Heterogeneous Catalysis and Catalytic Processes
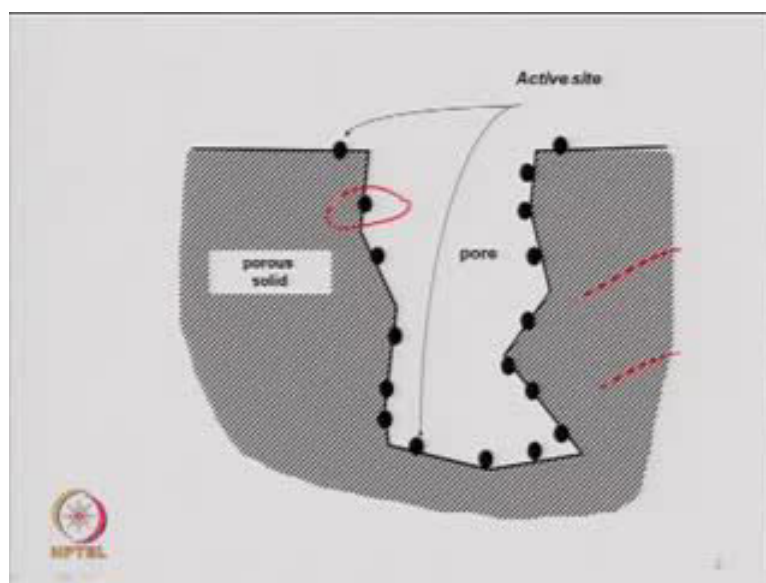**Prof. K. K. Pant**
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Lecture - 04

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In the last lecture we were discussing about catalyst pore system and we were just talking a pore geometry, right; solid heterogeneous solid catalyst pore system and we were talking about the catalyst pore geometry. So, if you look at this pore structure; so we have the metals here and this is the solid support right which is just providing a base for deposition of this, over the metals are deposited inside the pore of the catalyst and that we call the active sites.

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PORE SYSTEM

The pore system of a support is usually irregular in shape and contains macropores due to the spaces between individual crystallites, with diameters of the order of 100 nm, and micropores with characteristic dimensions of 5–10 nm.

A good support offers
(1) Controlled surface area and porosity,
(2) Thermal stability,
(3) High mechanical strength against crushing and attrition.

The pore system if you look at, it is very complex system, complex geometry and depending upon the catalyst preparation, you can get different kind of pores right micro pore macro pore misopore. So, if you look at the irregularity; so, generally we considered for modeling purpose straight cylindrical. The pores are straight and cylindrical; then, we add certain kind of non-geometrical parameter, non-cylindrical parameter like it maybe in terms of the torch structure of the pore, zigzag path of the pore and maybe the porosity itself that maybe another fraction. So, porosity, torchosity and that can be used to calculate the effective diffusion in a pore which are not straight cylindrical.

So, if you just see here the, they contains the micro pore which is nothing but the macro pore, when I say these are larger size relatively larger. So, maybe of 100 nano meter and diameter 1000 angstrom. And, these are nothing but the pores between the part. So, we have the two particles or then the space is created between them. So, suppose just like an cylindrical jar, you put large spherical ball; so you will find a lot of wides between them, right.

So. similar thing here when you are compressing and making a tablet from that; so, you will have the different kind of system or geometry depending upon the pressure which is applied and depending upon the morphology of that solid particle. So, particle chamber or crystal size. So, we can have a macro pore crystallites and the pores which can be

within the particle itselfm a single particle may have some kind of porosity. So, it can be called as a micro or mesopore which are roughly from 5 to 10 nano meter, right.

So, as you discussed last time also if you look at good support; so, it should have controlled surface area and porosity. So, that is a challenge when you look at a catalyst preparation; on especially when you look at Zeolite the catalyst which have very narrow pore size distribution, right. And, accordingly see in Zeolite catalyst, you will look at in terms of acidity you look at the pore size and that then they become the pore selective or safe selective for a given reaction. So, it should be thermally stable right and high mechanical strength against crushing and attrition. And, that is again equally important when you look at a moving bed reactor or fluid bed reactor or fixed bed reactor operating in the high pressure conditions.

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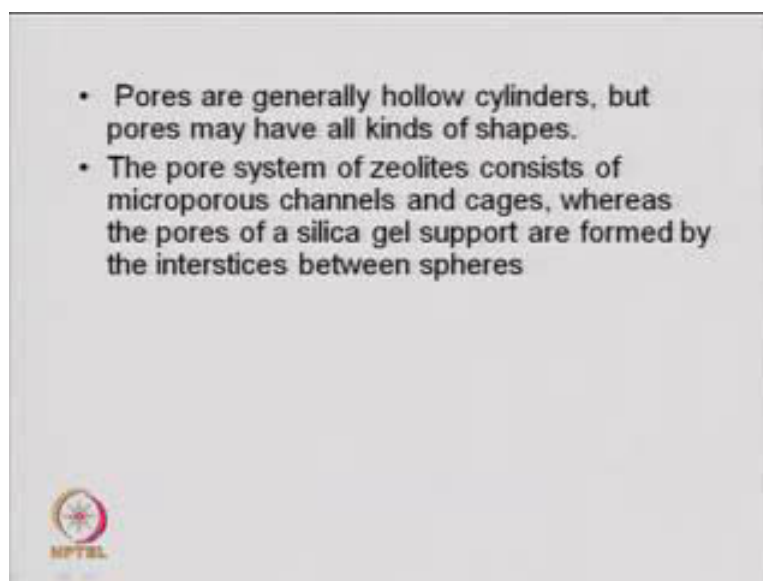
So, as I said the pores are generally hollow cylinders but pores may have all kind of shape. And, the pore system in Zeolite, if you look at they are mainly micro porous and they have the channels or cage type structure. So, hexagonal, pentagonal, octagonal; different type of cage structures can form depending upon the oxygen available in the ring or silicon oxygen aluminum which is connected and making a bridge. So, how these are connected and how different just like a football, if you look at or a buckyball structure. So, you can a different kind of geometry, though it can the one shape may be hexagonal, it can be pentagonal, it can be square also. So, depending upon that the cage

or you have just large number of balls kept in that then you get a gap between them. So, different kind of pores can form here.

And, aluminum carbon block, they are generally carbon block and they have platelet;s just like a slit type structure and resulting just a slit shape. So, again you can control the porosity of this or it can have a wedge type structure also. So, but in general when we are classifying, we are saying that they are strait cylindrical and interconnected. If they are interconnected or may be closed from other end; so, we can a different kind of model for different kind of pore system.

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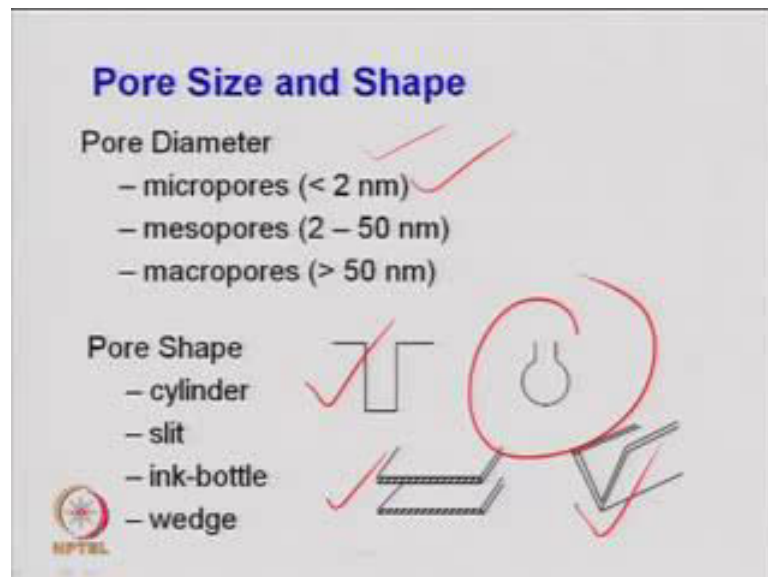
So, this is just if you look at here the micro pores by general definition less than 2 nano meter or 20 angstrom mesopore in between which is see 2 nano meter to 50 nano meter or 20 to 500 angstrom. But in some literature you may say just 200 angstrom also, 20 nano meter and more than 500 angstrom or 50 nano meter, you call them the macro pores. So, basically these are the pore space between the particles; where as these two, this is mainly the pore space within a particle. Within a particle intra, that is what you are talking the inter pallet or inter particle and intra particle.

