Heterogeneous Catalysis and Catalytic Processes
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Module - 04
Lecture -12

Good morning, in the last lecture I was talking about pores and distribution and discussed the algorithm for the evolution of the property or thickness of the pore whether, the absorbed layer thickness and the pores side distribution, which was accumulative pore side distribution or the change in pore radius as a function of pressure.

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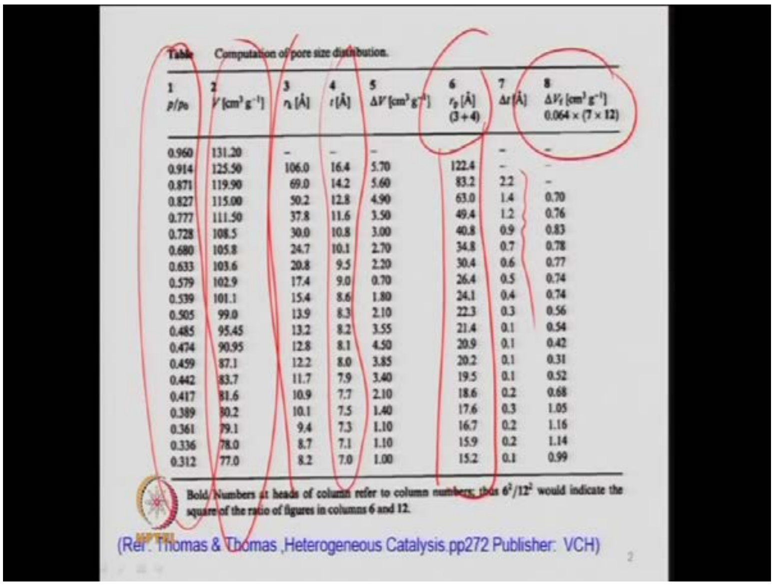

Table Computation of pore size distribution.

1 p/p_0	2 V [cm^3 g^{-1}]	3 r_k [Å]	4 t [Å]	5 ΔV [cm^3 g^{-1}]	6 r_p [Å] (3+4)	7 Δt [Å]	8 ΔV_f [cm^3 g^{-1}] 0.064 × (7 × 12)
0.960	131.20	–	–	–		–	–
0.914	125.50	106.0	16.4	5.70	122.4	–	–
0.871	119.90	69.0	14.2	5.60	83.2	2.2	–
0.827	115.00	50.2	12.8	4.90	63.0	1.4	0.70
0.777	111.50	37.8	11.6	3.50	49.4	1.2	0.76
0.728	108.5	30.0	10.8	3.00	40.8	0.9	0.83
0.680	105.8	24.7	10.1	2.70	34.8	0.7	0.78
0.633	103.6	20.8	9.5	2.20	30.4	0.6	0.77
0.579	102.9	17.4	9.0	0.70	26.4	0.5	0.74
0.539	101.1	15.4	8.6	1.80	24.1	0.4	0.74
0.505	99.0	13.9	8.3	2.10	22.3	0.3	0.56
0.485	95.45	13.2	8.2	3.55	21.4	0.1	0.54
0.474	90.95	12.8	8.1	4.50	20.9	0.1	0.42
0.459	87.1	12.2	8.0	3.85	20.2	0.1	0.31
0.442	83.7	11.7	7.9	3.40	19.5	0.1	0.52
0.417	81.6	10.9	7.7	2.10	18.6	0.2	0.68
0.389	80.2	10.1	7.5	1.40	17.6	0.3	1.05
0.361	79.1	9.4	7.3	1.10	16.7	0.2	1.16
0.336	78.0	8.7	7.1	1.10	15.9	0.2	1.14
0.312	77.0	8.2	7.0	1.00	15.2	0.1	0.99

Bold Numbers at heads of column refer to column numbers; thus $6^2/12^2$ would indicate the square of the ratio of figures in columns 6 and 12.

(Ref. Thomas & Thomas ,Heterogeneous Catalysis pp272 Publisher: VCH)

So, as I said that we have the data in the form of P by P 0, versus volume absorbed. So, this is the experimental information, which can be determined from the B T experiment. So, a different pressure by increasing the pressure to a saturation pressure the volume of the gas absorbed is measured and you can plot and this can be used to determine the B T surface area also an average pore radius average pore size, what I talked before but, if you want to get the in depth pore analysis, pore side distribution, you need to look at the plot. So, you need to find out the thickness, absorbed layer thickness, which we have talked last time based of wheeler's model and the Kelvin radius for that also we talked in terms of the vapor pressure release equation or Kelvin equation.

So, r k is the Kelvin radius here. So, this Kelvin radius as I said is less than the actual pore radius, so that is to be added. So, you get the pore radius here, this is your actual radius of the pore or which is used to determine the pore side distribution on that text part during the catalytic action. You want to get further analysis, you can find out the difference what between two pressure difference, what is the difference in the volume dissolved, because you are talking a desorption data here and simultaneously what is the decrement in the conest layer thickness.

So that is delta t, which can be obtained in two successive thickness layer thicknesses and you can find out these delta t. Which is related to your decrement in the friction volume, because in that delta t layer what is the volume of the gas liquid which is dissolved? so that can be calculated, so that you have seen based on that per meter square the nitrogen 5.23 square centimeter to cube volume and then, you can calculate it.

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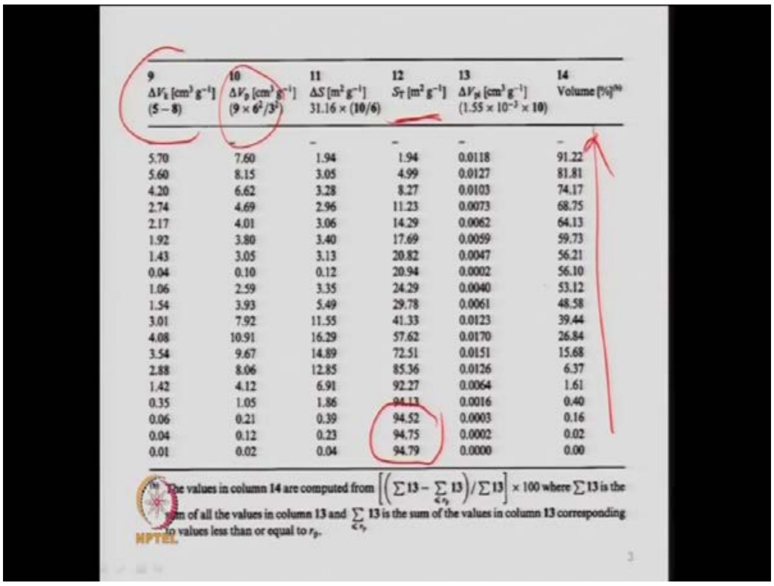

9 ΔV_k [cm^3 g^{-1}] (5 − 8)	10 ΔV_p [cm^3 g^{-1}] ($9 \times 6^2/3^2$)	11 ΔS [m^2 g^{-1}] 31.16 × (10/6)	12 S_T [m^2 g^{-1}]	13 ΔV_μ [cm^3 g^{-1}] ($1.55 \times 10^{-3} \times 10$)	14 Volume [%]$^{(a)}$
	–	–	–	–	–
5.70	7.60	1.94	1.94	0.0118	91.22
5.60	8.15	3.05	4.99	0.0127	81.81
4.20	6.62	3.28	8.27	0.0103	74.17
2.74	4.69	2.96	11.23	0.0073	68.75
2.17	4.01	3.06	14.29	0.0062	64.13
1.92	3.80	3.40	17.69	0.0059	59.73
1.43	3.05	3.13	20.82	0.0047	56.21
0.04	0.10	0.12	20.94	0.0002	56.10
1.06	2.59	3.35	24.29	0.0040	53.12
1.54	3.93	5.49	29.78	0.0061	48.58
3.01	7.92	11.55	41.33	0.0123	39.44
4.08	10.91	16.29	57.62	0.0170	26.84
3.54	9.67	14.89	72.51	0.0151	15.68
2.88	8.06	12.85	85.36	0.0126	6.37
1.42	4.12	6.91	92.27	0.0064	1.61
0.35	1.05	1.86	94.13	0.0016	0.40
0.06	0.21	0.39	94.52	0.0003	0.16
0.04	0.12	0.23	94.75	0.0002	0.02
0.01	0.02	0.04	94.79	0.0000	0.00

(a) The values in column 14 are computed from $\left[\left(\sum 13 - \sum_{\leq r_p} 13\right)/\sum 13\right] \times 100$ where $\sum 13$ is the sum of all the values in column 13 and $\sum_{\leq r_p} 13$ is the sum of the values in column 13 corresponding to values less than or equal to r_p.

That is based on that assuming 16.2 Armstrong square is the area of 1 nitrogen molecule and then, you can find out change in the Kelvin that is the pore volume, which is because of the Kelvin radius the volume of the liquid dissolved, so that is nothing but, calculation of the total pore volume minus volume of the liquid which had been vaporized from the absorbed that is delta v f.

So that can be calculated, this can be related to your pore volume, because I told that pore volume is related to the pore radius. So, delta v p upon delta v k is equal to r p upon r k whole square. So that you know, delta p is nothing but, pi r square pi that is volume of the 4 into cross section area of the pore into length. So, pore volume if I say area of cross section into length. So, pi r square into length. So, cross section area pi r square multiplied by length. So, length of the pore is same. So, you guess very easily co-relate delta v p and delta v k. So, which is given here in terms and this multiplied by that square of the radio catic r p or r k whole square. So, we can very easily calculate that.

And then, we can also calculate this change in the surface area b e t surface area, which you have calculated, or between two successive delta p, what are the numbers of molecules gas molecules, which have desorbed from the surface and area of one molecule is known. So that is the decrement of change in the surface area of the molecule gas molecule imam not talking in terms of a surface. So, but, that is equivalent to the layers of delta t, that is equivalent to a delta t also.

So, we get total surface area, so that is just similar to your d t surface area but, for cos 1 in layer thickness finally, if I look at this value you see here, it is almost a constant value and this is the surface area of that solid, which is similar to your b e t surface area it is the type electron area. So, total number of molecules which have been disrobed from the surface and that is related to the surface area. Then, there are some additional information this delta v p l, which is written, that is corrected, because you calculated at the adsorb condition, you can convert it into the styptic conditions.

So, we just co-related with the density of the gas and density of the liquid. So, this is ratio of density of the nitrogen gas divided by the density of the liquid nitrogen. So that will give you nothing but, the volume at standard condition and finally, this is your accumulative pore volume. So, volume that is when, to have total nitrogen, which is dissolved that the gas molecule or absorbed molecule, which has dissolved from the surface as a function of p y p z, which, I have shown before. So, this is a kind of accumulative product. So, 0 to 9 to 112 so that is the total volume of the gas dissolved and you can plot it, so that when you can have a delta V from here as a function of for radius r p which you have seen.

