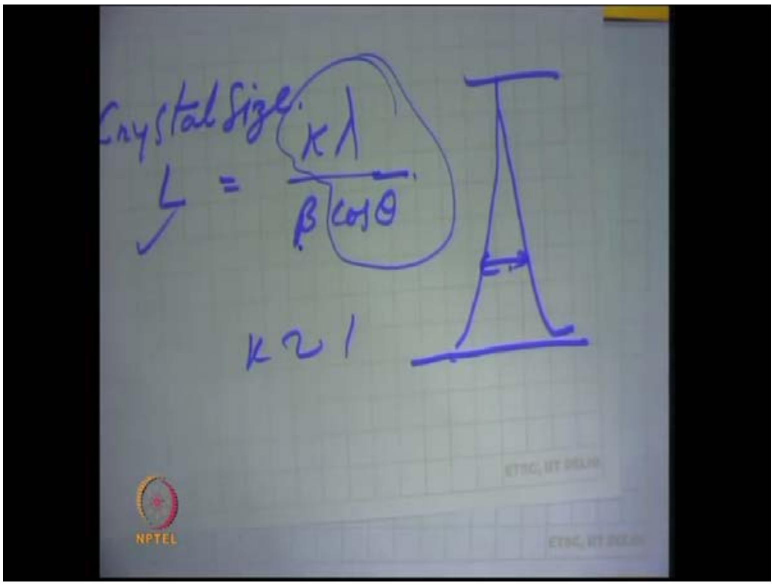
So, you have here, 2 theta and that depends on the some preliminary survey that is what range of 2 theta is required. So, it can be say 10 degree to something like 70 degree but, if you see that, you need sometimes a smaller angle. So, you need a small angle x-ray diffraction also when you need the diffraction patterns these are smaller angles. So, then you have some this side, you have some what you call some orbit unit and intensity. So, this is the. So, suppose if you have done this analysis.

So, you will have a diffraction pattern something like this. So, if the material is crystalline then, you will get these peaks, because the phases are formed if the material is not crystalline then, there would not be any peaks. So, you will get just like line, like this. So, this is for a non crystalline material but, for a crystalline material you get peaks like this. So, these are at different 2 theta values. So, this is your 2 theta value like this. So, you can identify from the calculation, which is your lambda is equal to 2 d sine of theta. So, you are getting this d value. So, if this is 2 theta values. So, lambda is known to you. So, this will tell you that, this is which phase suppose you have calcium aluminates.

So, it can have Caa, it can have 12c equal to 3 what I said earlier. So, you can have the information about this phase.

So and also simultaneously, the intensity some relative number suppose, this is the highest peak. So, I can make this 100 number some orbit number and then, the intensity of rest of the peak can be defined in terms of ratio of the peak heights. So, this height is highest one. So, this can be number intensity 100 and the other peak intensities can be determined based on this. So, it can be something like i over i 0, some orbital and useful information, which you get from this is your peak width gives you the indication about the crystal size.

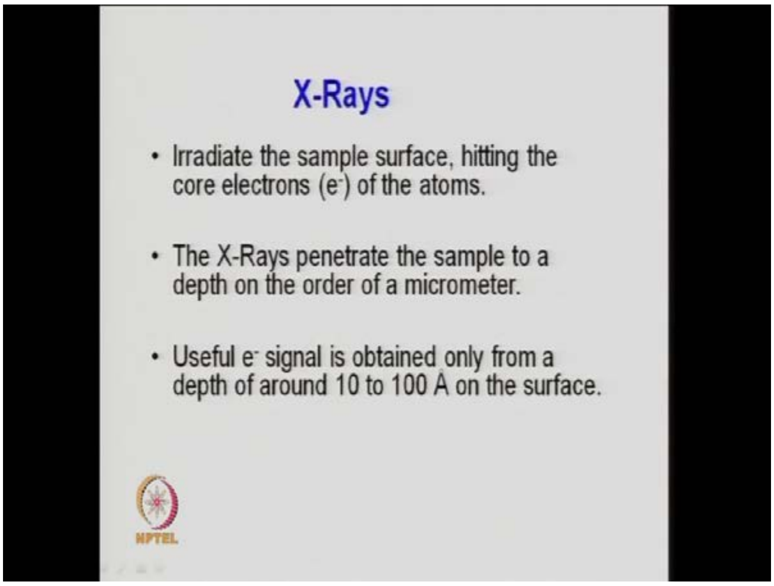
(Refer Slide Time: 31:50)



So, crystal size which is sometime represented by l is equal to k lambda over beta cos of theta something likes this. So, this is the constant, all this k is roughly 1, it is a property basically 1. So, beta is the peak of half height. So, it means if at a given angle of diffraction 2 theta, this is the total height. So, this is something like here, beta is the peak width of half height and radian units.

So, this can be calculated and wider the peak, because beta is inversely proportional to peak width. So, if wider the peak then, you can have the information about the crystal size. So, wider peak means smaller crystal. So, you can get the crystal size also from this and that can be compared from your chemisorptions study. So, this is useful information, which you can get from the x-ray diffraction pattern.

(Refer Slide Time: 32:00)



X-Rays

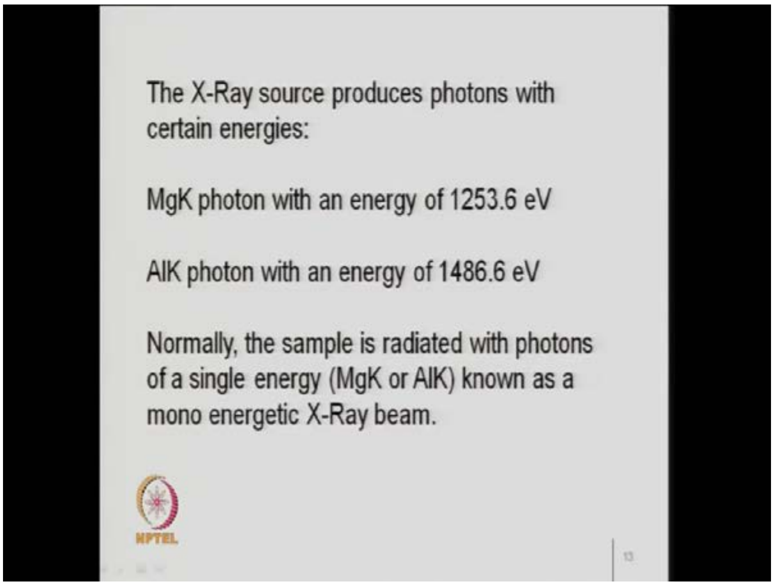
- Irradiate the sample surface, hitting the core electrons (e^-) of the atoms.
- The X-Rays penetrate the sample to a depth on the order of a micrometer.
- Useful e^- signal is obtained only from a depth of around 10 to 100 Å on the surface.