So, that we will talk later because they have lot of importance in terms of diffusion control reaction or when you are looking a diffusion of a gas molecule into the pore of a catalyst. Then, you have to look at the pore geometry and depending upon the size, you

can have the diffusion resistance in certain kind of pore and free from diffusion resistance, when the pores are larger.

So, pore shape this is just like a cylindrical pore right and this is a kind of ink bottle right. As I said that narrow from the mouth pore, mouth and then wider right; so, ink bottle type. This is just like a slit; so, aluminized structure, what I said or a wedge type structure. So, these kind of all kind of pores may be seen in the pallets. So, the different type of play materials they can have these kind of structure chain as well; so, it can change depending upon the solid material.

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Schematic illustration of the difference between roughness and porosity
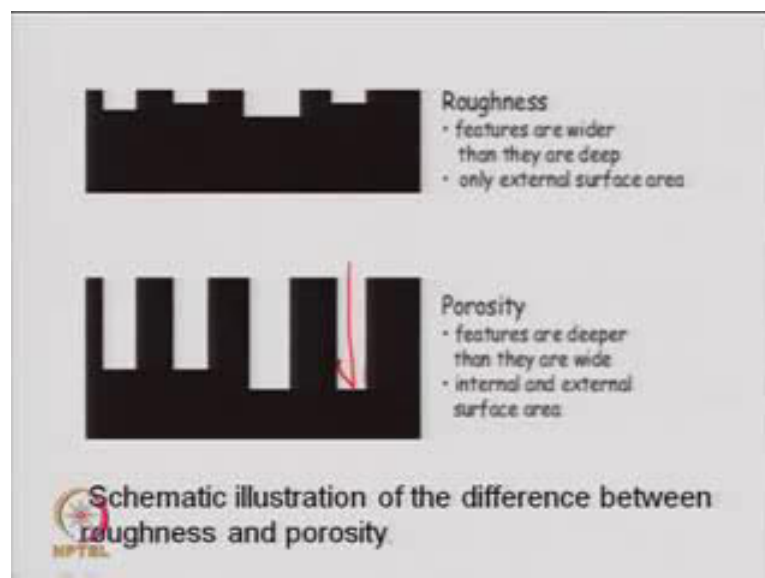
We have to understand the difference between the roughness and porosity. So, porosity we are generally defining that this is a straight cylindrical, so this is gap right and this is just a kind of roughness on surface. When you say even if you look at the fraction factor in a pipe, you define a term roughness which is nothing but the micro; say micron level depth right and which is nothing but a surface which is corrugated basically, not a smooth surface. So, a rough type of surface. So, this term is just of a small order of length or depth in one way and you calculate ((Refer Time: 06:56)) by d in the pipe and calculate the fraction factor. So that, that is a kind of; so roughness is basically the features are they are wider, then they are deeper. So, the width is more compared to the depth.

But when we talk pore the features they are deeper and less wider in terms of the internal and external surface area. So, this is just a difference between the when you say wedge surface, when you look at the surface where you are talking a porosity. So, it has sufficient length basically and the diameter l by d of that pore equally becomes the important; so, narrower pore and larger depth right.

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Adsorptive	Gas to be adsorbed
Adsorbent	Material on which gas adsorbs
Adsorbate	Adsorbed gas
Micropore	Pore width ≤ 2 nm
Mesopore	Pore width 2–50 nm
Macropore	Pore width ≥ 50 nm

So, some terminology because we use this terms again and again, when we look at the modeling or when we look at a heterogeneous catalyst, a gas comes on the surface of the solid. So, we call a gas which is coming is just a surface, on the surface where it is being adsorbed right. So, that is known as adsorbent right. So, adsorbent is the material on which gas adsorbs.

So, this is a solid basically and this is what we are calling here catalyst right; solid catalyst. And, the gas which comes on to the surface for adsorption that is known as adsorptive gas or you call it adsorbate. So, this is adsorbent and this is adsorbate. So, same thing here; this is what the property of gas right. And, micro pore I have already defined less than 2 nano meter roughly, macro between mesopore is between 2 to 50 nano meter and that macro pore more than 50 nano meter.
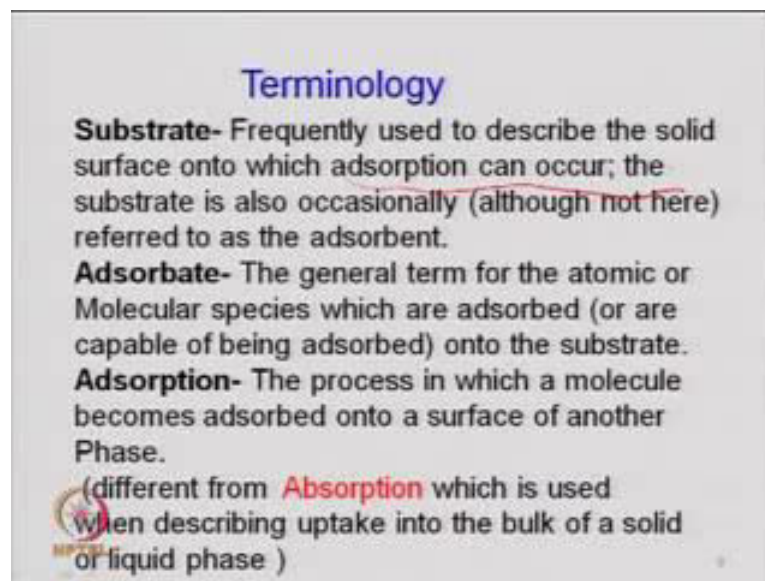
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So, now, we do understand, try to understand the mechanism. So, basically when you write a catalytic reaction mechanism understanding or demystifying the surface chemistry, that is important when you look at a metal, a support and a gas which is coming onto the surface. Because for all heterogeneous catalyst reactor design. the reaction mechanism is very important. Because you are depending upon the reaction mechanism, you identify the rate controlling step, then optimize the process parameter and then you think for the scale up of the process. And, that will be a kind of optimum design where you can have highest productivity with respect to conversion. So, that is what we are looking here.

So, first we have to understand the surface phenomena here. So, before catalyst preparation, I am just talking a brief of this and then again we need to go with different kind of models which have been developed for adsorption of a gas on the surface of a solid. So, in general if you look at, the adsorption can be two types; basically one the physically gas is coming on to the surface which will be a very weaker kind of bonding. That is known as physical adsorption. And, the in contrast to these, when the surface is active for some specific gas and the gas chemically binds to that surface under certain condition; that is very important under certain condition means, that is equivalent to a reaction condition. So, the gas be a chemisorb gas; so, it is a kind of chemical adsorption.

So, the physical adsorption is that it is a very weak bonding or Vander Waals type; weaker type forces between the that is the force of attraction is weaker between the gas and the solid surface. So, there is no significant redistribution of electron density in either the molecule or at the substrate surface. So, this is just a physically the gas is adsorbing.

So, it is a basically condensation of the gas molecule which is related to your critical temperature and pressure. So, this steam, at if you have the steam at 100 degree and then just you just apply the pressure on it; it will condense on the surface. So, basically it is a condensation; if you increase the pressure, the more and more molecule will come and adsorb on the surface. It have nothing to do and if you heat it again, they will leave the surface. So, that is what the physical adsorption.

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So, again the because to understand physical adsorption or chemical adsorption, we have to look at those terms. So, substrate is the same method what we have discussed a solid substrate, right. When you call substrate the gas which is adsorbing on the substance; so, basically to describe a solid surface on to which adsorption can occur. So, on the substrate, in fact we are talking the surface which has some property for adsorption either physical adsorption or chemical adsorption. So, occasionally what we refer here is the that a solid surface on which the adsorption takes place. And, adsorbate I have already

defined; that atomic or molecular species, then I am talking on a gaseous species which are adsorbed or they have a capability of adsorbing on the surface.

Adsorption is the process in which the molecule becomes adsorbed on the surface of another; which is not adsorption. So, absorption is basically a superficial addition of a gas molecule on the surface of the solid. Whereas if you look at absorption, it is nothing but the bulk of a solid or a liquid phase the gas penetrates to that depth. So, there is a difference between the two. Coverage; because we will talk many times the fractional surface coverage.

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Coverage- A measure of the extent of adsorption of a species onto a surface.