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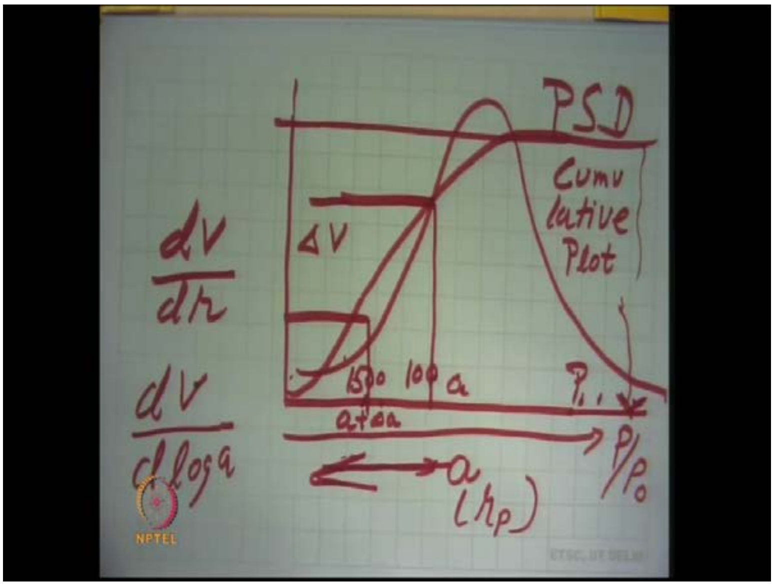

So, delta V upon delta r, which I was talking a pore side distribution. Now, you can have a plot from this, which can be in terms of d v over d r between two successive pore radius and this can be as a function of pore size as I said earlier also, this can be a function of pore radius which I am talking here, a or r p total pore radius. So, this is between two successive pore radiuses. So, where if I am talking a pore side distribution, which is related to your p y p 0 if you look at here. So, this is your pressure which is higher on this side.

So, where the smallest pores are also filled and this so that time it will give a total pore volume and that will be you are the smallest pore, which I have been filled and starting from the largest pore. So, first largest pore gets fills and then, the small one. So, a desorption takes place first, when you talk from the largest pore, because it is related to the radios, the vapor pressure in a small pore so that will fill first. So, pore filling is first in the small pore and then, when we look at desorption and again, it will be because it is universally proportional to the radius of the capillary.

So, the pressure is released. So, immediately the pore will get vacate and that is the reason, you get a kind of hysteresis during this. So, this d v upon d long, what we are saying will give you accumulative pore side distribution I am sorry, this pore side distribution, this is a pore side distribution.

So, getting back just take this to delta V, you just take to delta between 2 cos running radios and you can take this or sometimes you will see it like this also, d v upon d of log of a.

So, if I just plot it like this, pressure I can have p by p 0 values also or just as function of pressure and then, if I am writing pressure increasing in this. So, probably the radius will go in this side. If your radius is increasing in this side then, pressure will come here about the highest pressure means, the smallest pore side, so that means, if I am just talking accumulative pore 0, pore volume, then it will go again something like this. So, it will go like this, something like this, so that is the total pore volume if I write and that is a pore volume distribution.

And this is something like you had the largest pores that are filled, so that is in that case the all pores are filled here. So, this is the highest pressure and here, the pores are smallest pore. So, this is total pore volume, that all the pores are filled from this point to this point and when I say accumulative pores side this is your accumulative pore side distribution that is cumulative plan related to the pore value but, this one is the pore side distribution. So, this gives you the idea between 2 radii if I write like this. So, this is your as I said this is the smallest pressure. So, this is the pore larger.

So, this will be a plus delta a here and this is a. So, this that is between two radii a and a plus delta a, what is the pore or you take volume of the pore which you have just filled t. So, total pore volume between 2 radii if I just say that, suppose this is your 100 Armstrong and this is your 1500 Armstrong. So, I can have the idea that, between 2 pores, 100 and 1500 Armstrong, what is the volume of the pore which got filled and that is your delta V.

So, this will manage your pore size distribution in a catalyst. So, whether in a catalyst you can have a just narrower pore size distribution or just like a zeolite catalyst you see and molecular catalyst you see, it can be wide pore size distribution like a different kind of activated carbon material or aluminum materials. So, valid pore size distribution. It may have only the micro pace like in zeolite micro pore or sometimes it can only the macro pore which is nothing but, between the particles, so that the particle itself, one particle if I look at fine particle that may be a non-porous material but, but when you make a pallet from that. So, the is nothing but, the pore space between the particle, so that will the kind of macro code and depending upon the pressure as I said, when you make a tablet from that you apply the pressure.

So, depending upon that pressure you get different kind of pore size distribution. So, the molecular seeds are excluded, generally where we want that the pores should be sufficient, it should have large surface area. So, recommended is that you draw, it you make the excluded rather making a pallet, because the excluded will have larger porosity then, the problem is that you have to balance it between porosity and the strength mechanical strength pallet, because the excluded may not hold that larger pressure space in a fills reactor or when you are ((Refer Time: 11:16)) activation of the particle mirror.

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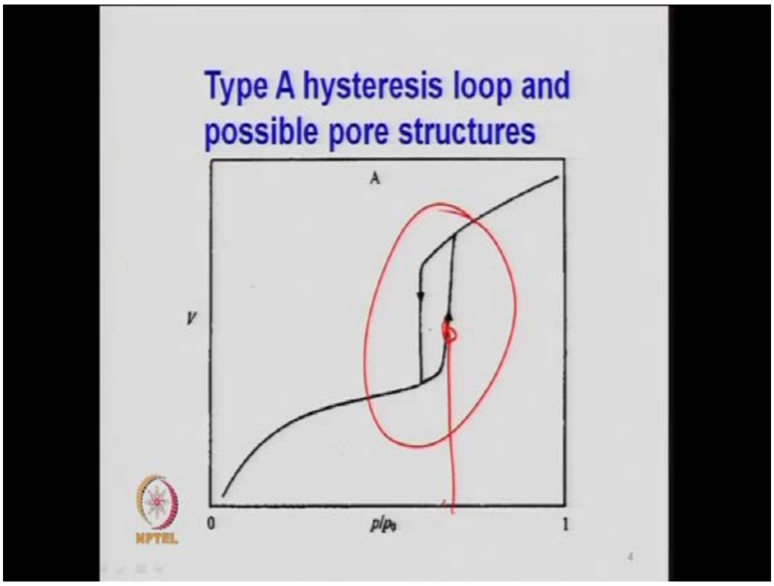

Type A hysteresis loop and possible pore structures

So, these things are has to be here. So, again I was talking a kind of hysteresis also, now you can have some idea, why hysteresis is formed the that is what we talked that, the because of the pores may not be closed from an end the pores are open from both end because the hysteresis will not get when the pores are split cylindrical and placed from one end, because ((Refer Time: 11:49)). So, basically the meniscus formation is related to the hysteresis.

So, when there is formation of meniscus hysteresis will not form but, when there is delay in formation of the meniscus depending upon the shape of the pore then, you may get the hysteresis. So, what is the meaning of hysteresis.That is related to the Kelvin equation. So, when you are applying pressure, absorption is taking place. So, the lower pore will fill first or whenever the capillary which is smaller size, that will get filled but, a larger one something like ink bottle old fashion ink bottle upon if you look at the larger pore may not get.

So, when that desorption takes place? What will happen? Because you know that desorption is again, when you are releasing the pressure. So, at the same pressure, what is the adsorption take place when, the condensation start the molecule may not leave the surface. So, it is stable you have to make it unstable so that raises of the net has to be unstable for relieving the gas molecule. So, you may relieve the pressure more and you have to release the pressure more than desorption will start.

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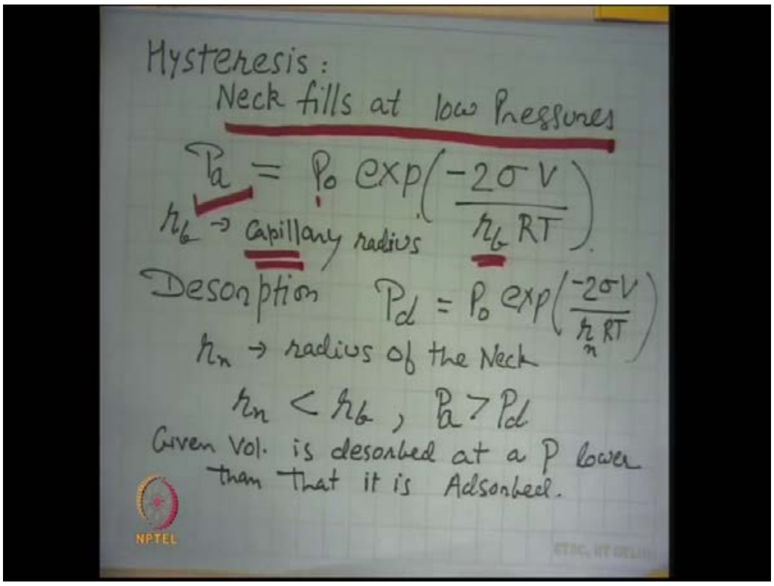

Hysteresis:

Neck fills at low Pressures

$$P_a = P_o \exp\left(\frac{-2\sigma V}{r_b RT}\right)$$

$r_b \to$ Capillary radius

Desorption $$P_d = P_o \exp\left(\frac{-2\sigma V}{r_n RT}\right)$$

$r_n \to$ radius of the Neck

$r_n < r_b$, $P_a > P_d$

Given Vol. is desorbed at a P lower than that it is Adsorbed.

So, that is the reason of hysteresis. So, what we have talked last time also, I am just showing this slide for hysteresis formation, which is similar to that, what we discussed that is the neck fills at the lower pressures then, you have a narrower area narrower volume, narrower radius of the that neck or pole then, the conversation will start in a smaller pore first that is what I said. So, this is related to our Kelvin equation, this is the same equation.

So, this is the pressure required for absorption in a pore is equal to whatever the saturation pressure time’s exponent or minus 2, sigma V divided by r b RT. So, this is your Kelvin equation. What we have seen earlier in terms of log scales so that time it was log of p y p zero is equal to minus two sigma V r upon r 2, V is the volume of the liquid at job r b is the radius of capillary. So, this is P, a adsorption pressure, which are related to your radius of that capillary. Now, when there is desorption.

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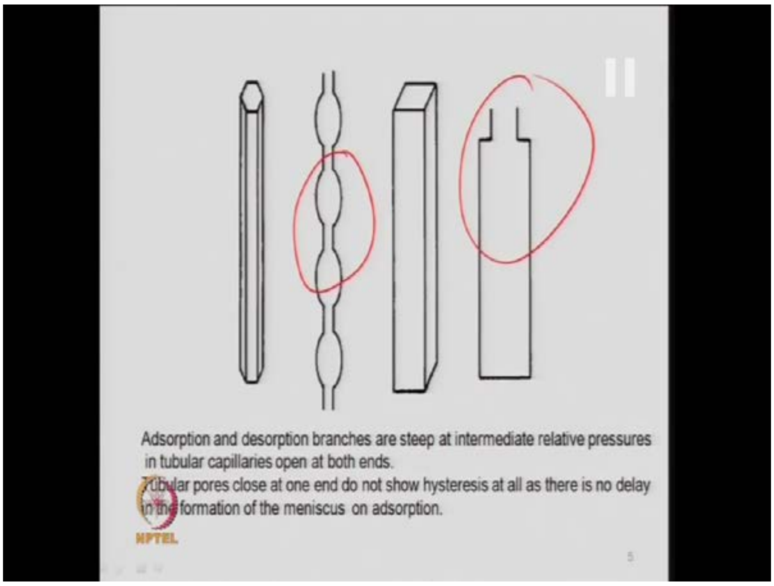

Adsorption and desorption branches are steep at intermediate relative pressures in tubular capillaries open at both ends.