So, generally as I discussed that x-ray irradiate the sample surface hitting the core electrons of the atoms. Now, core electron is another term, which I will just talk little later. So, that is important, because we talk core electron, not the outer based electron. So, this is related to something like fermilevel. So, we have to just look at the atomic level and the structure of an atom, how the electrons s p what we talk work function fermilevel vacuum level. So, these are related from which are the electrons are emitted.

So, outermost core may not give you the good information, because it is far away from the nucleus the atoms, which are closer or electrons, which are closer to nuclei, they provide you the better information, because that is for a given material. So, most of the time we look at that and that is what, it is a core electron of the atom where, the x-rays are hitter and you need the information of all the core electrons. So, x-rays penetrate towards the sample to a depth on the order of a micrometer. So, that depends on the intensity of x-ray radiation wavelength of that radiation or energy provided.

So, useful electron signal is obtained only from a depth of around 10 to 100 angstrom on the surface. So, that is. So, x-ray basically, scans the surface and then, during the scanning it identifies that, whatever the different theta angle, whatever the diffraction and it just talk on that at different diffraction angle and then, it talks about the crystal, because it has a definite shape. So, from that, the diffraction takes place if it is not crystal x-ray, you would not get any peak and no diffraction will come.

(Refer Slide Time: 33:45)



The X-Ray source produces photons with certain energies:

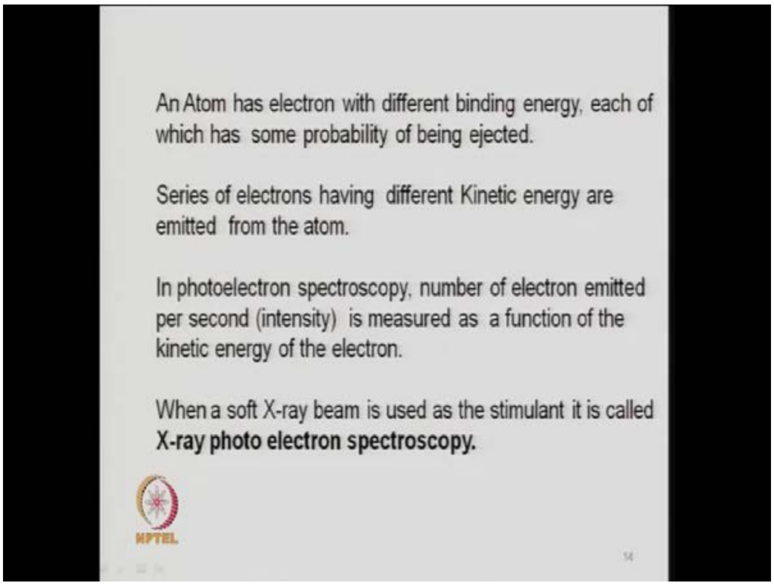
MgK photon with an energy of 1253.6 eV

AlK photon with an energy of 1486.6 eV

Normally, the sample is radiated with photons of a single energy (MgK or AlK) known as a mono energetic X-Ray beam.

So, x-ray source, they generally produce photons with certain energy. So, that is h nu type of energy which you get. So, just like magnesium potassium photon if I was talking. So, that has energy of roughly say 1.25 kilo electron volt and whereas, aluminum potassium photon, it has energy of 1.486 kilo electron volt. So, different type of source, it has the different source of energy. So, that is your h nu type whatever the nu. So, nu is the frequency. So, that can be used. So, normally the sample is radiated with photons of a single energy. So, that we have to call monochromatic energy source. So, single energy like magnesium potassium, alpha aluminum potassium, copper potassium and which is known as mono energetic x-ray beam.

(Refer Slide Time: 34:40)



An Atom has electron with different binding energy, each of which has some probability of being ejected.

Series of electrons having different Kinetic energy are emitted from the atom.

In photoelectron spectroscopy, number of electron emitted per second (intensity) is measured as a function of the kinetic energy of the electron.

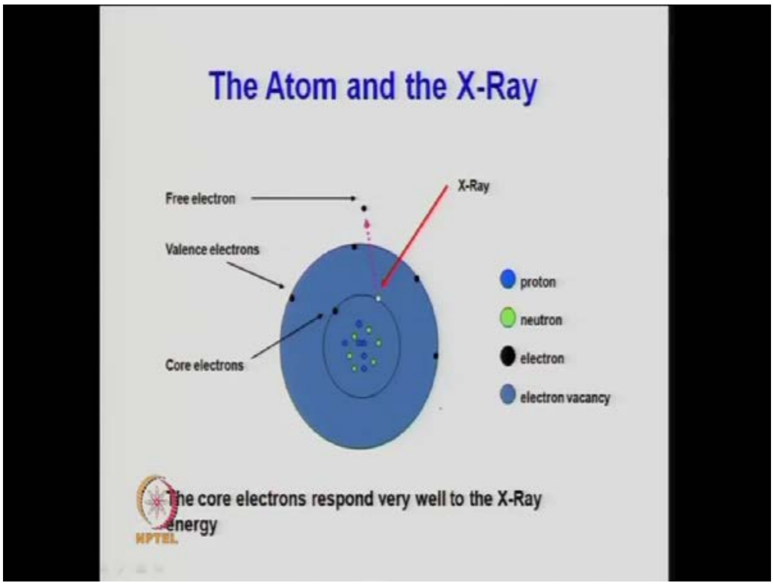
When a soft X-ray beam is used as the stimulant it is called **X-ray photo electron spectroscopy.**

So, now just that is in the order to look at these electrons, we have to just look at the atom. So, you know the atom has an electron with different binding energy. So, binding energy is different, because we are talking. Now, in terms of energy which is required and electron will leave the surface. So, binding energy is different depends on the kinetic energy, it depends on the work function, it depends on the potential, that is the work potential of the instrument also. So, every atom will have if you look at the electrons, they will have different binding energy and each of which has some probability of being ejected.