Exposure- A measure of the amount of gas which as surface has seen; more specifically it is the product of the pressure and time of exposure.
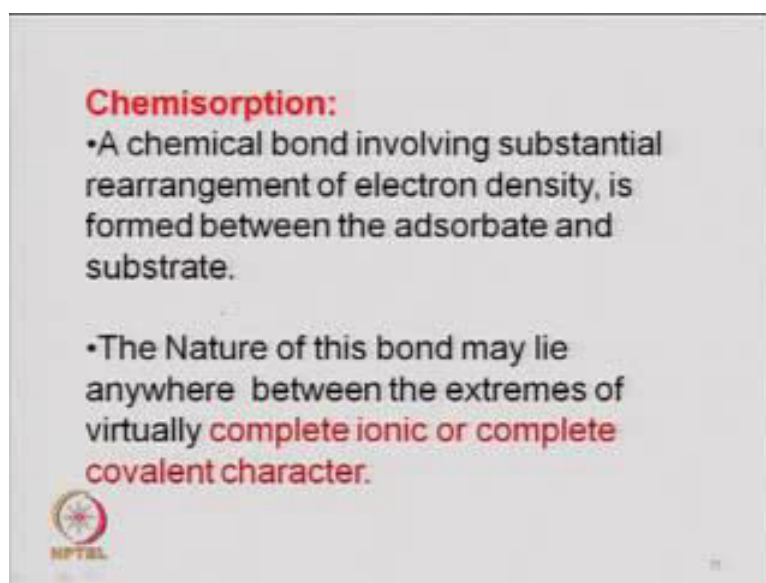(normal unit is the langmuir ,where $1 L=10^{-6}$ Torr *s).

So, it is nothing but the extent of an absorption of a species on to a surface. So, they are there are two terms now; as I discussed last time sticking coefficient right or sticking probability. So, for how much pressure right what is the pressure of the gas at what pressure on which substrate and for how much time the gas is in contact? So, we have to look at the exposer also. It means the terminology will be defined exposer; it is nothing but at a certain pressure the gas has been in contact with the solid for a given period of time. Time is also equally important; if you just give it and just for a fraction of second adsorption may not take place. Because initially the molecules are colliding with the substrate and the force is, there is a kind of bonding which is start taking place. If you release the pressure immediately, it will leave the surface.

So, that is important that exposer again we talk in terms of the value which we call Langmuir. So, that is pressure multiplied by time right pressure in the unit of torr right. So 1 torr is 1 millimeter of mercury. So, torr multiplied by the time is second. So, basically the amount of gas which is surface has seen more effectively it is the product of pressure and the time. So, this is gives you the idea that for how much time gas in contact with surface of the solid and this will decide your sticking probability. So, whatever the number of molecule which have been adsorbed on the surface will depend on the sticking probability as well as the exposer time also.
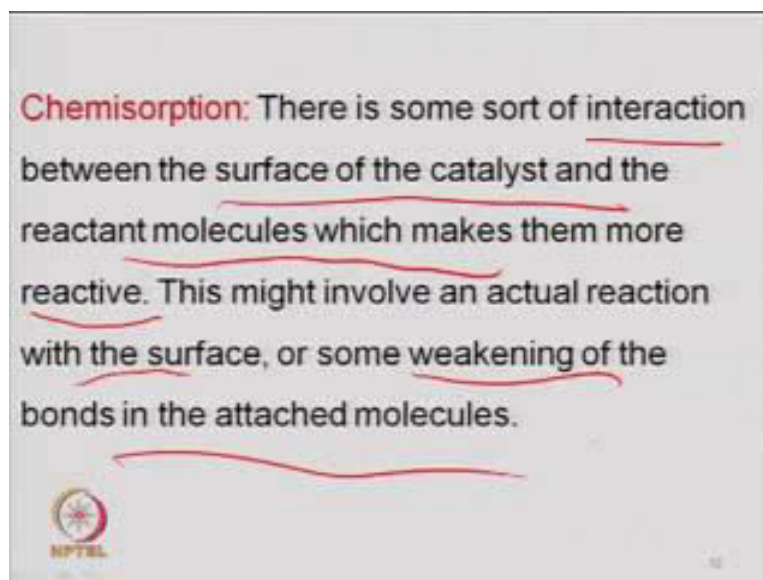
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So, in trust to physical adsorption which is related to Vander Waals force, the second one is known as chemical absorption or chemisorption. So, a chemical bonding here is that. So, it is a kind of chemically the molecule are adsorbed chemically on to a surface of the solid. So, all gases may not adsorb chemically here. A some kind of chemical binding is required. So, the nitrogen, if you consider it as an inert; so, under normal condition nitrogen will not adsorb right on the surface of a solid. But it can be absorbed physically. So, if you reduce the temperature, it will reach to a condensation temperature of nitrogen then it can condense on the surface. So, that is very important. So, chemical adsorption is related to the rearrangement of the electron density.

So, that is what I told, when you are looking a chemical reaction; then, chemical structure or electronic structure of a gas molecule should have certain kind of binding

with electronic structure of the metal species or support species. So that criteria or that fundamental thing which is from chemistry, we have to find out in terms of the adsorption or chemisorption property of the gas molecule and select a suitable metal as a catalyst.
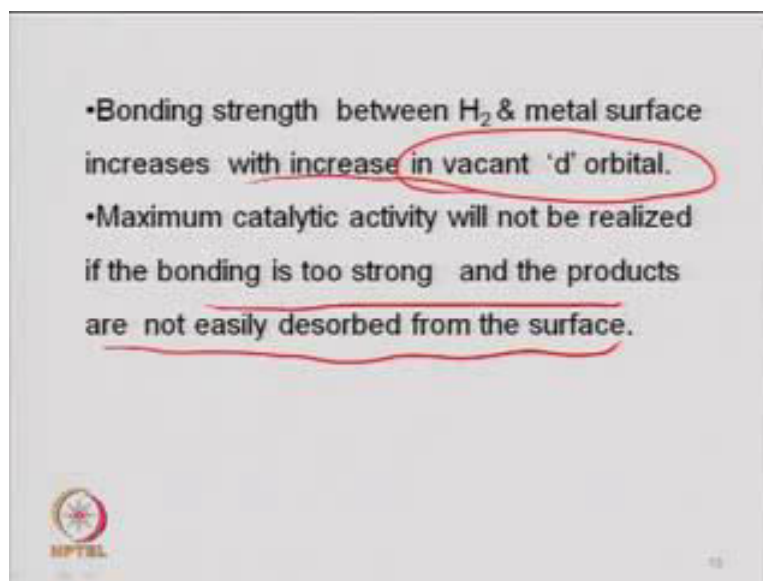
So, that helps in selecting the most suitable material for a given catalytic reaction. So, the nature of this bond may lie anywhere between the extends of complete ionic or complete covalent. So, it can be any type of bonding, ionic bonding and covalent bonding right. And, the force may also very wide range right. The energy that is the activation energy because it is a kind of chemical adsorption; it may be wide number. It may be of 200 kilo calorie also, it may be just 25 kilo calorie per mole also, right. So, it may vary.

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Chemisorption: There is some sort of interaction between the surface of the catalyst and the reactant molecules which makes them more reactive. This might involve an actual reaction with the surface, or some weakening of the bonds in the attached molecules.

So, during chemisorption, there is a sort of interaction between surface of the catalyst and the reactant molecule which make them more reactive. So, this is how these two interacts; that is the one thing and what is the kind of bonding between these two. So, at what condition of temperature and pressure that is the time of exposer is equally important. So, this might involve the actual reaction with the surface or some weakening of the bond in the attached molecule; just like a chemisorption of hydrogen. And, you can find out that dispersion, that is the fraction of the surface which is covered by a gas molecule. So, these kind of studies can be done for the characterization of a catalyst by using this fundamentals of the chemisorption.

- Bonding strength between H_2 & metal surface increases with increase in vacant 'd' orbital.
- Maximum catalytic activity will not be realized if the bonding is too strong and the products are not easily desorbed from the surface.

So, bonding strength is an example of, I just say that the bonding strength between the hydrogen; suppose you have a hydrogen, oxygen or carbon monoxide which may be the chemically reactive gases. And, it will adsorb on some surface. So, now depending upon the metal, suppose you have a copper, suppose you have a nickel molybdenum; so, different metals will have different kind of bonding structure. So, hydrogen on metal it increase with the increase in vacant d orbital right. So, for having a good catalytic activity the, there should be some kind of unpaired electron in the d orbital. So, that is a kind of vacant d orbital right. So, the vacant d orbital's are more; then the binding will be more and more strong. If they are less then it will be weaker.