Tubular pores close at one end do not show hysteresis at all as there is no delay in the formation of the meniscus on adsorption.

So, desorption will take place smallest pore and the bulb has the larger size volume is larger, that I am talking just like a ink bottle at this kind of system here, this something like this or it can be like this, also say something like this and this pores are open from both ends. So, problem is in terms of meniscus formation, which will form easily in the case of the closed end port that is a kind of wetting the surface, because we are talking contact energy is 0.

So, affects the surface. So, meniscus forms there. So, here this is the pressure for adsorption and then, desorption starts. So, you will write the pressure required for desorption P, d and this pressure is again equal to this same equation, that is P, 0 e x p minus twice sigma V upon r n and RT not, because of desorption is will take place from the neck, first the pores are filled, when the adsorption has taken place. So, because of the neck have lower radius and the lower percentage this larger radius.

So, it means, desorption will take place in this according to this equation. Now, this neck radius is less than the bulk radius or the actual pore radius. So, this is what, the radius of the neck r n is less than r b. So, what will result, the pressure for adsorption is higher than desorption. So, you will pressure just take the ratio. So, adsorption required, the pressure will be higher to adsorb a given volume but, when you want to relieve that volume, we need to release a pressure to a larger extent.

So, what does it mean? This symbolism is that at the same condition of pressure here, if I just look at this point, this was the pressure required for adsorption where the volume adsorbed is this. Now, here when the desorption started at the same pressure, when larger volume had dissolved or to relieve the same volume a lower pressure will be required, if I just look at this point which is equal to the same volume this much pressure will be required.

You have to release the pressure and this is that called either the ink bottle effect, because of the ink bottle effect, it can be lowered the structure also, it can be the reason that pores are open from both end not state cylindrical for all kind of complex genetic pore can be looked into once you have this desorption once again. So, by having this plot that is pressure or volume versus P by P 0, you can have the information in terms of this hysteresis adsorption hysteresis what you call.

So, given volume, which is here is dissolved at a pressure lower than, that is absorbed, that is what you call the adsorption hysteresis. So, that can be a b c d e different five types of adsorption from hysteresis have been absorbed experimentally depending upon the type of solid material. So that what I said that, the structure will be of different nature hexagonal like this, it can be this ((Refer Time: 17:39)) channel and it can be ink bottle type but, ink bottle also here, that this radius is length is larger compared to this net length, there can be a different kind of hysteresis in the other system.

So, what I have just described is here, that adsorption and desorption branches are steep at intermediate relative pressures in tubular capillaries open at both ends that, this what you have seen type A, it is somewhere at the intermediate that it can start from here, also in some of the materials, that we that is known as type B type adsorption hysteresis. So, which are open from the both ends, because this comes at an intermediate pressure, where the hysteresis is absorbed the tubular pores closed to one end, do not show hysteresis at all as there is no delay in the formation of meniscus on adsorption. So, this desorption is related to the counter structure, which is found in the hill. So, when there is a pore, which is closed from this end.

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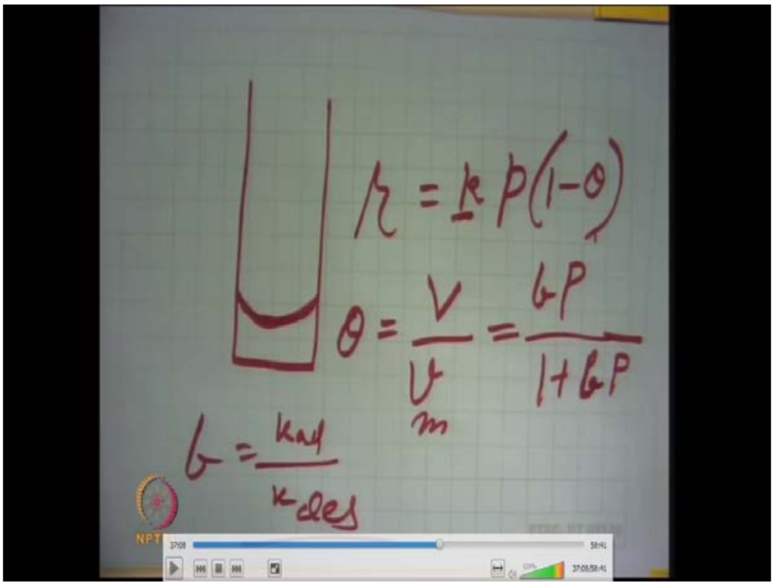

$r = k P(1-\theta)$

$\theta = \frac{V}{V_m} = \frac{bP}{1+bP}$

$b = \frac{k_{ad}}{k_{des}}$

So, you will have a kind of meniscus but, in open, you do not have this kind of meniscus to lose in that, because that is the reason, that you do not get if the pores are closed from one end you will not get any hysteresis.

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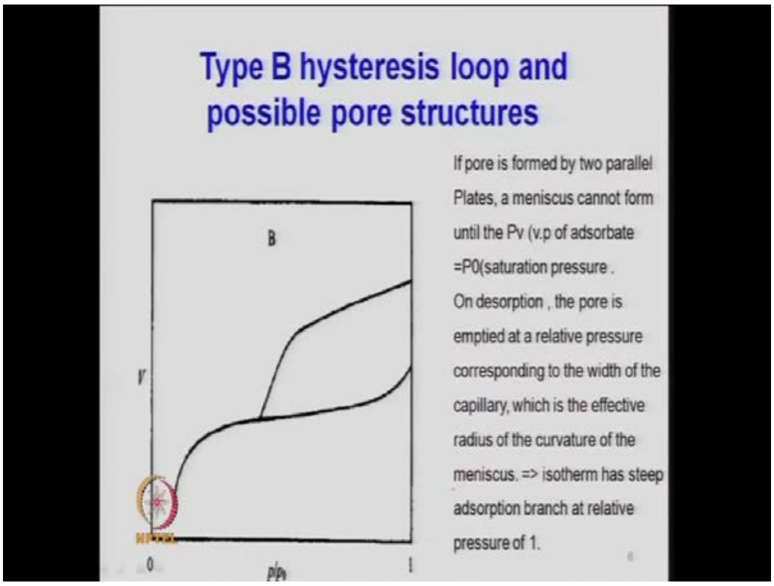

Type B hysteresis loop and possible pore structures

If pore is formed by two parallel Plates, a meniscus cannot form until the Pv (v.p of adsorbate =P0(saturation pressure . On desorption , the pore is emptied at a relative pressure corresponding to the width of the capillary, which is the effective radius of the curvature of the meniscus. => isotherm has steep adsorption branch at relative pressure of 1.

This is another type b, that you can see, it is released to the saturation pressure higher, that is PYP0 press to one and then, the hysteresis is formed well in that case and in this case, it was the intermediate, it is an intermediate point so that is exponential and this will be same in this kind of structure layered structured.

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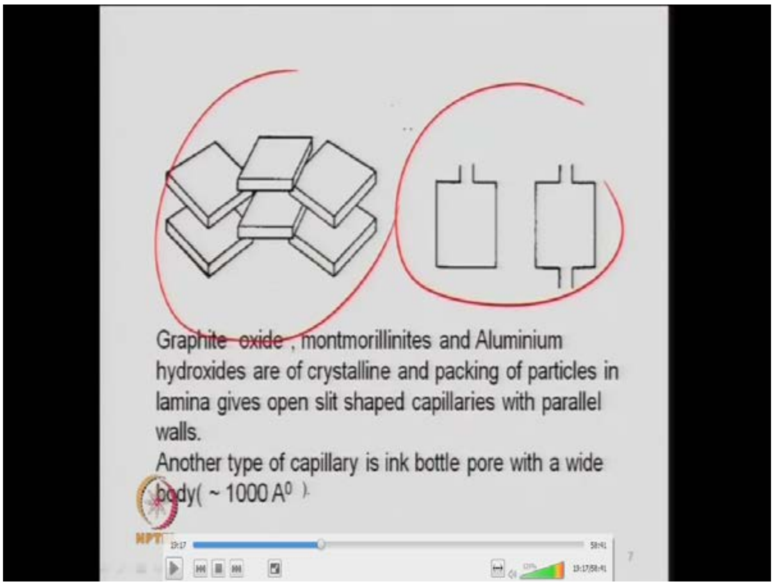

Graphite oxide, montmorillinites and Aluminium hydroxides are of crystalline and packing of particles in lamina gives open slit shaped capillaries with parallel walls.

Another type of capillary is ink bottle pore with a wide body(~ 1000 A^0).

If the pore is formed by 2 parallel plates like ((Refer Time: 19:25)) type, meniscus cannot form until the vapor pressure of the adsorbed is equal to saturation pressure, you have to go to the high pressure with the, because it is a steep type structure. On desorption, the pore is emptied at a relative pressure corresponding to the width of the capillary which is effective radius of the curvature of the meniscus. So, this kind of width of capillary is equivalent to the equivalent radius of the capillary not the gap. So, width at the capillary, which is effective radius of curvature of the meniscus. So, this simply results, the isotherm has steep adsorption branch at relative pressure of one here, something like this, the reason for desorption is that the meniscus formation is delayed.

So, and at it goes to the saturation pressure PYP01. So, what I mean to say, depending upon the type of material, you can have the different kind of complex between the pore structure for results what you say. So, the pore side distribution or the hysteresis of that. So that is again you can see here, this gap is also wider so that means, when it reach to the saturation pressure and if you look at the two cos ((Refer Time: 20:48)) pressure here and here, if I just look at the same volume significantly high pressure deduction is required, we have to release the pressure to a significant low level then only the desorption will start.

So, and the results the adsorption layers may not be correct in terms of kelvin radius, because desorption is related to the capillary condensation and the terms that desorption takes place. So, generally the correct results are from desorption, when you calculate the values of surface area pores side distribution then, desorption values are taken as a finite results. So, all these materials like graphite oxide, montmorillinites, clay type structures, aluminum hydroxides are crystalline and packing of particles in lamina gives open slit shaped capillaries with parallel walls. This type of structures will have with type B adsorption hysteresis like desorption similarly, the ink bottle pore with a wide body, which are more pore side wider than that is 1000 Armstrong approximately then, also you will have a kind of those hysteresis.