So, they will leave the metal, when the energy beam has strike on that. So, series of electrons they may have different kinetic energy and they are emitted from the atom. So, we are basically, what doing we are measuring the kinetic energy of those beam, the photoelectron spectroscopy that is another one x p s, which we will talk later, the number of electron emitted per second. So, that is something related to the intensity of the number of electron emitted per second the known as intensity. That is measured as a function of kinetic energy of the electron.

So, when a soft x-ray beam is used as a stimulant, it is known as x-ray photo electron spectroscopy. So, that is the x p s is different instrument, which relates the binding energy, that is the kinetic energy or binding energy and then, it gives the composition of the metal throughout. So, the composition can be determined in depth analysis can be determined, you can get the bonding type of bonding also, a variety of information can be obtained by using this x-ray photon spectroscopy, which is based on the binding energy. So, all of you know this.

(Refer Slide Time: 36:36)

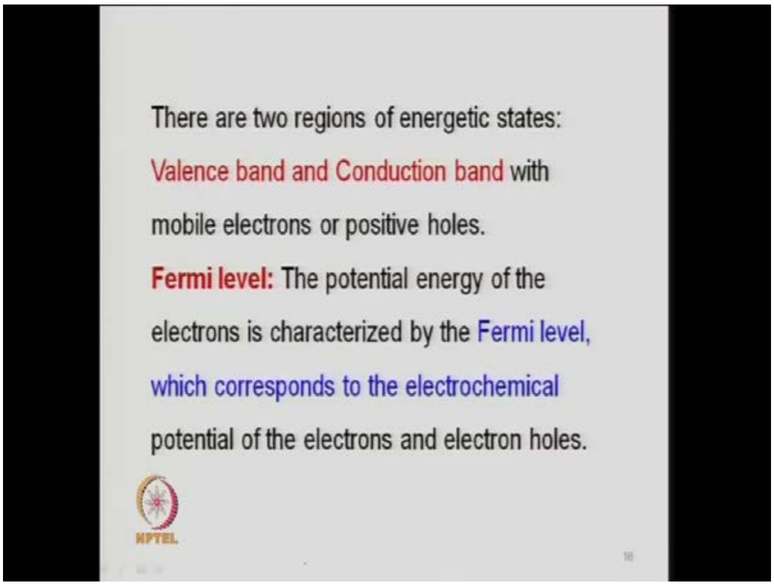


The Atom and the X-Ray

The core electrons respond very well to the X-Ray energy

So, just to recall the things that every atom, it has some proton, neutron and then, electrons and they are just like this is what, I am talking core electron, because it is closer to the nuclei. So, this electron, the energy beam strikes here. So, we are looking at the reflection of this electron. So, like this. So, this is the source of energy x-ray and it strikes here and then, it leaves some free electron here and here, the valence electron which is on the outermost side. So, they are free to move in fact they are just binded but, free to move anywhere. So, very mobile. So, these are known as valence electron. So, core electrons respond very well to the x-ray energy so that is why, the information what is required is important information is from the core electron.

(Refer Slide Time: 37:37)



There are two regions of energetic states:

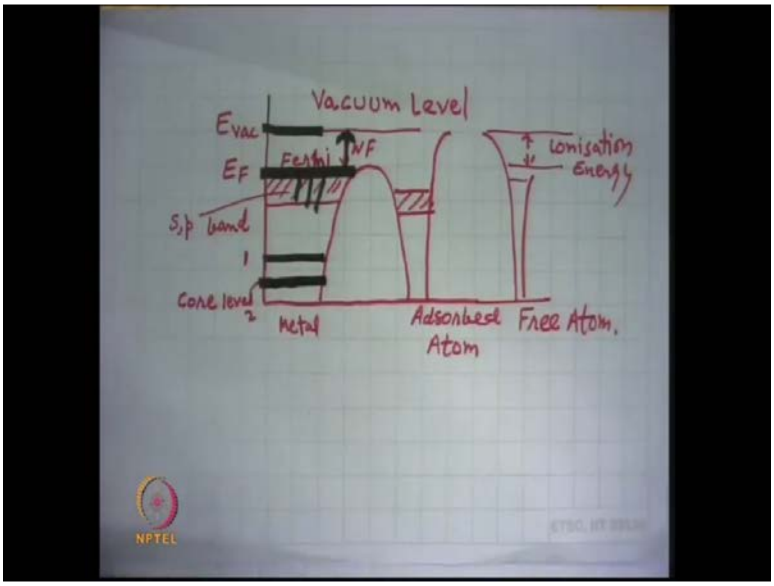
Valence band and Conduction band with mobile electrons or positive holes.

Fermi level: The potential energy of the electrons is characterized by the Fermi level, which corresponds to the electrochemical potential of the electrons and electron holes.

So, the valence band conduction band, which is this semi conductive materials when you say the catalytic property the metals. So, the two regions of the energetic states that are what we are talking in this form of core energy and x-ray styles. So, you look the information or we need the information in terms of the core electron. So, valence band and conduction band. So, there are two types of energy, that is the semi conductors, when we say, they need a certain kind of energy and then, they have the gap and that can provide the electronic activity just like in titanium dioxide for u v when, you have a u v source it can activate as an catalytic activity but, otherwise it is no more good as a catalyst. So, that is a semi conductive material.

So, you mix a kind of mobile electrons or these are also known as positive holes. So, a gap related to Fermi level. So, Fermi level it is a potential energy of the electron that is characterized by the Fermi level, which corresponds to the electrochemical potential of the electron and the electron holes. So, generally Fermi level, above Fermi level the energy is minimum basically and below that the energy is maximum. So, it is a gap between there. So, what we call work function as I was talking. So, that we are measuring it above the Fermi level, that is the vacuum level energy minus, the Fermi level, that is the kind of work function. This is the amount of energy, which is required to release an electron so that is important, Fermi level is important and this will this gap will be different. So, if I just show you, which you must have read earlier.