So, generally the maximum catalytic activity will not be realized, if the bonding is too strong as I said before and the products are not easily desorbed from the surface. Because the one thing is that either the adsorption is not possible right or if the adsorption is possible, it is very strong that is because of the d orbital's is more. And, simultaneously if the adsorption is suppose weak or the products are weakly adsorbed, then again they will not convert to the final what you need; secondary reaction which are taking place. Some intermediate may form which may not be desired product. So, all kind of problem may occur, if your adsorption is too weak or if the adsorption is too strong; then product has been formed. But it is not leaving the surface.

So, if you your either you give a more higher temperature, your energy consumption will increase. So, all the phenomenon need to be considered for selecting a best metal for a given catalytic reaction or for a given reactant for a given reactant to chemisorption. So, these are very important here.

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So, just as an example if you look at here; so, generally we say that the group 8 metals right or noble metal group; p g m platinum group metal. They are more active as a catalyst; platinum, palladium, rhodium. So, these are more active right also group 1, 8 these are also active. So, all the metals if you look at cobalt, nickel, rhodium, rubidium, osmium, vanadium, iridium, platinum; so, they have one vacant d orbital per atom.

So, they have certain kind of binding; not too weak no too strong. On the other side, if you look at vanadium, chromium, mobalt, molybdenum, tungsten; these kind of metals have a large number of vacant d orbital. So, when they are large number of vacant d orbital; then they will strongly bind. So, chemisorption is very strong. So, molecules will not diffuse when the specie were adsorbed, it is strongly binded on the surface of the solid; and now it will not be able to move or able to diffuse further towards the surface for second heat reaction or for transformation in to the product. So, it remains there and adsorb species.

So, this is not a good kind of catalyst. But when you take the oxides of this and there may be a active catalyst. So, as a metal they are not very effective right because they strongly chemisorbed these again; the picture pictorial view.

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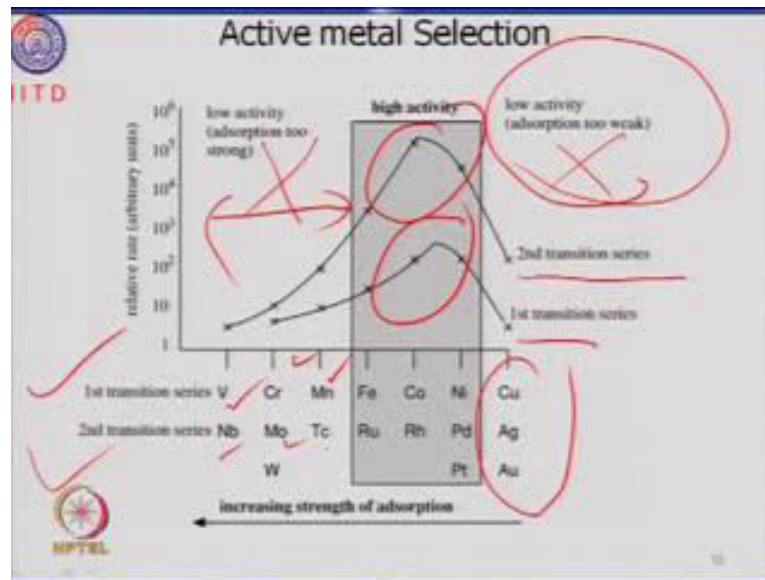
So, here just we are show that different metal. So, first transition series, second transition series; so you can see this is the zone see; this side the adsorption is too weak here low activity; so very weak adsorption. So, molecules all the metals they have the adsorption that is second transition series and first transition series if you look at. So, there adsorption if you look at relative rate on terms of arbitrary unit rate of adsorption increase; and then it is maximum here. And, then again in this unit decrease. So, this is low activity because here adsorption is too strong in the side. So, very strong chemisorption in this zone for all these metals. So, they are very strongly chemisorbed; same thing in the second transition series also strong chemisorption and this is for copper, silver and gold the adsorption is very weak.

So, these zones are not effective as a catalyst or not good for the catalytic activity. But this zone where you have a iron, cobalt, nickel and p g m group metal, platinum group metal this zone is effective for catalytic activity. So, based on these a depending upon the reactive gas molecule; we select the particular kind of metal support combination for a given chemical reaction.

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So, a chemical reaction once happens so both the reactant molecules will attach to the surface and one molecule will attach to the surface; other may be in the gas phase. So, this may hit freely that is which you moving in the gas phase or liquid phase; so the adsorb specie will attach with the gas specie.

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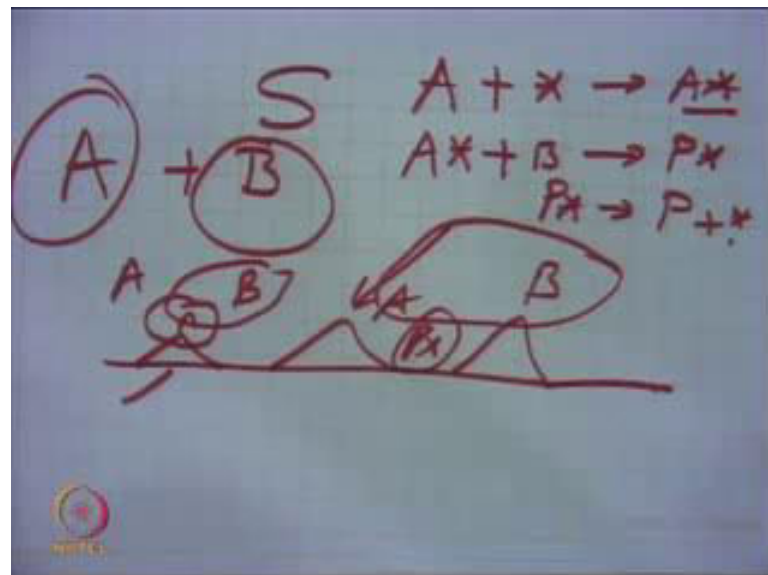
So, what I mean to said that the possibility maybe like this the a suppose; I am saying s is my substrate A and B are the reactant it tells will see later. But suppose this is a reactant, this is a reactant. So, possibility maybe that the on this substrate which have some active

site or which has some active site. So, A is coming and adsorbing here but B may remain here and these two are reactant. So, B is not adsorbed the second possibility maybe there that A is adsorbing here and B is adsorbing here; and then these two are reactant both possibility may happen. And, this will depend on the type of reactant specie and the support specie. So, the nature of the electronic structure of the reacting molecule and the metal support molecule is very important.

So, sometime one specie is an in the gas phase itself and other another is adsorb. So, if you look at here; so the products the reaction will take place and the product molecules will form. And, then it is a adsorb product specie which is transforming between the reaction on this and this suppose and then it is a p adsorb specie like this. So, I can write it something like A plus say star and gives you some kind of A star which is an adsorbed specie. And, same thing suppose b is on the gas phase so A star will react with B and it will it can form some p star like this which is a chemisorbed specie.

And, then p star will release the surface and will give you p plus star a free site again as a catalyst right which is again available for catalyst. So, finally the product gets desorbed. So, this is your desorption step where the product which is adsorbed on the surface leaves the surface; and gives you the product. So, desorption means the product molecule break away and this leaves the active site available for a new set of molecules to attach and react. So, the that is what the catalytic activity. So, catalyst effectively it is taking part in a reaction but at the end it immerse as an unreactant component.

So, this table gives you the idea about a difference between physical and chemical adsorption. So, the force of attraction in the case of physical adsorption is weaker Vander Waals type forces. So, Vander Waals type forces they are very weaker kind of force. So, and when you have just apply the just reverse the condition they will release or they bond will break; whereas the chemical adsorption it is a chemical binding; it requires some kind of energy. So, it is a stronger force. So, molecules are strongly binded with the substrate; if you look at their specific action right so physical adsorption is weaker bond. So, low right their activity is very low specific activity whereas in the case of chemical adsorption it is high; quantity wise if you look at the physical adsorption can adsorb a large number of molecules.