So, this structure is different, when compared to the first one here, the structure. So, this 1. So, here this is very large and this are relatively low compared to this case or it is larger. So, the hysteresis will depend on these kinds of structures and geometry so that is the case of physical adsorption. So, you have seen the milky surface area and the determination of the pores side pores volume thickness of the layer, absorbed layer, adsorption hysteresis based on the nitrogen, adsorption, desorption, isotherm and that is the case of physical adsorption.

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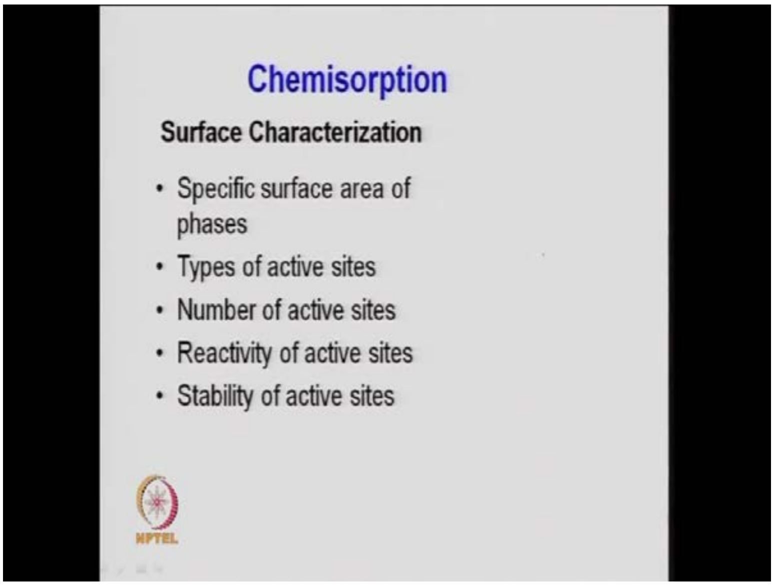

Chemisorption

Surface Characterization

- Specific surface area of phases
- Types of active sites
- Number of active sites
- Reactivity of active sites
- Stability of active sites

That just talks about the textual property of the catalyst morphology, there are some other methods by which we will talk on that morphology can be evaluated in terms of spherical shape and particle size or the crystalline size crystalanity. So, there are other methods also, which will talk on that based on the let us say destruction patterns and here now I am talking the chemisorptions.

So, it means some reactive gas which comes and absorbs on the surface of the active metal. Now, so far the adsorption throughout the surface, whether there is the active metal or not, adsorption will take place, because it is the condensation of the gas molecule as you said that it is the physical adsorption. Here, what we are talking, this is stress in nature, only a reactive gas which a type of reactive gas will adsorb specifically on a surface, which is active for that gas otherwise there will be no adsorption. So, this is what I said that, chemisorptions require the higher amount of activation energy compared to the physical adsorption that you have listened.

But, this is very important tool for the determination of the chemical behavior of the catalysis and that is related to your catalytic activity, you can have the same reactive gas also which is being used in the reactor for further investigation can be used as a chemisorptions study also, turn over frequency, turn over number we should determine based on this study. So, this case should have specific area of the quizzes. Now, I am saying, because it is a chemical adsorption. So, specific surface area of that crystal which is active from the reaction, not the physical adsorption physical adsorb surface area maybe very high 220 meters per gram but, this area just may be ten meters square per gram or 5 meters per gram.

Also gives you the idea about the active phase. So, which phase is active during a catalytic reaction, you can get the information from this, you can just make different catalyst you can just give the different plain and then, look at the adsorption property. Then, number of active sites, that is you are the ((Refer Time: 25:14)) dispersion and then you calculated turn over frequency. So, you can get the number of active sites, reactivity of active sites can do that chemisorptions at different condition of temperature and then, you can talk on the reactivity also and you can calculate activation energy also from this ((Refer Time: 25:33)) study.

And the stability of the active sites, which is again important for the catalytic activity, that stability of the catalyst or for how much time the catalysts can be used or after resonation it can be recycled back into the system. So, this kind of investigations maybe made or can be termed from this chemisorptions study.

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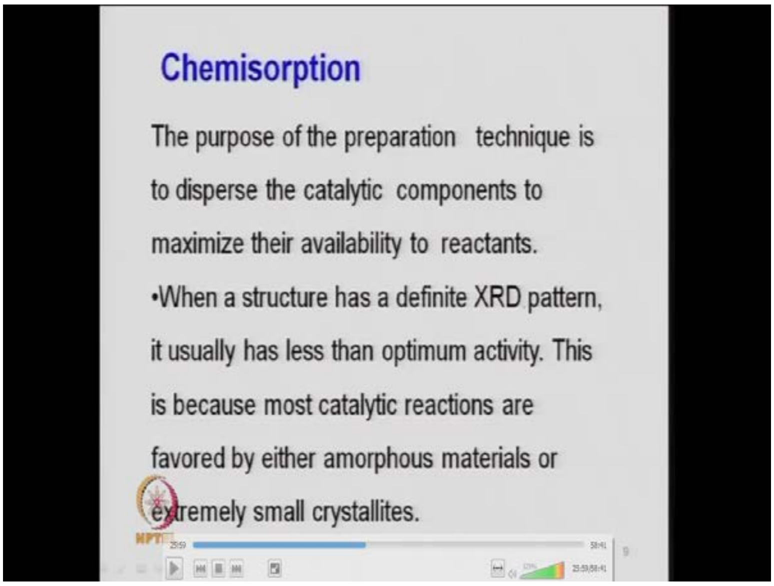

Chemisorption

The purpose of the preparation technique is to disperse the catalytic components to maximize their availability to reactants.

- When a structure has a definite XRD pattern, it usually has less than optimum activity. This is because most catalytic reactions are favored by either amorphous materials or extremely small crystallites.

So, what are chemisorptions? All of you know but, quickly I have discussed this thing earlier that the purpose of these chemisorptions pack may is to disperse a catalytic components to maximize their availability to reactants. So, when you prepare a catalyst here aim is to have high dispersive of the matter. So, matter disperses on the surface on the solid. So, how good or how bad they are distributed on to the support that is the first information, you can get from chemisorptions.

So, we want to maximize the availability of the metal species for the reactant and you know the end or you should learn this also, highly crystalline metal menu may not be good and before ((Refer Time: 26:49)) gives large number of p’s but, that is being, that is good for catalytic activity. You need to have a fine disperse particle, when there is small particles crystallites and nano particles and that may not be digit ((Refer Time: 27:02)) from the ((Refer Time: 27:05)) and that maybe very good for the catalytic activity.

So, this is also important, when a structure has a definite XRD pattern, it usually has less than optimum activity, because we need more and more defects on the surface to have a good catalytic activity as structure. So, not necessary that the metal is crystalline for a good catalytic activity, it can be amorphous also. So, you know that, this is because most of the catalytic reactions are favored either amorphous materials or extremely small crystallites. So, if you are developing the crystal the crystal size should be as small as possible and then, you have a small crystal size then they may not be detected by that

((Refer Time: 27:50)). Crystalline materials may not be good or degree of crystanality may not be related to the catalytic activity.

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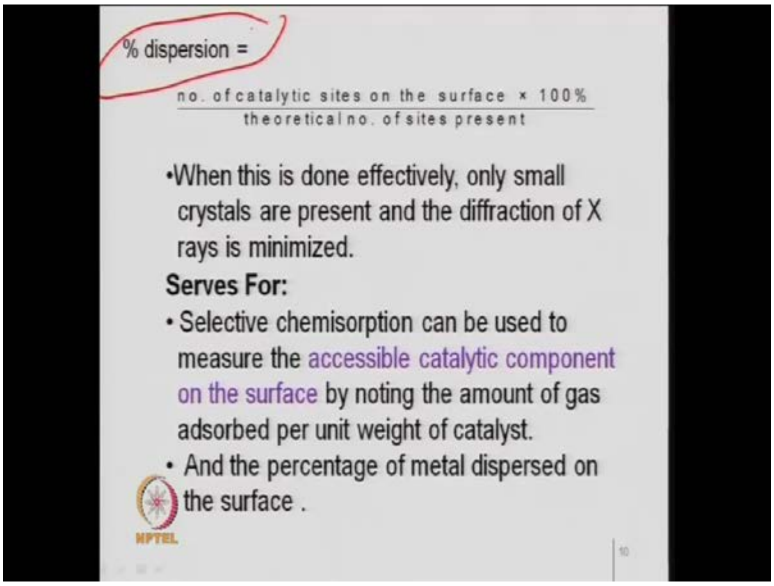

% dispersion =

$$\frac{\text{no. of catalytic sites on the surface} \times 100\%}{\text{theoretical no. of sites present}}$$

- When this is done effectively, only small crystals are present and the diffraction of X rays is minimized.

Serves For:

- Selective chemisorption can be used to measure the accessible catalytic component on the surface by noting the amount of gas adsorbed per unit weight of catalyst.
- And the percentage of metal dispersed on the surface .

So, we talked dispersion, which are already defined at number of active sites on the surface, divided by the theoretical number of sites, which are present on the total number of sites which are ((Refer Time: 28:12)) the theoretical means, you have calculated for the preparation of the catalyst, you have to pertain the person a platinum on alumina. So, this you know that, that should be the theoretical represent and also should be confirmed by some catalysation method like atomic adsorption spectroscopy or in the two coupled plasma r c p technique.

So that will give you the actual number of the metal which is present on the catalyst. So, one is from your initial calculation but, during the heat treatment there may be some loss to get it concerned from chemical methods. So, r c p is one atomic adsorption spectroscopy or u v spectrophotometer can be used. You can find out that is your theoretical metal concentration. Actual concentration now, it will be which is related to the catalytic activity and from chemisorptions.

So, this number of active sites on the surface is actually the sides which will be responsible for catalytic activity. So if you are 100 metal species on the surface, 100 atoms out of that 10 may be available on the surface and this 10 will give you the catalytic activity, remaining 90 is a waste. And that is why, the atom efficiency what we talked in the concept of green chemistry becomes important when you look at the catalyst preparation.

So, instead of having hundred percent of the platinum, try to have 0.5 percent of the platinum with more than 90 percent. This percent or more than 70 percent the percent is present, that should be your target that good efficiency from the small concentration which is used and ((Refer Time: 30:00)) height should be active for the catalytic reaction. So, dispersion becomes very important and this is based on the turn over frequency also from this you calculate the turn over frequency that is the number of molecules which are reacted per unit time and per unit active side, which is available on the surface. So, you can put dispersive here, total number of side where, the type of dispersion will not be on the other side, which are at the surface.

So, if you have done that effectively and the dispersion is good on a small crystal are present and the diffraction of X rays is minimized. So, the particles are finally, dispersed your particles are of the order of the nanometers small, the crystallite side their better disperse external will not detect that, all the specially may not detect it either because of low concentration or because that, the crystallite side is. So, small, because wavelength is important for that. So, the ray, what is the wavelength of that and then, accordingly you can calculate that.

So, when you have this. So, selective chemisorptions can be used to measure the accessible catalytic component on the surface that is dispersed by noting the amount of gas adsorbed per unit weight of the catalyst. So, it is similar to your physical adsorption here, the only thing that now you have a chemically reactor gas. So, this will absorb only the active sides of the surface. So, how may molecule of those gas species or that gas species is absorbed on the surface, the volume of that gas can be measured and that volume can be related to the number of atoms and you know the atom area. So, you can find out the surface area.