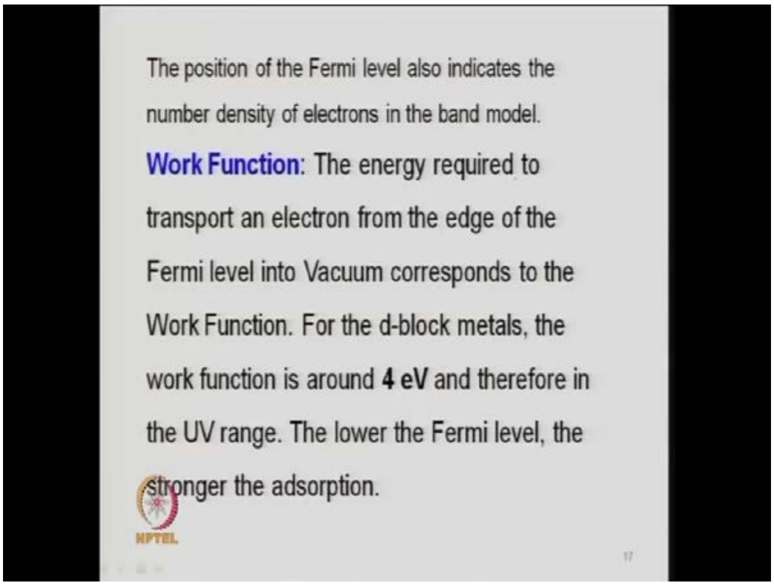
(Refer Slide Time: 40:30)



So, this is a kind of structure of the metal or electron atomic structure in the metal atom. So, this is a core level like here. So, core you have different levels, core level 2, core level 1 and which is based on the different their SPD bands. So, core level 1, core levels 2. So, that depends upon the number of total number of electrons which are distributed and for. So, and this is your the SPD, SP band here, which is the electrons are just free and they are just filled here. So, and then, the Fermi level this is your Fermi level.

So, here it is the energy is highest here, in this side and here it is the vacuum level, which has the electron are free to leave move in this zone, what I was outermost core of that and in between this, the difference of this is your work function. So, if you look at here, it is something related to your ionization energy, again the energy required to let remove the electron from the outermost core and that is nothing but, the ionization energy to create an ion. So that is a free atom, when you have this kind of adsorbed atom. So, when this is a metal, this is adsorbed atom. So, energy band shifts when, something this is chemisorptions, which is related to the electron transformation. So, that is what, the structure is related here and that is the Fermi level.

(Refer Slide Time: 41:00)



The position of the Fermi level also indicates the number density of electrons in the band model.

Work Function: The energy required to transport an electron from the edge of the Fermi level into Vacuum corresponds to the Work Function. For the d-block metals, the work function is around **4 eV** and therefore in the UV range. The lower the Fermi level, the stronger the adsorption.

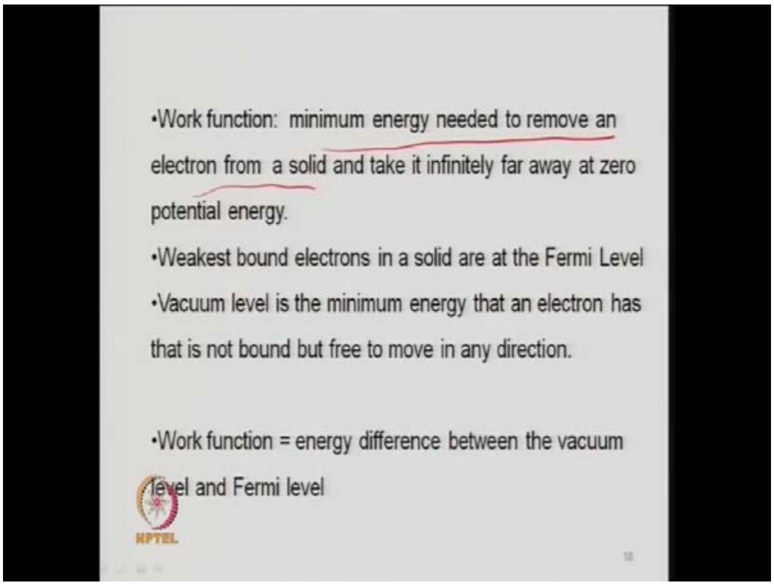
So, position of Fermi level is very important. So, this shifts moves. So, position of Fermi level indicates the number density of electron in the band model. So, s p band is below the Fermi level where, all the bands are filled by the electrons they are. So, it is the energy is associated to that band and above that, when I am taking vacuum level the energy is the electrons are free to move that is minimum energy and Fermi level where, the electrons means below that high energy and above the electrons have the low energy.

So, work function the energy required to transport an electron from the edge of a Fermi level into a vacuum. So, after that, the electrons are free to move that corresponds to the work function. So, difference of that is the vacuum energy minus, the Fermi level energy is you are the work function. So, that is the energy you need. So, electron has to move from the core.

So, for d block metal if you say because most of the d blocks metal, the work functions are roughly 4 electron volts. So, low number if you look at in terms of the high h nu energy, which is of the order of kilo electron volt and therefore, this is in the ultra violet range lower, the Fermi level stronger the adsorption. So, your chemisorptions whether, it is strong metal support interaction what we are talking or the gas molecule adsorbs strongly on the metal that is related to the Fermi level.

So, if Fermi level is on a lower side, your chemisorptions will be stronger the adsorption. So, you have to tune it, in fact the metal selection, because this is for a given metal, the electrons are distributed in their cores s p d k shell, what we could see defined in that l shell. So, the electrons are distributed. So, when you select the metal for a given reaction the adsorption should not be very strong, adsorption should not be very weak also, this is what the related to the electronic theory or electron how they are distributed in the cores or shells.