Because it is nothing but a condensation of the molecule. So, saturation happens but there will multiple layer adsorption. So, multi-layered adsorption can happen but in chemical adsorption when the site is covered it cannot take other site. The first it has to get vacant and then only the further chemisorption can take place. So, it is a limited number heat effects. So, the generally we consider adsorption as an exothermic process right release of it. So, in this case if you look at the physical adsorption the heat of reaction or heat of adsorption is very low of the order of 1 to 15 kilo calorie per mole right a kind; because it is a weaker kind. So, does not require a high temperature for chemisorption because exothermic reaction and a if you look at chemical reaction. So,

activation energy is required; just you have to activate the molecule then only it will adsorb, right.

So, the gas molecule if I take hydrogen on a surface of platinum it may adsorb on the surface at a lower temperature. But if you have a nickel molecule and again the hydrogen it may take a higher temperature. So, because they are specific in their activity and it is a kind of chemical bonding. So, whatever the amount of energy required to adsorb which you call heat of adsorption. So, that is for chemical binding it will be higher; so order of magnitude maybe from varies from 10 to 100 kilo calorie per mole very high activation energy; as I just sort physical adsorption, right.

The activation energy is low less than 10 kilo calorie per mole right but chemical when you say chemical activation. So, when the it is a just a chemisorptions; so there may be activated chemisorption also which may require higher temperature. So, there activation energy maybe very high; so for chemical adsorption the activation energy is high. So, it means a certain temperature is required to activate the molecule to form the activated complex; and then it will transfer into the product. So, chemical that is when you are saying that hydrogen in adsorbing the platinum it will adsorb only at certain temperature. Because it is forming a kind of platinum hydride a bond right. But when you look at a condensation of a steam on the surface of a solid just you have to release the pressure right; just you have to reduce the temperature.

So, either we you can allow it to condense on the surface right based on thermodynamics. Effect of temperature. So, physical adsorption; so it is very rapid at low temperature and recheck them quickly because condensation of the molecule. When the partial pressure that is the vapor pressure you have to find out and at that condition just you condense you keep p by p 0.

So, you can very easily saturate it these are relative pressure. So, that is the physical adsorption. But in the chemical adsorption the because the temperature when it is low because it requires a kind of activation energy; so your temperature is low. So, rate of chemisorption will be low because it is a kind of chemical reaction right. It needs a kind of k 0 into the power of minus e by r t from RMS equation a kind of that depending upon the value of activation energy you need a certain temperature.

So, the if your temperature is low your chemisorption rate will be low. And, this will increase with temperature just like as I said rate equation. But here it is a condensation of the molecule the only thing that your critical temperature is the very important. So, till that when you reach the equilibrium. So, rate of adsorption will be if you have a cryogenic condition the molecule will keep on condensing. And, when it reaches to saturation no further condensation rate of adsorption will be equal to rate of the vaporization.

Adsorption, when I say physical adsorption basically a condensation of a molecule and desorption when I say it means the desorption of a molecule. So, condensation reaction is always exothermic reaction right. Effect of pressure. So, as I said when you have a higher pressure more and more molecule will come to the surface or physical adsorption there is nothing to do with activity of a surface. It has nothing to do with type of metal anything any gas if it is below its critical temperature it can be allow to adsorb or allow to condense right.

So, nitrogen, liquid nitrogen if you have the temperature a minus 198 degree centigrade it will condense on that. So, that is the crucial point same thing for oxygen also so and same thing for the steam also; what I said carbon dioxide all these gases So, they are whatever the critical temperature you condensate it below that and will get a condensation. Surface the whole surface area is active because physical adsorption has nothing to do with a surface.

But when I say chemical adsorption it will be only on the active sites which I have shown here these are the active site. So, chemisorption will take place on these spots. So, this is the important in terms of dispersion. So, how much metals are active or how many metals are active on a surface that is important in the case of chemical adsorption. So, physical adsorption as I said it is a physically no nothing to do with the chemical activity. So, it can be multi-layer, right.

So, multi-layer physical adsorption but when you look at a chemical adsorption once the layer is saturated no molecule come on to the surface because chemisorption is on the active sites. And, once you see that your active sites are covered right and no further chemisorption will take place. So, this is the same thing what I said deactivation of the catalyst or poisoning of the catalyst. So, it is a poison precursor the seeds there and it is

not removing being removed from the surface your catalyst is dead; you need to replace the catalyst right.

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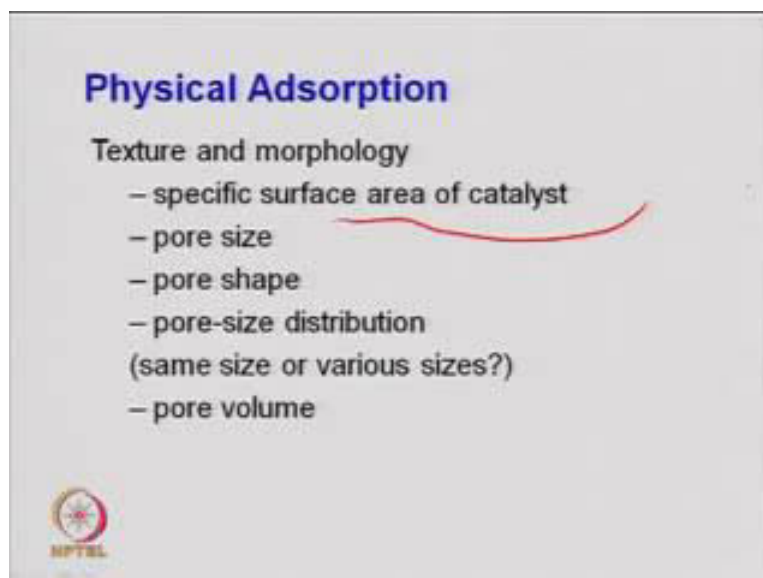
So, the application now physical adsorption also had very wide application in terms of demystifying the surface property or surface morphology. So, it is used for determining by specific surface area of the catalyst; because it is b the surface area which you report right that is internal pore surface area; the number of pores which are inside in a catalyst. So, whatever the 2 pi r bar L if I say area of one cylinder and there are millions of the pores. So, you can very easily find out the total surface area of the kind catalyst. Now, you are saying that how many molecules of the gas which is inert gas adsorbed on the surface? If you know the area one molecule of that gas; so multiply with a total number of molecules you can find out surface area right.

So, this fundamental thing which is related to your kinetic theory of the gases also we will talk later on this how to find out the surface area? But this is used to determine the specific surface area of the catalyst; b the surface area which you relate basically from that isotherm. So, will talk on that later; same thing this can be used to find out pore size, pore size distribution, pore shape also, ink bottle effect also; the that is what I talked nitrogen adsorption desorption methods. These are generally used which is based on the Kelvin's equation right capillary pressure of pressure in a capillary fundamental thing which is used to the kinetic theory of gases; which is related to the whatever the

condensation of that to how much how many molecules of the gas will condense. And, that will depend on the radius of that capillary, right. So, we will see that part later right so pore volume. So, all these information even the bulk density of the solid, apprehend density, porosity all these information you can find from the physical adsorption.

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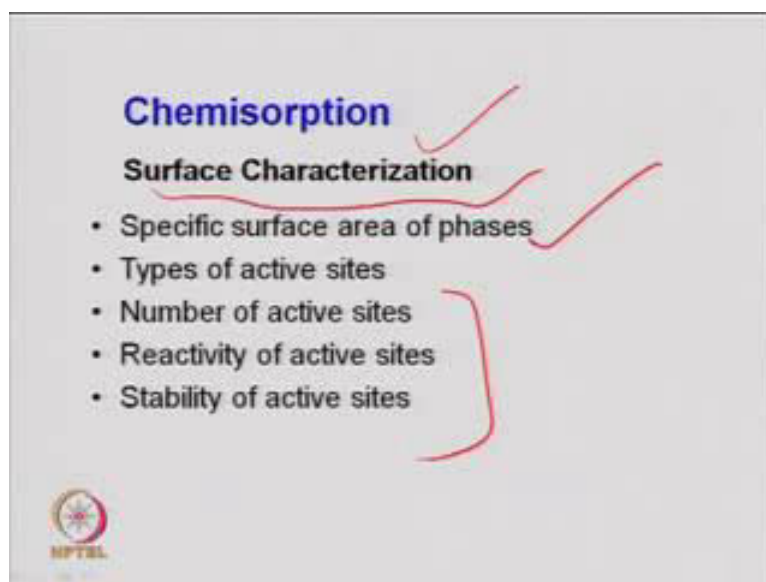
The chemical adsorption is again very important. Because when you prepare a catalyst you have to identify the surface reactivity or the concentration of metal specie which are available on surface right what you call dispersion. So, the chemical adsorption had the surface characterization information that we specific surface area of the phases right. Now, I am saying that the metal; the first one physical adsorption is related to the total surface area right where the physical adsorption take place. But when I say here because the this type of adsorption will be only on the active sites which are exposed to chemical reaction or on which the adsorption will take place. So, these site concentrations can be determined when you have any chemical reactive gas, right.