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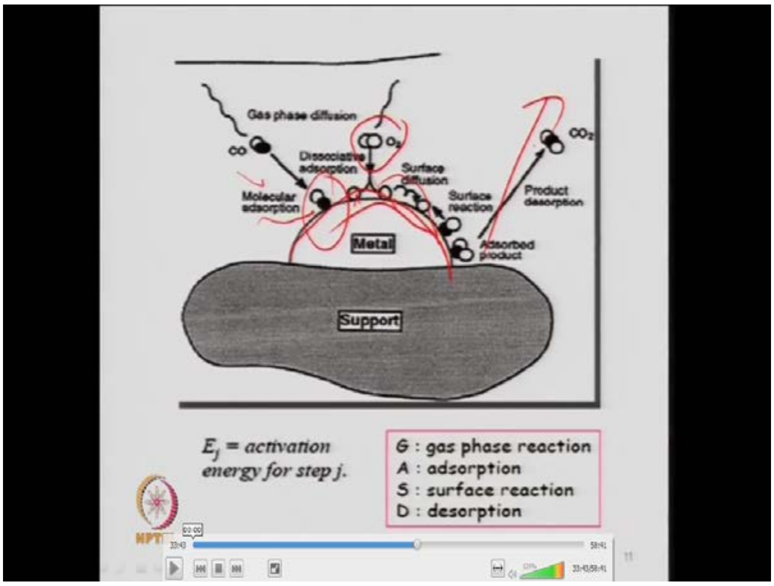

E_j = activation energy for step j.

G : gas phase reaction
A : adsorption
S : surface reaction
D : desorption

So, percentage of matter dispersed on the surface can be found out. So, when you look at chemisorptions, it is a kind of chemical reaction mechanism, which we will see in detail later but, this is a support on this the metal has been deposited like this, it is a metal and then the gas is ((Refer Time: 32:11)) which maybe hydrogen, which maybe carbon-mono-oxide or carbon-di-oxide or nitrogen oxide and to any gas can be a reacting gas. So, gas phase diffusion like COH coming here like this and this is what, we have shown in molecular adsorption.

So, I will talk of that later also, the same molecule SH is absorbing on the centroid maybe dissociative also. So, a combined molecule of carbon-mono-oxide this absorbs on the surface, if it is dissociative then, it could be something like that carbon-mono-oxide will split, first and then, it will two more to carbon and oxygen and then, they are absorbing just like in case of oxygen it is shown here.

So, oxygen is splitted into two. So, one oxygen here and one oxygen here, like splits on the surface, if I talk in terms of sites covering two sides, two active sides and then, they are migrating onto the surface, because to have the catalytic activity, these molecules have to be mobile on the surface. So, this is because of the surface diffusion phenomenon like this and then, this is the chemical reaction at the surface product forms and then, desorbs.

So, this crystal is still up like a chemical reaction where, just you can talk see oxidation. So, you can find out this, that is why the actual mechanism depending upon the temperature, because this will be a function of temperature. Different condition of temperature, how many molecules are reacting and then, you can calculate the activation in the chemisorptions.

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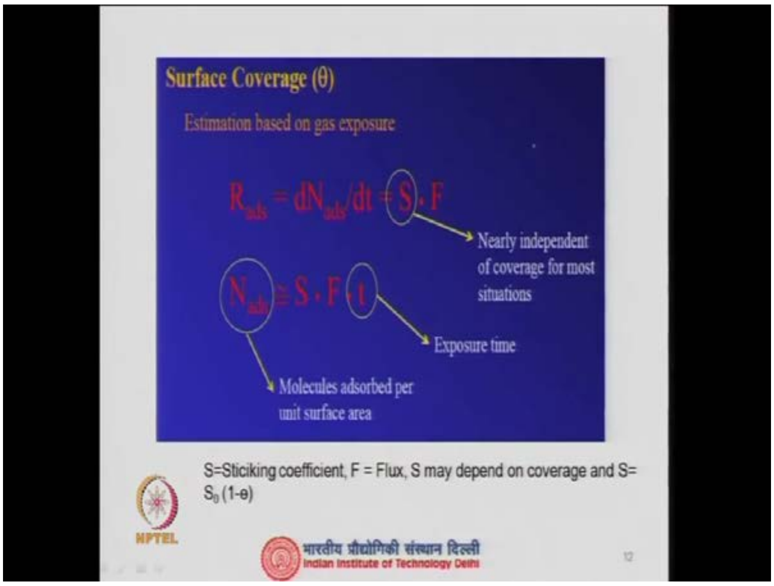

Surface Coverage (θ)

Estimation based on gas exposure

$R_{ads} = dN_{ads}/dt = S \cdot F$

Nearly independent of coverage for most situations

$N_{ads} \cong S \cdot F \cdot t$

Exposure time

Molecules adsorbed per unit surface area

S=Sticiking coefficient, F = Flux, S may depend on coverage and S= $S_0(1\text{-}\theta)$

Here, now I am talking just a graphitization of the chemical reaction like, what I have shown before, that is the rate of adsorption, you know that ((Refer Time: 33:56)) d on by d t the number of molecules which absorb on a surface and that is related to some s sticking coefficient and times the flux. So, F, now already said earlier, we have already seen the calculation for F, which is just nothing but, under one upon under root of two pi m k be key some into p. So, pressure related.

So that is in general, you write your rate of adsorption r is equal to k rate constant, adsorption rate constant times bar, say pressure and times the suction of the surface which is getting. Same thing I have written here, now only thing that sticking coefficient s generally is given, we have assumed here almost independent for most of the case sticking coefficient but, generally decrease with the surface coverage like this. So, as theta one minus ((Refer Time: 34:53) and this flux F is proportional to the pressure P under root up to pi n k b t, that we have seen last time in the flux calculation. So, in general you calculated like this. Now, if you just intimate this equation is here through here that is S into F into t. So, I was talking the exposure time earlier.

So that is also important, it means your adsorption will depend or chemisorptions will depend, what is the flow rate of that gas, number of molecules, which are coming onto the surface and for how much time. Time of exposure is also equally important so that is the total number of molecular surface will related to the sticking coefficient or probability of sticking and the flux multiplied by the exposure time. So that, this is the idea of the surface coverage or chemisorptions, that is the reaction, number of molecule which adsorbed.

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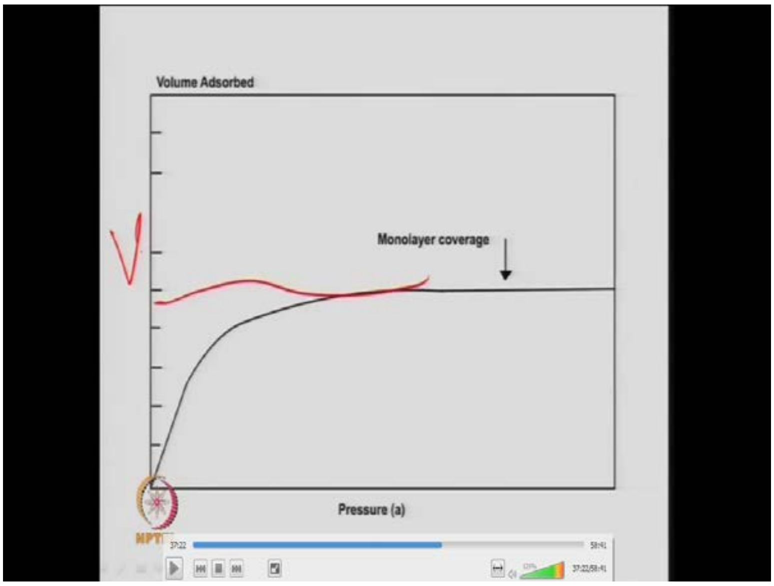

So, once you have that, that is the volume adsorbed as a function of pressure ((Refer Time: 36:00)) absorbed during that, we already talked that, because line man isotherm talks in monolayer coverage. So, this is a kind of monolayer coverage here in this case. So, here, it is the volume of the gas absorbed as a function of pressure and you will have something like V P upon 1 plus B P, last time that we talked or K P upon 1 plus K P per capital K P per that adsorption equilibrium constant, rate of adsorption is equal to rate of desorption.

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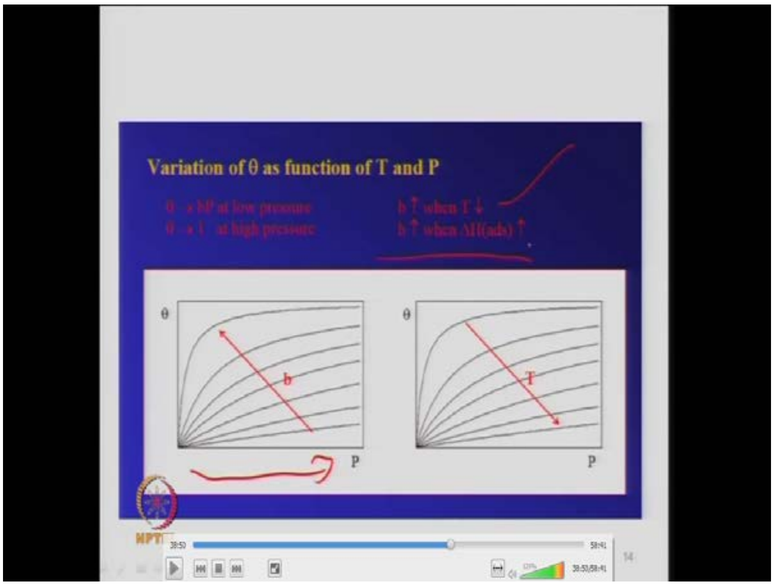

Variation of θ as function of T and P

$\theta \approx bP$ at low pressure
$\theta \approx 1$ at high pressure

b ↑ when T ↓
b ↑ when ΔH(ads) ↑

So, this is a function of temperature and pressure, just like in the lineman equation you have seen. So, lineman equation, we have seen last time theta related to v by v m and known on their coverage and that ((Refer Time: 36:47)) K P upon 1 plus K P or b p upon 1 plus b p where, b is the adsorption equivalent constant, we simply p adsorption divided by k desorption thing. So, this equation has been used and. So, always there will be a monolayer, when you are talking chemisorptions no multilayer will form. So, there is a monolayer but, this will be a function of pressure.

So, partial effect will start from here anyway. So, this is already shown here, that is the theta, the rate of adsorption increase with pressure that is the first thing from this equation adsorption in case with pressure. But how this b which is the adsorption equivalent constant, also how does it affect the adsorption, that is also if you have increasing the k value or equilibrium constant for adsorption or small b which is simply your adsorption equilibrium constant.

So, increasing your surface coverage and increase suction of the surface cover increase. So, rate in the formal direction is increasing in one way. So that is the equilibrium constant is high then, your surface coverage will increase. It is exothermic most of the time the consumption exothermine. So, it is always decrease with temperature. So, this is the effect of temperature.