(Refer Slide Time: 43:22)



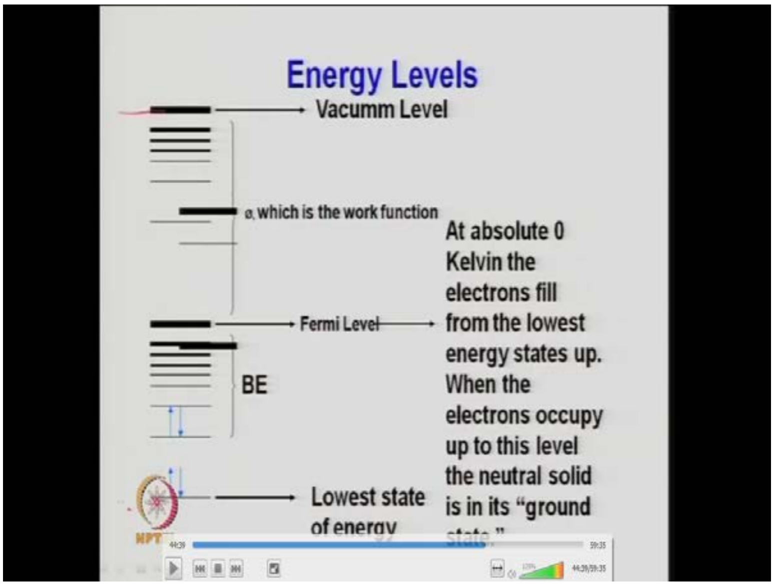
- Work function: minimum energy needed to remove an electron from a solid and take it infinitely far away at zero potential energy.
- Weakest bound electrons in a solid are at the Fermi Level
- Vacuum level is the minimum energy that an electron has that is not bound but free to move in any direction.

- Work function = energy difference between the vacuum level and Fermi level

So, work function we have talked, it is the minimum energy needed to remove an electron from a solid and take it infinitely far away to 0, potential energy to vacuum level. So, vacuum level has the minimum energy 0. So, electron has to be taken from the Fermi level and transfer it to the vacuum level. So, that is your work function. So, weakest bound electron in a solid are at the Fermi level, because below their energy is high. So, vacuum level is the minimum energy that is an electron has that is not bound but, frees to move in any direction.

So, this definition I already discussed. So, there is you need to see vacuum level work function, which are the property of the atom of a metal. So, work function definition is energy difference between vacuum level and Fermi level. So, if Fermi level is on a lower side, that what I said the Fermi level is on a lower side then, work function required will be high. So, that is what, that is high, it means you need high energy to release the electrons from the hole. So, the same, what discussion has been made is shown here now.

(Refer Slide Time: 44:30)



Energy Levels

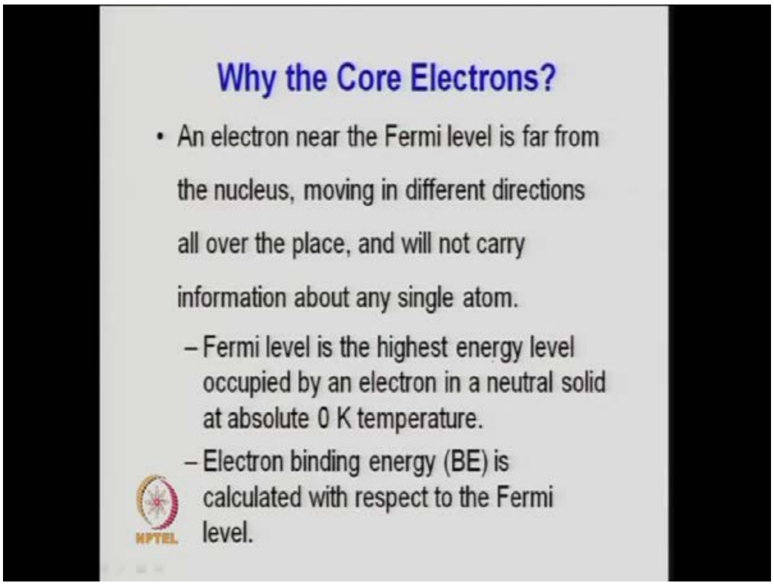
At absolute 0 Kelvin the electrons fill from the lowest energy states up. When the electrons occupy up to this level the neutral solid is in its “ground state.”

So, this is your vacuum level and this is your lowest energy state. So, that is what, we are talking the cores core electron and this is the work function, which we are defined the. So, this is your Fermi level. So, this is your work function phi. So, vacuum level minus Fermi level and this binding energy. So, I told that, the core electrons are required. So, binding energy gives you the idea about that how strongly this core electron is attached to a nucleus or that is what, the energy intensity between the nucleus and the core electron, because you have to relieve that electron for catalytic activity. So, that is related to the binding energy. So, when you have the x-ray photo spectroscopy, you just look at that. So, binding energy we are measuring in fact which is the property of a material, now by giving a kind of kinetic energy.

So, this is a Fermi level, vacuum level difference in the work function and from the core when, the electrons are relieved. So, that is the nothing but, how the electrons are attached to nuclei and that is you are the binding energy. So, at absolute 0 Kelvin the electron fill from the lowest energy states up when electron occupy up to this level, the natural neutral solid is in it is ground state.

So, that is the normal condition when, they are neutral. So, that is at 0 degree Kelvin, you want to say I mean that, the electrons everything that is the stagnant position. So, there is no. So, that is the lowest energy state. So, electrons fill from the lowest energy state then, the electron occupy up to this level, the neutral solid in its ground state, when there is no activity.

(Refer Slide Time: 46:33)



Why the Core Electrons?

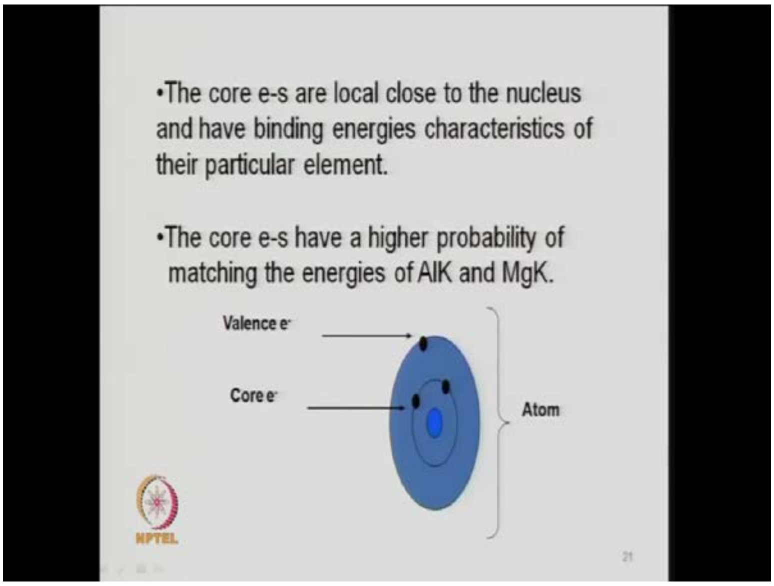
- An electron near the Fermi level is far from the nucleus, moving in different directions all over the place, and will not carry information about any single atom.
  - Fermi level is the highest energy level occupied by an electron in a neutral solid at absolute 0 K temperature.
  - Electron binding energy (BE) is calculated with respect to the Fermi level.