The any chemical reactive gas will adsorb on this at specified condition. So, how many molecules of that gas adsorb; and if you know the area of one molecule you can find out the area of this right. So, this information can be obtained from chemical; same thing for type of active sites right. So, type of active sites means it can be a Bronsted type, it can be Lewis type; suppose if I talk acidity, right. So, basicity same thing that strength of the acid site concentration or basic site concentration.

So, stronger type of sites means they will adsorb a higher temperature; same thing if the something is adsorbing at a lower temperature means a kind of weaker site for the same type of specie. So, you can get and that is what the initially I was talking the metal support interaction. So, whether your metal support is now interaction is strong. Then it mean, the chemisorption will take place at a higher temperature. So, these information can be obtained by chemical study.

So, you have the a reactive gas say hydrogen or carbon monoxide; and just allow it to react or in touch or whatever I said that pressure into time at a given condition expose it for a given period of time over a range of temperature. And, then you can very easily find that when there is a the fraction a kind of peak will you will get; where you can see that there is a kind of adsorption. Because you have when the gas is passing everything will come out because nothing can be adsorbed right.

But when there is chemisorption the volume will decrease in one way right. So, you can very easily find out the decrease or you integrate it in terms of the reference. And, you can have the concentration of the gas which is adsorbed on the surface and that is related to the concentration of the matter. So, that we will see later how the stoichiometric coefficients are correlated? So, all type these kind of information can be obtained from chemical adsorption.

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So, we were talking a term dispersion again and again. So ,this is very important number besides your turnover frequency. So, turnover frequency, turnover number but first thing is that this dispersion. So, when you have a catalyst system or a catalyst for a reaction or you are prepared a catalyst for a reaction; the concentration initial concentration is not important. The important is that what is the actual concentration which is exposed to the surface? Because for chemical reaction dispersion or fraction which is exposed to the surface is more important.

So, your chemical reaction will take place depending upon this. Suppose this number is just 1 percent; it means whatever the initial mass of the metal which has been deposited only one percent of that has been active, right. So, last is wasted 99.9 percent is waste and 1 percent is effective. So, especially when you have a noble method because they are very costly platinum, palladium, rhodium these are ruthenium these are very costly material.

So, we need only a small concentration of these active metals. Because the small concentration itself is enough right for catalytic reactivity; the only thing that how well it is dispersed on a surface that is important. So, in fact it is just in the form of cluster then it most of the surface of this active metal is a waste. So, that is a crucial part of the catalyst preparation; especially when you have a precious metals or any metal even nickel, cobalt, molybdenum. So, all the need to deposit on the surface in such a way that every part of that metal should be well utilized.

So, this is again a part of green catalysis; there we are talking in terms of the E factor right the waste. So, if you are saying 1 percent dispersion 99.9 is waste right; and that is just a changing the economy of the process over all process. So, dispersion definition now you know it is mainly the number of surface atom. Number of surface atom I am talking in terms of the which is exposed to the surface divide by the total number of atom which are in the beginning you have taken right or total number of metal as which were deposited on the surface.

So, suppose you have prepared with 10 percent 10 with percent of the nickel. And, now in 10 gram of catalyst you have 0.1 gram of the nickel is actually and if you have taken the steady to chemisorption say. So, you can find out how many molecules of hydrogen

adsorbed on the surface? So, this will adsorb or chemisorb only on those active nickel sites.

So, you can very easily find out what is the concentration of nickel which is available on the surface? So, this is your n s right. So, the number of surface atom or concentration of the nickel on the surface divides by the total concentration of the nickel on the surface. So, this is a very important number. And, this is related to your turnover frequency also when you calculate the rate or turnover rate. The most of the time the compare a catalytic activity rather you write rate of reaction per gram of catalyst per unit time most reacted per unit time per gram of a catalyst.

But the good definition will be if you define it moles of the reactant that is converted into product per gram of these metal right per unit time. So, suppose you have 10 gram of metal 10 percent of metal a, 5 percent of metal b and 1 percent of metal c. So, you just define in terms of that and then you compare the activity. So, then you can have a better idea in terms of the screening of the catalyst or you can define.

So, basically the turnover rate is the more specific or better definition to define the rate of reaction. So, chemisorption when you have titration of the surface site basically when you are titrating your calculating the acidic site and basic site. So, it is related to the stoichiometric as I said; because say hydrogen when you are taking hydrogen molecule H_2 right. So, when you have a platinum now hydrogen may dissociate fast and split fast in H and H; and then it will adsorb on platinum right. So, it is known as dissociative chemisorptions. So, there the possibility may be something like this that stoichiometric very important.
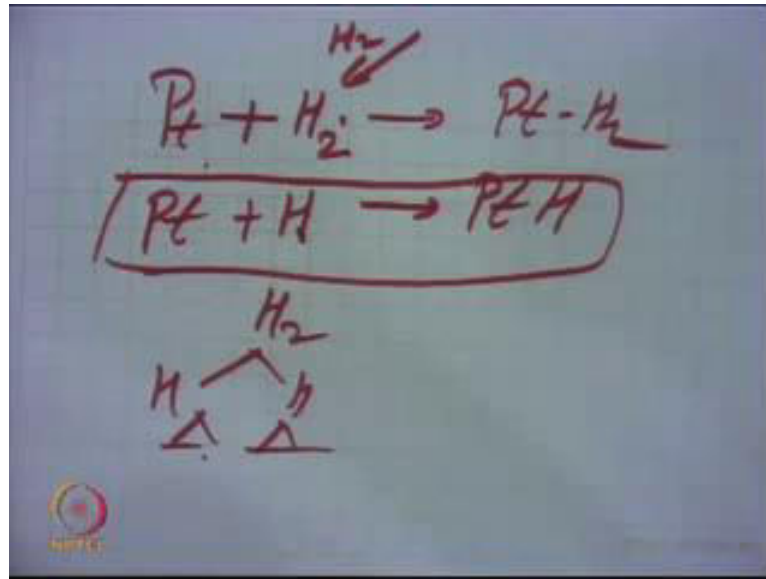
So, you have a platinum right and you have a hydrogen which is coming from here. So, whether hydrogen is directly attaching to this or platinum is this hydrogen is dissociated fast; and giving you like this and then it is making a platinum hydride right. So, a complete molecule whether it is hydrogen or carbon monoxide. So, whether the it is a associative chemisorptions.

So, associative chemisorption means this whole thing is combined together like this and dissociative means this. So, in the case of hydrogen on most of the surface it is a dissociative. So, hydrogen it means one hydrogen molecule when comes it will chemisorb first like this. So, H H; so it will cover 2 nickels, 2 metal sites platinum or palladium or nickel. So, it will cover 2 platinum sites right.

So, that is the meaning of this that is how many sites are required to have a chemical adsorption of this specie. So, you need to look at these stoichiometric. So, this is very important that this is what I am saying that adsorption versus pressure. So, this is saturation to monolayer form. So, when you have chemical adsorption you will have monolayer no further chemisorptions.

So, surface is saturated. Now, we are talking in terms of the stoichiometric that is how many molecules consumed, molecules are hydrogen consumed? But before that you should understand the chemistry that hydrogen chemisorpion dissositively on the surface. So, that is why it every hydrogen molecule will cover the two platinum site. So, when

you are defining the turnover rate or the dispersion then you have to take care of that; so will talk on that later.