So, b increase when temperature decreases and b increase also when heat of adsorption increases. So, heat of adsorption can be calculated from ((Refer Time: 38:35)) Capron equation. So that can be used to determine the heat of adsorption. So, heat of adsorption, if b is higher, heat of adsorption will be higher that k d over d t of l and k is equal to delta upon r t square that is equation that can be co-related with this.

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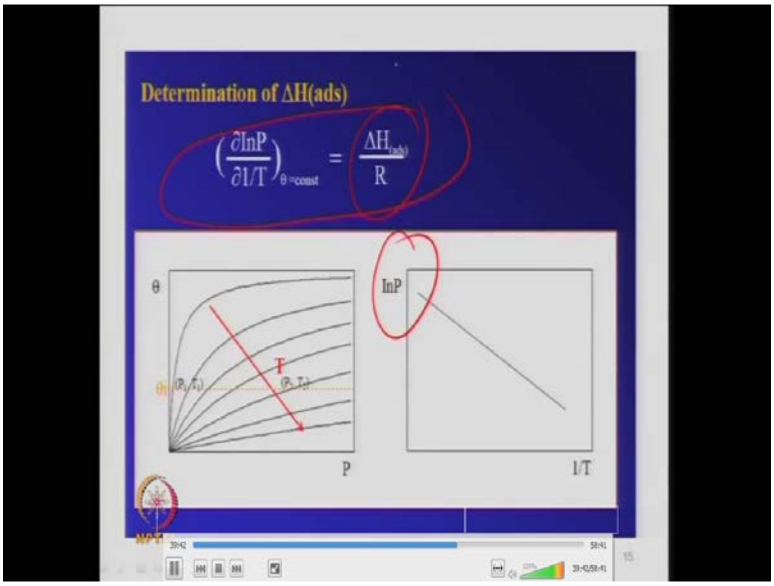

Determination of ΔH(ads)

$$\left(\frac{\partial \ln P}{\partial 1/T}\right)_{\theta=\text{const}} = \frac{\Delta H_{(ads)}}{R}$$

So, this is what I was talking ((Refer Time: 38:59)) Capron’s equation. So, del over or del l n P of divided del of 1 by T at constant coverage is equal to delta H adsorption divided by R if you get this, you can just simplify the equation in own type of equation or this equation is nothing but, d over d t of l n P 0 minus delta h upon r t square, that equation is known to you.

So, this equation co-relates, the heat of adsorption or can be used to calculate the heat of adsorption. So, a plot of log plot of l n P versus 1 by T, will get a straight line and from that we can find out the heat of adsorption this ((Refer Time: 39:42)) to yourself. So, you can very easily find out this and as a function of pressure and temperature different pressure, different temperature, you can have the surface value. What I mean to say by using the chemisorptions study you can find out the heat of chemisorptions or the heat of adsorption, you can find out the effect of chemical reactive gas as a function of pressure or temperature, which can be used for further investigation in the reactor.

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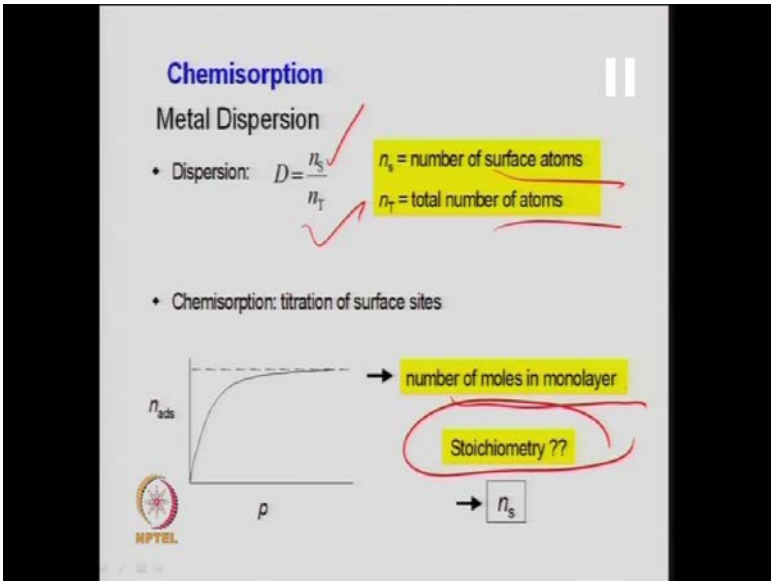


Chemisorption

Metal Dispersion

- Dispersion: $D=\frac{n_S}{n_T}$

n_s = number of surface atoms

n_T = total number of atoms

- Chemisorption: titration of surface sites

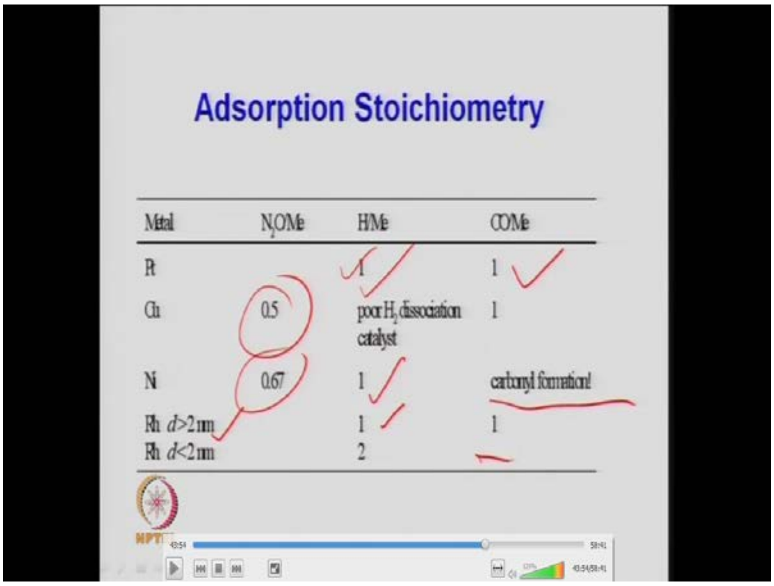
→ number of moles in monolayer

Stoichiometry ??

→ $\boxed{n_s}$

Initial investigation can be done in a micro reactor and then, go in a larger reactor. So, dispersion we have talked, fractional dispersion number of surface atoms divided by total number of atoms percentage, that we have multiplied chemisorptions; we have seen which can be determined in touch of volume or in types of number of molecules. So, molecule adsorb as a function of pressure, the number of mole in the monolayer can be calculated provided you know the stoichiometry. So, stoichiometry means, whether it is associative chemisorptions or dissociative. The hydrogen adsorb dissociative on most of the surface. So, it means if hydrogen one molecule of hydrogen you are taking, it splits into two atoms and then, it will cover on two metal sides. So, one hydrogen molecule will take two sides of that map plat ((Refer Time: 41:00)) I suppose.

(Refer Slide Time: 43:54)



Adsorption Stoichiometry

Metal	N_2O/Me	H/Me	CO/Me
Pt		1	1
Cu	0.5	poor H_2 dissociation catalyst	1
Ni	0.67	1	carbonyl formation!
Rh d>2 nm		1	1
Rh d<2 nm		2	

So that is the stoichiometry here, these are defined or can be calculated on different metals say platinum say hydrogen one at stoichiometry one which is written here in terms of determination of this adsorption, that we are calculating the number of molecules, which adsorb on the surface and if imam saying that one molecule of nitrogen or hydrogen absorbed disassociatively. It means the number of sides one molecule of the gas has absorbed. It will cover two platinum sides, it means the total number of molecules if I am calculating hydrogen absorbed, I multiplied to find out the number of platinum sides on the surface so that is the meaning.

Find out the number of platinum sides on the surface. So, the surface area ultimately we are calculating for the metal not for the gas. So, we have to see that, the molecule which adsorb or chemosorb in what way it covers the surface of that species active site so that is what, the stoichiometry and here if you have platinum. So, hydrogen metal hydrogen for hydrogen metal. It is one for cobalt also it is one. So, it is shown here one is to one dissociation.

Copper nitrogen oxide on metal. So, it is 0.5dissociation. So, for hydrogen if you have for this metal copper is there for hydrogen. It is poor hydrogen dissociation on the catalyst, the metal if the hydrogen absorption of copper is poor. So, poor hydrogen dissociation catalyst, then only catalyst hydrogen should not be used.

Cobalt if you have and if you take sorry carbon-mono-oxide gas if you take then, it is 1 is to 1. So, you can absorb 1 molecule, you will absorb 1 copper. Nickel it is roughly 0.67 for n 2 adsorption for hydrogen it is 1, 1 nickel for cobalt it is the formation of carbonyl, nickel carbonyl forms. So, mainly for nickel this should not be used if you are calculated number of active sites.

So, it will make nickel carbon and with that and that has been checked from the X-ray defection. It is only of rhodium, it depends on the particle size also and its diameter is more than 2 nanometer and this is not used for rhodium generally, because it is an oxidation gas, it can be used for treatment but, here the hydrogen it is 1 associative adsorption and then, you take carbon-mono-oxide it is again 1.

For less than 2 nanometer and that is the nano particles of that it becomes dissociation. For this confirmation, it is not ((Refer Time: 43:56)). So, what I mean to say, the stoichemetry should be known on a ((Refer Time: 44:00)) that who whether the adsorption is associated or dissociative so that can be calculated based on the bonded energy or binding energy then, one can have the idea whether, it is associative or dissociative chemisorptions and then, calculate the number of active matters.

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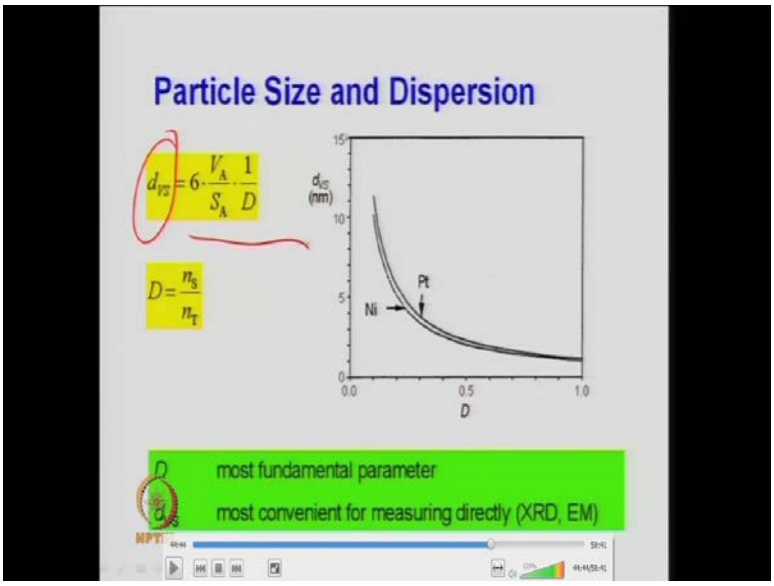

Particle Size and Dispersion

$$d_{VS} = 6 \cdot \frac{V_A}{S_A} \cdot \frac{1}{D}$$

$$D = \frac{n_S}{n_T}$$

D most fundamental parameter

d_{VS} most convenient for measuring directly (XRD, EM)

So, once that is done then, you can find out the crystal size also, there are other methods also for determining the crystal size and exceed a fraction can be used electro-microscopy can be used horizontal ((Refer Time: 44:41)). These are technique by which you can find out the crystal size or particle size and also that can be co-related with this, because you know the volume of the particle simplified by d p by 6 and surface area from particle, because we are talking of projected area.