So, why core electron, I have already discussed this but, the electron near Fermi level is far from the nuclei that is one thing. So, core level is below the Fermi level. So, it is moving in different directions at all over place. So, this may not give you very useful information, because at a Fermi level, they are free to move up that is the work function I told and then, the vacuum level. So, lowest energy is in vacuum level and below Fermi level there is energy.

So, this may not give you the useful information about any single atom. So, Fermi level may not give you the any useful information but, if you have the core electron, you get the useful information, because they are binded to the nuclei. So, Fermi level is the highest energy level occupied by an electron in a neutral solid at absolute 0 Kelvin. That is what, the discussion discussed. So, electron binding energy is calculated with respect to the Fermi level.

So, that is from core to the Fermi level, which is shown here, Fermi level this is core and that is really important here, the electrons are free to move in between. So, they may not give the useful information but, for a given atom we are given metal, the atoms are attached to a nucleus, the proton neutron and then electrons. So, it means, what is that kind of energy when, the electron is released and level comes to the Fermi level. So, that is important. So, that is your binding energy basically. So, that may be giving you the useful information, because it is related to the number of proton in the nucleus.

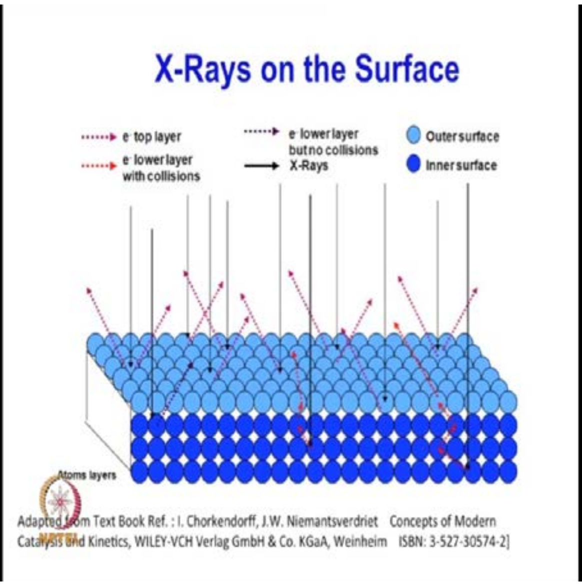
(Refer Slide Time: 48:20)



- The core e-s are local close to the nucleus and have binding energies characteristics of their particular element.
- The core e-s have a higher probability of matching the energies of AlK and MgK.

So, core electrons are local close to the nucleus. So, locally they are close to the nucleus and having a binding energy characteristic of that particular element. So, that is why, the core electrons are useful and they have higher probability of matching with the energies of whatever the alpha potassium or magnesium potassium, which is used for the x-ray analysis. So, valence electron core electron atom. So, we are looking something like here in this course.

(Refer Slide Time: 48:49)



X-Rays on the Surface

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]

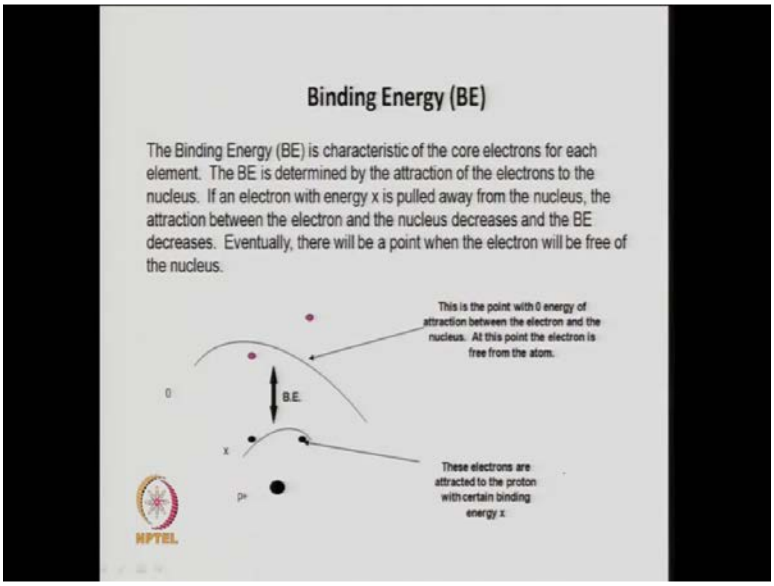
So, when a beam strikes the surface as I said before also that, these are just the x-rays features shown by dark arrows here. So, that is the different x-ray beams here. So, these all your x-ray beams here, which strike it, can strike on the surface top surface. So, this is your top layer, outer surface, this one is your outer surface and this is your inner surface of a metal depth. So, electrons this is which the electrons or x-ray which are gone up to the depth, they may leave the electron and they may collide. So, these are with collision. So, with this is arrangement of the inner surface.

So, they are colliding with different surface. So, the energy will be decrease, because they are colliding with the substrate and the part of the energy will be lost. So, this is what the in depth analysis, what you are getting and sometimes this output energy may not be a significant number to give you any information thus, electrons again the x-ray which are gone to this, they may come out but, without collision unlike here, this is the another type of the refracted beam. So, this is electron lower layer with collisions like this but, here the number of collision may be less or may not be in this second layer or bottom layer.

The top layers, this is the electron which are released from the top layer, these all are the x-rays which strikes on the top surface and then, relieves here rho. So, whatever the analysis you can get, that is the phases which have been formed based on the diffraction angle or the whatever the intensity of these radius electrons, secondary electron when, you have the x p s, the information can be obtained in terms of the binding energy of that electron.

So, different types of information can be obtained from primary, secondary or the energy beams which I showed auger electrons or the diffracted electrons. So, if you have but, when you x-ray then, you have just the surface information in terms of the crystallographic nature crystal structure. So, binding energy already has been defined. So, it is the characteristic of the core electron for each element. So, this will be differing from element to element.

(Refer Slide Time: 51:07)



Binding Energy (BE)

The Binding Energy (BE) is characteristic of the core electrons for each element. The BE is determined by the attraction of the electrons to the nucleus. If an electron with energy x is pulled away from the nucleus, the attraction between the electron and the nucleus decreases and the BE decreases. Eventually, there will be a point when the electron will be free of the nucleus.