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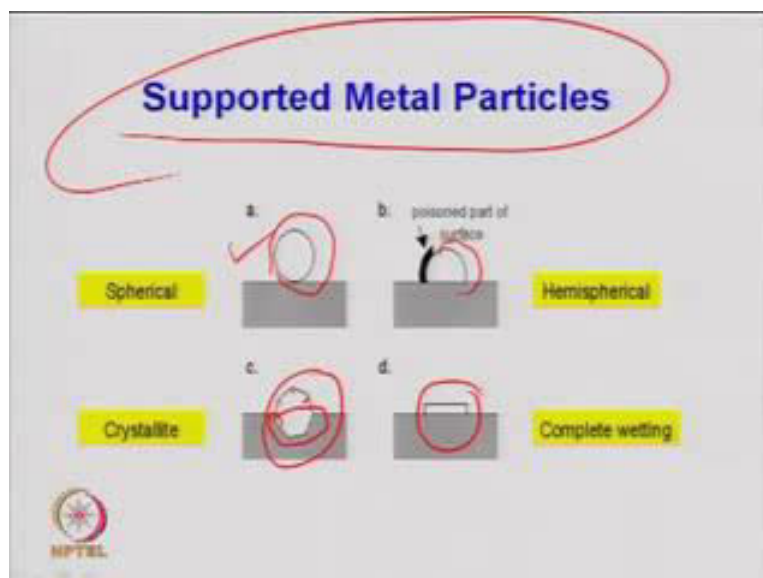
So, just we have shown some pictures here or for a supported metal particle. So, particle morphology maybe different as I said before right it. So, this is a crucial point in terms of the catalyst preparation; spherical particle or a hemispherical particle or a crystal like this. So, generally when you have a more edges the catalyst activity is more. because activity comes with from these as I said especially so suppose you have a carbon nano tube formation. So, nano tube may not form on this a spherical surface; the good kind of nano particles will form when you have a prism type of particle say on nickel suppose you are talking.

So, the structure of this or crystallites shape is very important. So, that is just an example but different cases may have the particle morphology what I am talking the catalyst morphology is very important. So, spherical or this type or prism type right so there can be a different kind of geometry of the particle; and that plays the important role that I did not tell. So, it is a kind of defect, it is a kind of lattice structure or what you are saying electronic structure because the shape is forming. Because of certain minimum energy requirement whatever the surface free surface which needs kind of a energy.

So, because of that this surface forms right on which the substrate is forming that is also equally important. So, here you can see that if you have this kind of surface. So, you can

see that every surface sphere surface is exposed for the reaction; most of the surface is available. But only the problem is that it may be a kind of weaker type interaction metal support interaction is weak.

So, it may happen that slightly high temperature or when you have certain this irregulation on the surface the metal may leave the surface. So, it is a that is a interaction is poor. But if you look at in terms of the activity or surface which is exposed chemically or chemical reaction; metal surface area which you are calculating. So, rate we can define per unit metal surface area also, crystallite surface area which you call that time it is better in one way but the bonding is weaker.

So, risk is that the molecule may leave the surface that is atom will leave the surface or metal may leave the surface during reaction. So, not very good or not very effective. Here, if you look at this as a hemispherical surface now. So, part of surface has been chemisorbed or interacting with the support. So, this maybe a case of strong metal support interaction. So, here the you have wasted part of the surface area of the metal but the bonding is strong, right.

So, metal will not leave the surface. So, a kind of tuning is desired that is this is for a hemispherical particle here and this surface the poison part of the surface this may records only this much is now effective for reaction. So, there may be different cases depending upon the chemical reaction and the time pores. So, this will the structure morphology; which you determine from the surface steady and a part big part of surface science and methodology surface structure, material science so or electronic configuration.

So, lot of theories are required in order to understand these surface or metal substrate interaction. If you look at here it is a good kind of it is a crystal basically; the partly it has been gone there inside. So, again a kind of crystal support metal interaction but the edges are more here right. So, every the dislocation which you call surface dislocation. So, here is the probability that molecule may interact here, it may interact here, it may interact here.

So more and more ((Refer Time: 44:27)) where the growth can become; the metal or the reaction can take place on this or adsorption or chemisorption takes place. So, and this is again a complete vacant surface; if you look at only a small portion of this is available or

exposed for the surface, right. So, there can be a different kind of interactions of a metal with the support. So, you have to tune for a given reaction; and then understand the surface.

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Adsorption at gas/solid interface.
Adsorption: Term used to describe the process Whereby a molecule(the adsorbate) forms a Bond to a solid surface(an adsorbent).
Fractional surface coverage θ

$$\theta = \frac{N_s}{N_a} \quad \begin{array}{l} \rightarrow \text{number of sites occupied by adsorbate} \\ \rightarrow \text{total number of adsorption sites} \end{array}$$

When $\theta = 1$, $N_s = N_\Sigma$ and an adsorbed monolayer is formed. The fractional coverage θ depends on pressure of adsorbing gas phase species. This $\theta = \theta(P)$ relationship is called an adsorption isotherm.

So, definition of adsorption we have already seen. So, I am just talking in terms of the fractional of the surface covered. So, most of the time when we talk a catalytic reaction the rate of reaction will depend or rate of adsorption will depend on the surface; which is available for adsorption; that is a vacant site concentration. So, what vacant site when I am saying I am talking in terms of n; number of sites which are available on the surface right. And, how many of these sites are already covered by an a specie.

And, you know in general the rate of adsorption will depend on the partial pressure that is one thing gaseous specie. And, also it will depend where the gas is coming and attaching. So, you physical adsorption is no problem but when it is chemical adsorption it is very specific in its success. So, chemical adsorption will take place only when there is a surface available for chemical adsorption; otherwise it will leave; it will go back, right. So, molecules are colliding and it will reflect there; because it does not find any space, right.

So, that is what the exposure timing is equally important special time. So, the molecules which are available on the surface that is what I said the sites which are occupied by an adsorbate. So, the fraction of the sites which are covered by a gas molecule will depend

on the fraction of the sites or the sites which are occupied by the gas molecule; which is your adsorbate divide by the total number of adsorption site. So, N s divide by N a sometime we write, sometime we write it.

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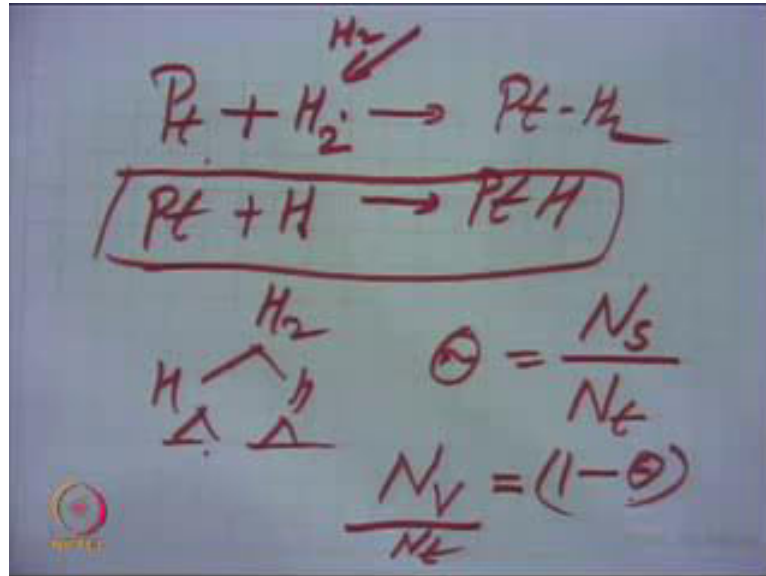
So, fraction of the surface which is covered is simply your number of sites which are covered divide by total number of sites surface on the surface are you getting it. So, it means theta is a fraction right because your rate is proportional to the fractional of the vacant site. So, what will be the vacant site I can write it N v number of vacant site that is 1 minus theta. So, the concentration which you write just like if I write a bimolecular reaction a plus b and I say that it is elementary type you simply write minus r a is equal to k times c a into c v right; the same thing here also.

So, the rate is proportional to the partial pressure of the specie; so p a multiplied by the fraction of the sites which are vacant. So, 1 minus theta right or concentration of vacant site so that will become N v upon N t, correct. So, this is the way that so I will not write it rather I will write it N v upon N t because I am saying fraction. So, 1 minus theta is fraction of the sites; which is vacant on which the adsorption will take place N v divided by N t. So, this is the very fundamental equation generally will come again and again when we will talk chemisorptions or catalytic reaction kinetics.

So, theta basically when it completely covered it will become 1; that is total sites are covered. So, that time there would not be any chemical reaction right. So, it maybe sites
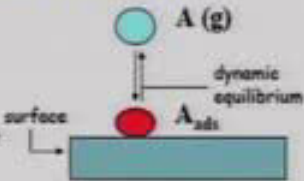
covered, it maybe poison some fights maybe poisoned also right; there not be available further reaction. So, this sites will decrease with time basically. So, sometime we write it c t concentration of site and which will be nothing but the vacant site c v plus t sites which are covered by the gas molecule.