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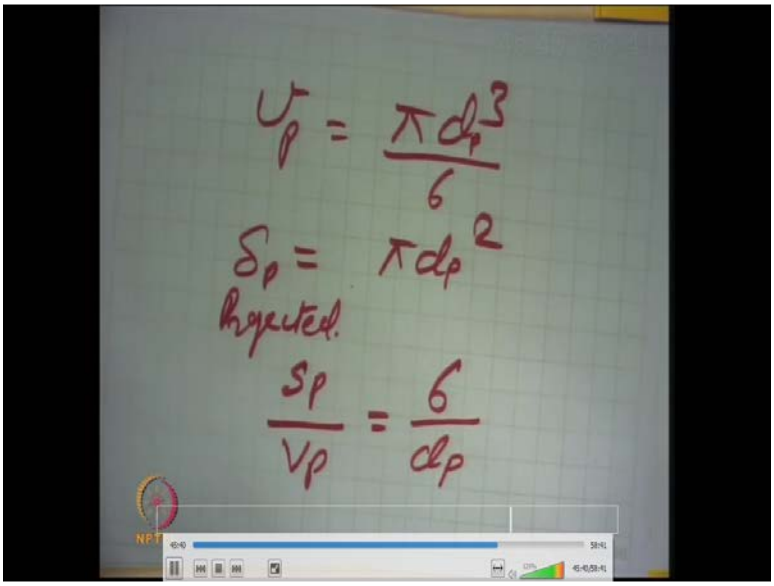

$$V_p = \frac{\pi d_p^3}{6}$$

$$S_p = \pi d_p^2$$

Projected.

$$\frac{S_p}{V_p} = \frac{6}{d_p}$$

So that is pi d p square. So, if you take this 2 ratio. So, your b p is related to your b p volume of particle if I write into pi d p by 6. So, pi d p cube by 6 volume surface area of the particle, I am talking about v t so that is your pi d p square. So, I am talking projected area. So, just if you take the s p by V p. So, this is a pi d p square. So pi d p square divided by pi d p cube and divide it by 6. So, this becomes six upon d p and since, you are talking dispersion number of matters which are expressed. So, we have to give total volume of the all particles and total volume of the surface area of those particles, which are being there and that can be co-related like this.

And dispersion we have already said. Now, if you look at the particles size and dispersion they are inter-related. So, as the dispersion increase, the crystal size decreases. In one way if you are ready to make a nano particles, the particles will have a better dispersion, because it is the enumeration of the particle crystals are enumerated or particles are enumerated, this crystal size is increasing, because of the enumeration.

Only that happens if enumerates then, definitely the dispersion will differ. So, it is the cluster of the particle now on 1. So, gas absorbs only on 1. So, number of sides are number reduced. So that is the reason that you need to look at the well dispersed particles on the surface, large surface area will be helpful in that equation of that kind of support.

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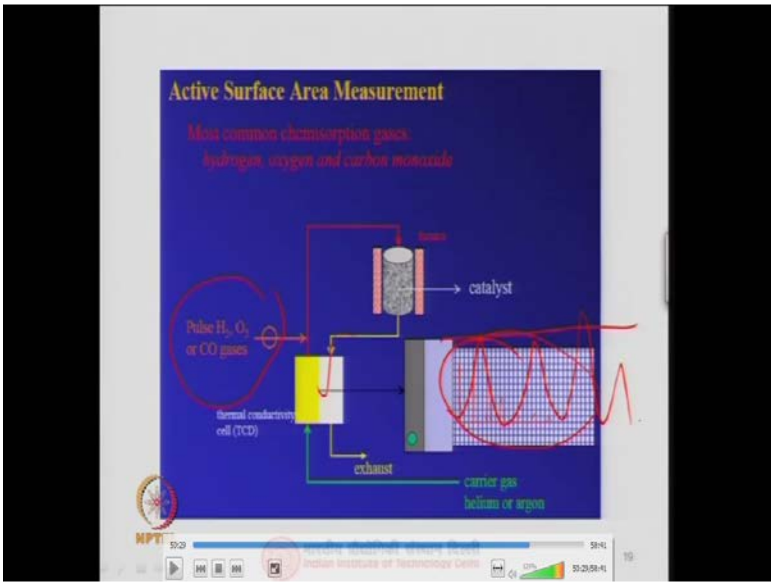

Active Surface Area Measurement

Most common chemisorption gases:
hydrogen, oxygen and carbon monoxide

So, D is the fundamental parameter, which is determined from chemisorptions, d VS can be determined by using XRD and EM also. Type of the setup if look at this is a kind of micro-reactor basically, for which can be used for temperature program reduction and temperature program desorption chemisorption. So, all these kinds of studies can be done, you can take any chemical reactive gas, you can give a pulse through a syringe also you can give chemisorption. So, idea is that you are this after recruitment of the sample, you give and these will a function of temperature.

So, chemisorptions which is ((Refer Time: 47:28)) and at a given temperature, you give the pulses of hydrogen was the catalyst well reduced, these catalysts and give the pulse of hydrogen and then, look at the response how and you have just the data pulsive hydrogen. So, it will chemisorp. So, allow it to chemosorb and then, you stop when you see the chemisorptions is complete, we will see that nothing gets absorbed ((Refer Time: 47:57)) after that.

So, now you just heat the ((Refer Time: 48:03)) gradually and then, just look at the response. So, at different temperature, because the surface matters we have the strong metal support interaction some of the metals which have the strong metal and support interaction they will have weak chemisorptions or the gas. So, they will relieve the gas faster or relieve gas faster.

But there is a tuning between the metal and support. So, the strong chemisorptions with the gas molecule may be there so that molecule will desorbs at a higher temperature. So, by knowing this kind of plots, you can have the idea about the interaction of the metal with the support. So, how many types of the sites which are strongly binded, metal site strongly binded with a support and what number or what fractions are related to the weak binded or intermediate binded, you can have some idea about the metal support interaction or we need to call s m s I, strong metal support interaction metal support interaction.

So, this kind of setup if you look at that you give repulse of any reactive gas, which can be your hydrogen, oxygen or carbon-mono-oxide, that is what general most of the time we assume but, sometime ((Refer Time: 49:20)) can also be used chemisorption and nitrous-oxide. This is your furnace, because it is chemisorptions. So, it can go up to thousand degrees centigrade even 1200 from room temperature, Indian temperature to 1200. So, you can have a program ((Refer Time: 49:32)) temperature ((Refer Time: 49:35)).

Then gas, this is the inlet cell and gas from this comes to a ((Refer Time: 49:40)) basically, it is a TCD type detector here, because all these suspended determined to thermal conductivity detector. So, reference i and vigilance i sample. So, you can have the signal something like this. So, you can have the peaks like this, depending upon the concentration, it may be constant when, metal is chemisorbed or it may decrease as I showed in the actual pressure, because the chemisorptions is taking place, the volume of the gas at the edged will decrease and when, the chemisorptions is complete and then, it will again the same.

So, by adding all these equi edges like this you can find out the volume of the gas adsorbed and this can be in the form of pulse, this can be in the form of stick changes also. This is again the same, it should be this active surface area measurement technique and here this is for catalyst surface area and dispersion calculation.

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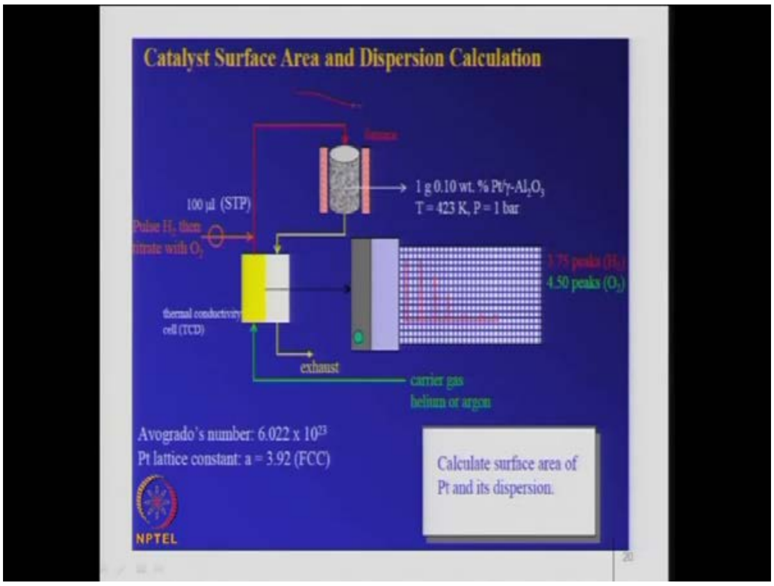

Catalyst Surface Area and Dispersion Calculation

Avogrado's number: 6.022×10^{23}
Pt lattice constant: a = 3.92 (FCC)

Calculate surface area of Pt and its dispersion.

So, basically the same figure. So, you have inducted a given volume at a standard condition and then, may I call it as a syringe that of a gas and then, you have to pass into this and this is measured the signal like this. So, it is constant initially then, it decrease and likewise as I said here. So, you can just leave for the given mass of the samples, one say, one gram which is 100 percent 0.1 width percent of platinum on gamma alumina. So, this is the catalyst and 0.1 percent platinum and gamma aluminum and it is 1 gram mass as the catalyst has been taken and heated at 423 Kelvin, that is adsorption of this hydrogen and 423 Kelvin.

And then, you can find out the area of this peak. So, which is written here, 3.75 (( )) hydrogen, 4.5 peaks of oxygen so that is for different gases. So, pulse with hydrogen then, ((Refer Time: 51:48)) with oxygen. So, how many molecules of hydrogen have been consumed during the process you can find out. So, basically, either this or these are connected to the software and then, you can directly you can find out that volume of the hydrogen consuming gas, which adsorbed on the surface. And once that is known. So, you know this, that 1 gram molecule of the gas of the standard condition have 6.032 into 10 by 23 molecules 1 gram of the gas has dismissed number of ((Refer Time: 52:19)).

And. So, there are some factor packing factor as I was talking earlier also, that is constant. So, generally that is not required at but, basically name the number of molecules and volume the same principle, same formula what we have discussed earlier, that is the surface area, earlier I was talking physical surface area.