This is the point with 0 energy of attraction between the electron and the nucleus. At this point the electron is free from the atom.

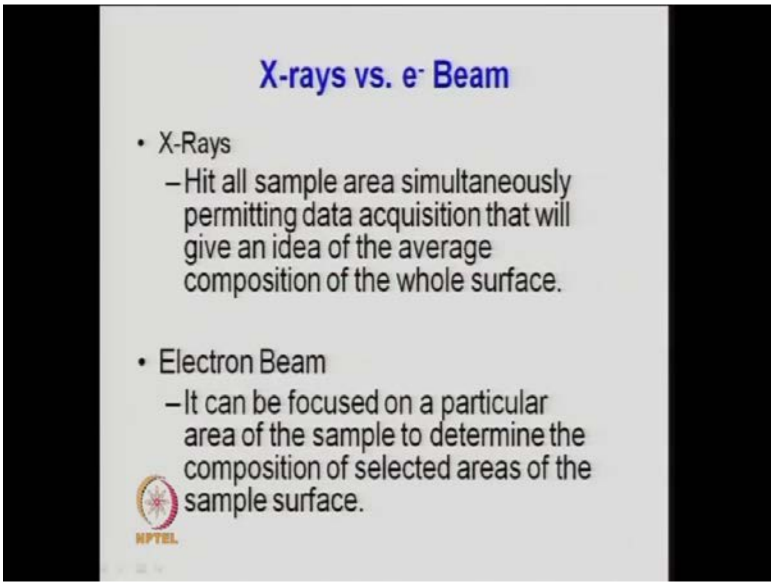
These electrons are attracted to the proton with certain binding energy x

So, the binding energy is determined by attraction of the electron to the nucleus if an electron with an energy x is pulled away from the nucleus. The attraction between electron and the nucleus decrease and the binding energy decrease. So, this is basically when, you do the x-ray photo spectroscopy, you get more useful information from that core. The electron release when you calculate, it is binding energy and which is property of the material or metal.

So, that gives you very important information in terms of the crystals in terms of the concentration of the metal, because different concentration metal will different type of metal will have different binding energy and nature of the spectra coke spectra also, that is mono layer, multi layer growth of the carbon materials. So, that information can be obtained from this. So, now there will be a point, when the electron will be free of the nucleus, when you have the given binding energy it increase. So, it will release the surface of that. So, that is what from here.

So, this is the point of 0 energy attractions between electron and the nucleus here, at this point. If you look at and the electron is free of the atom, which is this electron. So, here these electrons are attracted to the proton with certain binding energy x. So, all these are attached to the proton here. So, there is a kind of force between the core and the nuclei. So, you have to give certain amount of energy and that is what, the principle of the actual photo spectroscopy.

(Refer Slide Time: 53:00)



X-rays vs. e⁻ Beam

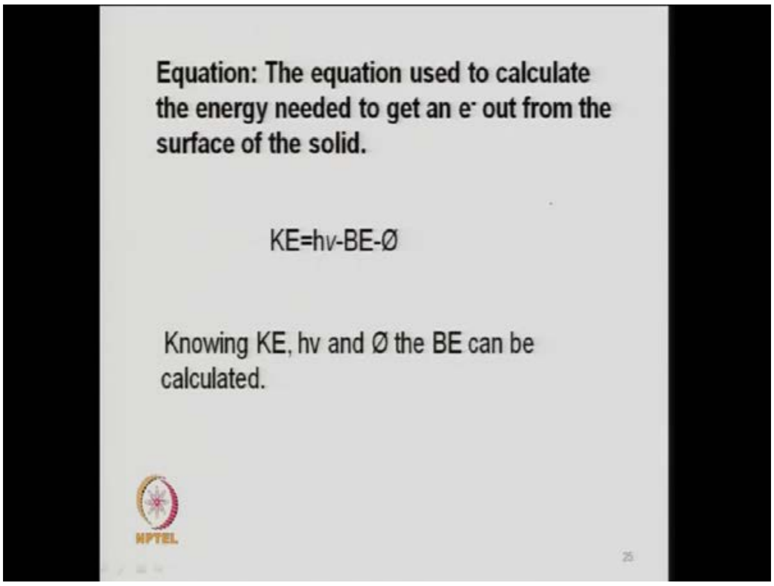
- X-Rays
  - Hit all sample area simultaneously permitting data acquisition that will give an idea of the average composition of the whole surface.
- Electron Beam
  - It can be focused on a particular area of the sample to determine the composition of selected areas of the sample surface.

So, with a x-ray versus electron beam as I said in terms of the surface scanning or a point to point analysis, that is another useful information both are important both gives the information about the surface but, depending upon the energy or intensity or the wavelength. So, x-ray hit all sample area simultaneously permitting data acquisition, that will give an idea of the average composition of the whole surface, just like the when you do the energy dispersive x-ray analysis, you get the analysis only at the average point localized point, not the throughout the sample.

So, if you look at the composition of the metal. So, you have to scan the surface point wise at different locations then, you can get the more useful information, because it hits the sample uniformly. So, only the localized information can be obtained when, you look at the composition, chemical composition but, when you look at crystal structure then, it is good electron beam, because it is of wavelength is one angstrom less than 1 angstrom, what I said it can be a focused on a particular area, localize of the sample to determine the composition of selected area of the sample surface.

So, this is your scanner electron micrograph transmission. So, they are for localized points. So, you get the information of that surface at the given sample for the given sample for a given local points. So, the again there may be. So, you have to take the average throughout the surface if you want to use the say number of atoms, number of metals, particle size then, you have to just take the average throughout the surface and then, determine the particle size.