So, there are different type of gas reactant molecule; then we will say sites covered by a, sites covered by b and so on so forth, right. So, sometime the product which may also be adsorbed product right before also; there will be a site which will also covered by the product also. So, this will be used again and again; in this picture we have shown here.

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So, there is always a equilibrium dynamic equilibrium between the gas which is coming. So, adsorbent and the adsorbate; so this is the adsorb specie and there is a kind of equilibrium on the surface. So, you are talking this part; so this very famous isotherm which was given by the scientist Langmuir and a based on that we call it Langmuir adsorption isotherm. And, further it was modified also later for kinetic studies. But basic fundamental thing is that there is a always a kind of dynamic equilibrium between the gas molecule and the substrate the surface. So, simple approach which is written as I said before that surface that is number of vacant site.
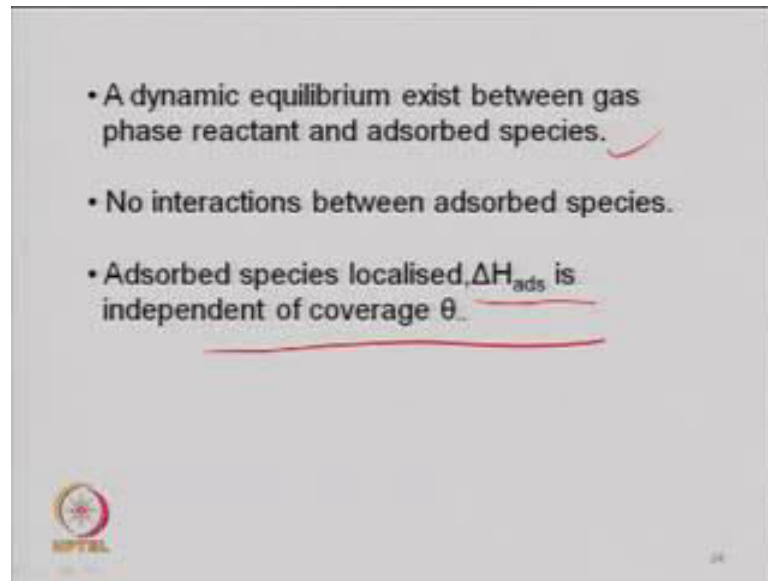
The sites which are available on the surface is nothing but equal to the vacant site plus the concentration of that sites on the surface. So, N v is the vacant site and N s is the sites which are covered by the gasses specie already covered. So, sum will be nothing but the total number of sites; solid surface generally there are several assumptions of the Langmuir. So, which we will talk later when we talk physical adsorption. But generally this Langmuir isotherm is more valid or more correct for that chemical adsorption.

So, will see that later but the surface we assume that it is a homogeneous. And, contain a number of equivalent sites each of which is occupied by single adsorbate molecule. So, if the gas molecule is attached on the surface no other molecule will come on to the surface. So, for chemical adsorption it is very correct because when the site is already covered; second gas molecule cannot come on to that right. Because it is an astrogas action reaction; but when it there is a physical adsorption a large number of other molecule can come.

Because it is nothing but condensation of the gas molecule. So, physical adsorption can happen. So, will talk on that later again there is another assumption is that these a dynamic equilibrium exist between gas phase reactant and the adsorbed specie. So, always the rate of adsorption is equal to rate of adsorption; when you are talking at equilibrium. So, whenever there is a saturation; so number of molecule which adsorb on

the surface which is equivalent to some kind of pressure; pressure proportional to the pressure.

And, the sites which are vacant right and desorption will take place from the surface which is covered by the solid. So, that will be proportional to theta fraction of the surface which is covered and desorption is nothing to do with pressure, right. So, the fraction of the surface which is covered from that the molecule will leave right adsorb a will vacant that surface which is already covered. So, it will depend only on the fraction of the surface which is covered to theta.

So, that is the meaning of this term and there is no interaction between adsorbed species. So, what we are saying that the molecules comes here; so a star, a star there are different a star. So, whatever the molecule concentration which is adsorbed here it has nothing to do with its neighbor. So, it means the rate of adsorption is independent of fraction of the surface covered.

So, it means the if n number of molecules have already adsorbed and you have remaining N v vacant sites. But rate of adsorption is not changing because of that right. So, it is independent of surface covered that is another assumption of Langmuir. So, we will discuss these terms later and adsorbed species which is localized and delta H adsorbed is independent of surface coverage which is the same thing which I said earlier also.

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So, when you do the modeling; so it is a wide if you look at the modeling of the catalytic reaction, heterogeneous catalytic reaction it is a very complex. So, you have to look at these adsorption phenomena, surface kinetics because you have a surface kinetic reaction. And, these will depend on the molecular interaction type of gas there heat of adsorption heat of chemisorption on these rate of adsorption or desorption. Because we are not talking just an adsorption and desorption; we are talking a transformation into some productive specie. And, the conversion of a into a product specie will depend on your partly thermodynamics; once thermodynamic is clear then you are talking in terms of just a kinetics that is rate.

But this rate is also a function of several resistance, mass transfer resistance because gas is coming to the surface. And, on surface there may be different kind of dislocation, different kind of other specie foreign elements right and because of that rate may effect. And, then the adsorb product is form which is desorbing, right. So, desorption rate may also be a function of temperature pressure or your environmental condition that is the reactor condition.

So, the total modeling of a heterogeneous catalytic reaction becomes a complex. It is a totally non-elementary type of reaction mechanic right. So, we have to look at that. So, reactor modeling is one of the most important aspect based on hydrodynamics and followed by the kinetic studies. So, very complex reactor if you look at the reactor design which involves your elementary reaction when you look at modeling; the quantum mechanics what I said chemistry, physical chemistry and so many so things like as I said nano catalysis, nano science, material science.

So, everything is a involved when you look at the reaction modeling. And, then reactor modeling because you have to scale up the process for a given catalytic reaction. So, reactor modeling starts from hydrodynamics and then you have to give the mathematical interpretation and representation the numerical method, micro-kinetics. So, this is now a days very important because you look a selective product, right. So, how the rate constant of each molecular reaction; what I am talking the molecular dynamics, molecular chemistry.

So, if you look at on the surface there are several thousands of the reaction may take place between these adsorbed specie right; just like a cracking reaction several reactions

are going on. And, you have to select a narrower or look at the selectivity for a narrow product. So, these are transcend condition they are products are forming; but we may be only for a fraction of the second right.

So, you have to control the rate equation you have to look at the rate constant, activation energy for each reaction and then only you can go for the details scale up of the reactor. So, micro-kinetics is very important in that regard. So, structure and efficiency heat and mass transfer very important because the when you look at a large scale commercial reactor it may be endothermic, exothermic.

So, heat release hot spot formation; so in a catalytic reaction the exothermic reaction is very difficult to control because it is a runaway condition. So, many problems are transcend condition unsteady state, heat balance. So, we need to look at all those when you look at a commercial reactor design. So, very complex phenomenon.

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So, when you look at a catalytic reaction process in general it is related to the heat and mass transfer energy, balance efficiency of process. So, first thing is that material energy balance you have to write for a given system. So, the different kind of reactors may used will talk discuss on that briefly. But a ten type reactors, CSTR a pluck flow reactor, batch reactor. So, most of the time we do the kinetics in the case of fix bed differential reactors. And, then when you look at the actual reactor system for exothermic it can be bubble column reactor like for Fischer Trop type reaction right; it can be just like a

crudile bed reactor, like an f c c cracking. So, you have to look at the reactor design and then you need to understand d a heat and mass transfer problem.

So, reactants and generally when you see the catalyst testing or screaming we add the definite amount of catalyst in a reactor. And, then we feed the reactor, feed the reactant and the exit we measure the concentration. And, then the look at the property of the product with it is a different space time if it is continuous reactor. And, then we just try to maximize the desired product; and also we look at the activity of catalyst and stability of the catalyst.

And, then we compare the catalyst and then we give some sort of solution in terms of screaming of the catalyst. And, then we go with the detailed kinetics and modeling and then you scale up the process. So, this over all it looks a small step; but if you look at the independent step they are very complicated. So, you look at that. So, I stop here and will continue it next time.