(Refer Slide Time: 54:50)



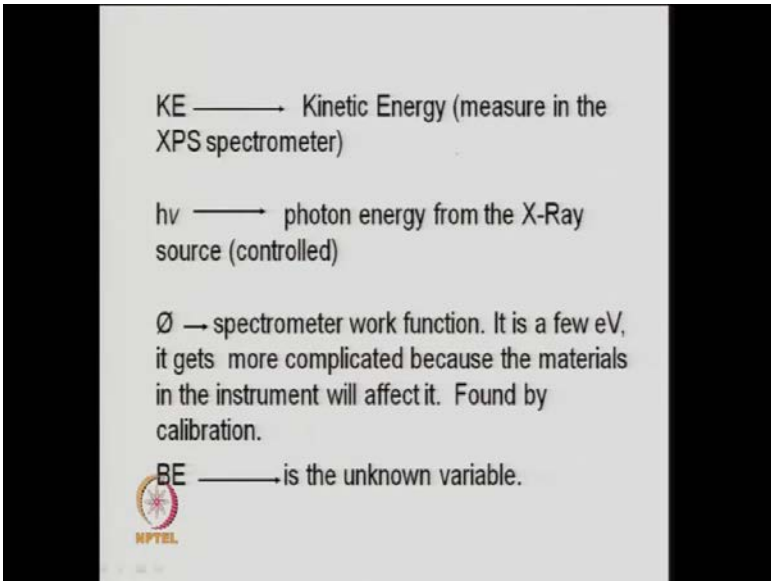
Equation: The equation used to calculate the energy needed to get an e^- out from the surface of the solid.

$$KE=h\nu-BE-Ø$$

Knowing KE, hv and Ø the BE can be calculated.

The equation for energy that is the kinetic energy, which is related to h nu, the energy of the photons minus the binding energy and minus, the work function, work potential all over work function. So, because the, energy needed to get an electron from the surface of the solid. So, the kinetic energy is equal to h nu minus binding energy minus the work function. So, kinetic energy is known, because it is a output intensity, you can measure that or depending upon the source and the reflection beam h nu is the input energy source where, it is also known as binding energy is to be calculated and work function is the property of the metal. So, that can also be determined just as I said 4 electrons volt for most of the metals surfaces.

(Refer Slide Time: 54:50)



KE ⟶ Kinetic Energy (measure in the XPS spectrometer)

$h\nu$ ⟶ photon energy from the X-Ray source (controlled)

Ø ⟶ spectrometer work function. It is a few eV, it gets more complicated because the materials in the instrument will affect it. Found by calibration.

BE ⟶ is the unknown variable.

So, kinetic energy, when you measure in the x p s spectrometer. So, this is the h nu is the photon energy from the x-ray source. So, this is controlled 1 monochromatic energy phi is spectrometer work function. So, it is few in electron volt it gets more complicated, because the material in the instrument will affect it. So, generally 4 electrons volt is required and this is found generally by calibration, because it is for instrument and binding energy is unknown variable. So, this can be determined by using the information.

(Refer Slide Time: 56:22)

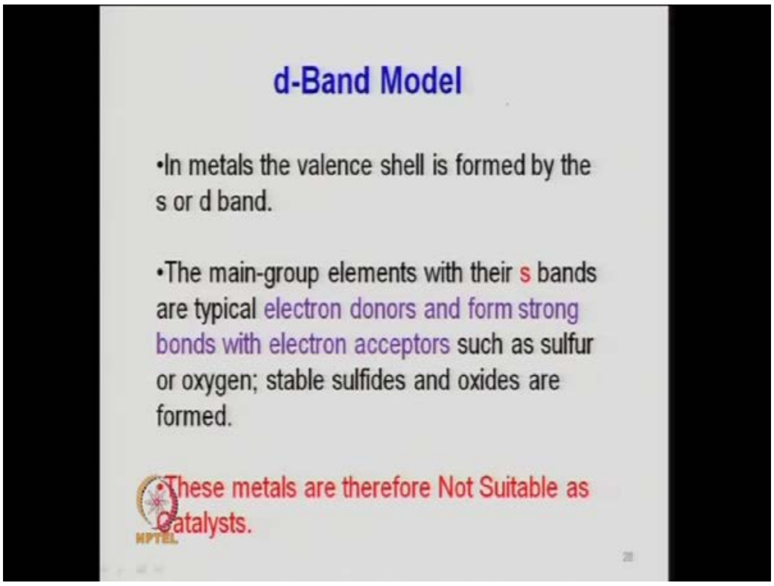
Metals normally have a narrow d band. The catalytic properties are strongly influenced by the occupational density of the electrons in this band.

In many cases a direct relationship has been found between the catalytic activity of transition metals and the electronic properties of the unfilled d bands.

Now, we should look at the metals. So, metals normally have a narrow d band. So, I told, I was talking just about the d band theory basically, the same. So, all the metals, we have, narrow d band, the catalytic property properties are strongly influenced by the occupational density of the electrons in this band. So, how many electrons are available in that d band, that is what we are talking for the selection of the transition metals are good and unpaired the electrons in that d band.

So, that is very important in this band. So, d band s and p bands as I said that, they have the sufficient electrons available and they are already filled in that but, d band is one which is the number of unpaired electrons in the d band that gives the kind of catalytic activity. So, in many cases if you look at the direct relationship has been formed between the catalytic activity of transition metals and the electronic property of the unfilled d band so that is related to the catalytic activity.

(Refer Slide Time: 57:25)



d-Band Model

- In metals the valence shell is formed by the s or d band.
- The main-group elements with their s bands are typical electron donors and form strong bonds with electron acceptors such as sulfur or oxygen; stable sulfides and oxides are formed.
- These metals are therefore Not Suitable as Catalysts.

So, it means your d band theory is very important, d band model, when you look at why copper, why nickel, why cobolt, why radium, why uranium they have been selected as a catalyst. That is a first thing and then, when you select them the volcano plat, what we were talking initially, when you select them for which kind of reaction for a given reaction, you say that for hydrogenation nickel is good, platinum is good but, what is the basis of selection of a metal so that becomes important, when you look at the electronic structure of that metal.

So, the peace will remains where, whether these principle what we are talking XRD sam tam or x p s so that is for characterization but, the fundamentals for the catalytic reaction it remains the same, that is we are selecting, that in when there is a reaction they will emit a kind of electron and how strongly they are adsorbed on the surface or how weakly they are adsorbed depending upon these two situation, there will be a kind of reaction and that is the theory or that is principle behind transformation of that adsorbed species into product species.

So that is what, the importance of the d band and that is based on the electronic theory or what you say the total the structure of that metal and electron. So, there may be a different theory for the catalytic activity but, this is one. So, the main group element with their s-bands are typically electron donors and form strong bond with the electron acceptors we talk acidity basicity. So, I will continue this next time.