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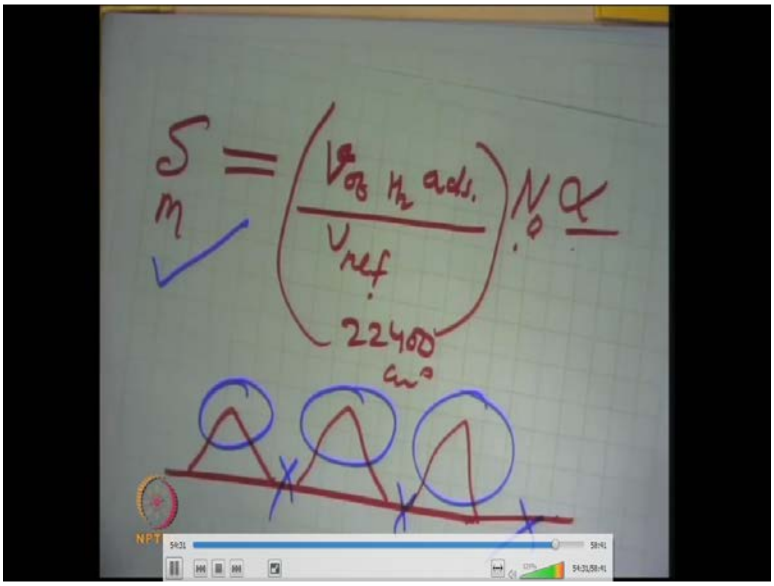
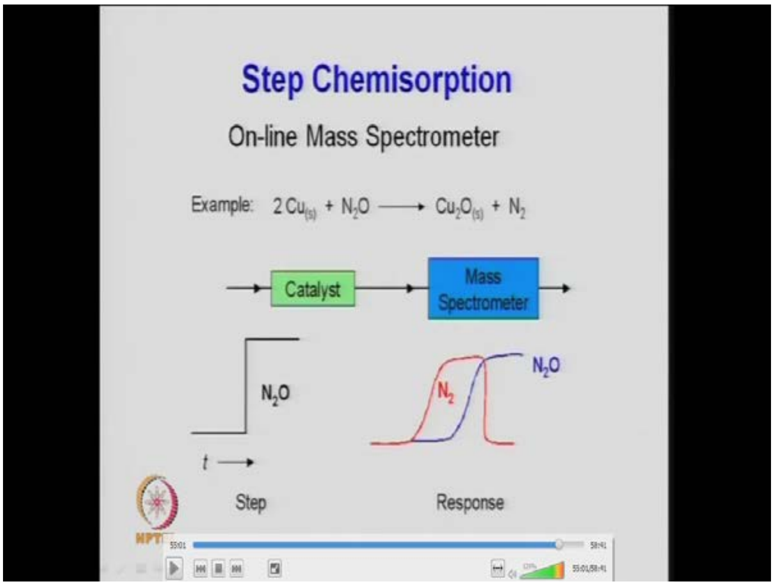


Now, it is a chemical surface area. So, surface area of the Mattel if I write like this is equal to the volume of chemisorptive gas or hydrogen adsorbed divided by volume of the reference condition multiplied by number of molecules, which are available at standard condition that is n 06.02. 21 by 23 and then, it becomes 2400 centimeter cube and times, the area of 1 molecule. So, basic reaction remains the same, because now, you know that chemisorptions are on this side then, no adsorption on this side their surface can be no chemisorptions.

So, here the gas will absorb here, it will absorb. So, we just calculating, we are assuming that, there are arranged in a closed pack or array and we are just talking a projected area of one molecule of hydrogen and we know that, 1 molecule of hydrogen adsorption of 1 metal species 1 site. So, I can very easily find out the volume of the hydrogen gas, which is adsorbed. And you know that at the standard condition of temperature 1 gram mole of this have 22400 volumes and which will have n 0 or algorithm number.

So, in that and area of 1 molecule of hydrogen if you know just like for nitrogen, we saw 16.0 ((53:48))square. So, you can find out the total area of the surface which is chemisorptive theory. So, this method can be used for the determination of the surface area of the metal that is active surface area and in that active surface area how many metals are there, that can also be measured if you know what is the area of one metal. It is a platinum 1 platinum atom has what is the area of that and just you know the total area. So, number of atoms can also be find out like ((Refer Time: 54:18)) active site of platinum that is used to determine the concentration of the active sites.

(Refer Slide Time: 55:01)



Step Chemisorption

On-line Mass Spectrometer

Example: $2Cu_{(s)} + N_2O \longrightarrow Cu_2O_{(s)} + N_2$

So, the approach, what we have discussed. So, just this is same for copper nitrous oxide absorption on copper, this takes 2 sides, the 2 metal sides. So, adsorption and this goes to something like this, because it is a chemical adsorption copper oxide forms. So, you have taken catalysts pass it through the mass spectrometer and then, you determine the concentration of nitrous oxide, which is absorbed on the surface by difference.

So, if you have given the state output. So, you will get a peak like this and then, a constant like this, after that on pulse it will increase. So, you can find out the response of that gas and you can use it for the determination ((54:45)) that I save here in terms of this same to your pulse chemisorptions.

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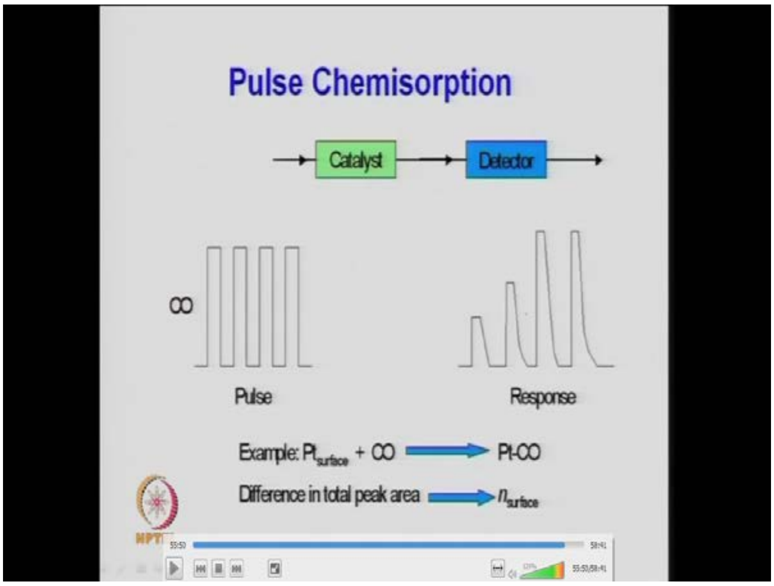

Pulse Chemisorption

Example: $Pt_{surface}$ + CO → Pt-CO

Difference in total peak area → $n_{surface}$

This is the carbon mono-oxide gas. It is your pulse has been given. So, response is something like this. So, simply say's that detector, this detector response from the detector. So, platinum and ((Refer Time: 56:06)). So, is to just associative platinum, CO carbon-mono-oxide. So, difference in total peak area is nothing but, the number of surface. So, this is what for chemisorptions operators, which is generally known rate for determination of the metal dispersion or the metal surface area, number of metal atoms temperature program itself is also similar.

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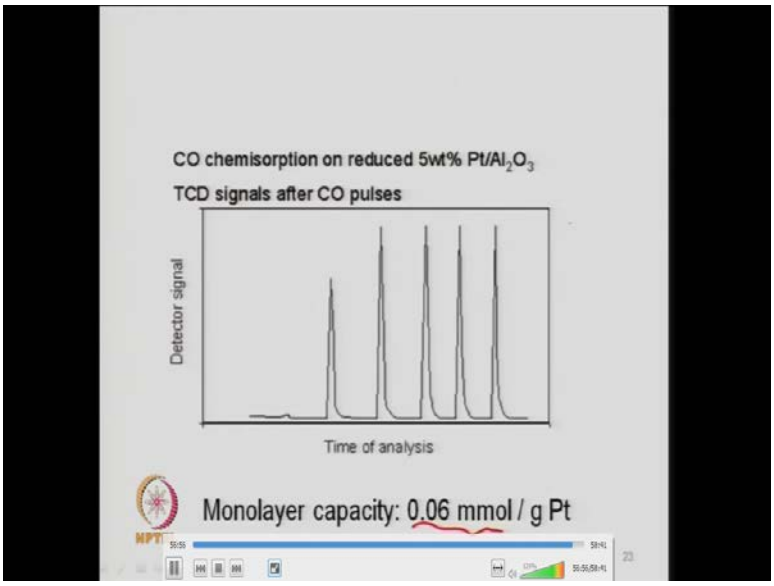

CO chemisorption on reduced 5wt% Pt/Al_2O_3

TCD signals after CO pulses

Monolayer capacity: 0.06 mmol / g Pt

So, we can do that. So, these are here just monolayer capacity per gram of platinum roughly upon 0.06 mille mole of the carbon-mono-oxide gas chemosorb. So, this is the kind of signals at time for the pulse CO, chemisorptions on that at platinum alumina catalyst. So, there are different types of catalyst can be obtained different condition of temperature.

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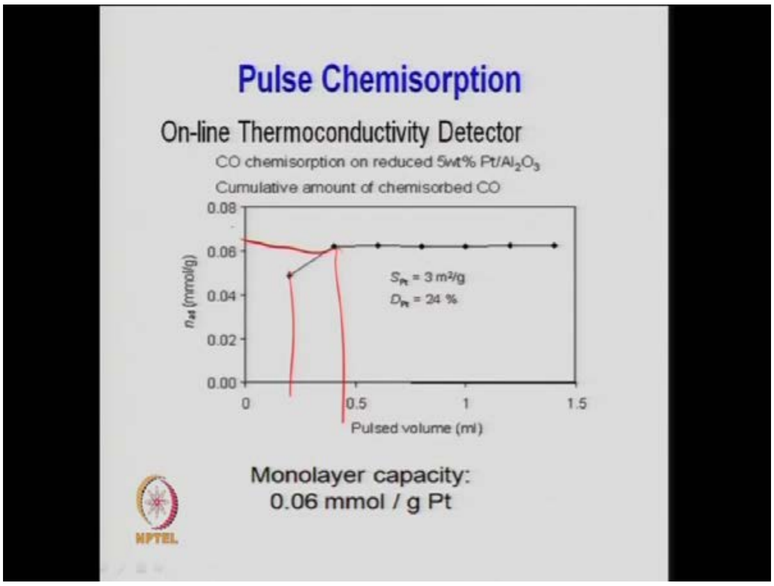

Pulse Chemisorption

On-line Thermoconductivity Detector

CO chemisorption on reduced 5wt% Pt/Al_2O_3

Cumulative amount of chemisorbed CO

Monolayer capacity:
0.06 mmol / g Pt

So, you can have the cumulative collation. So, whatever the pulse volume and the number of mille moles per gram of the catalysts if you calculate. So, you can have the curve like this, mille mole per gram as a concern of volume when you injected the different pulse. So, the pulse volume and we can find out the number of molecules. So, here it is now saturated and. So, you increase the pulse volume the saturate. So, this is something like per co-related and that can be related with the surface area. So, you can find out what I said here. So, ((Refer Time: 57:31)) square per gram.

So, the surface area support is 200 meters square per ((Refer Time: 57:35)), the metal surface area will be low so that is how the always in the first phase most of the time but, you are very high loading something like 60 or 70 percent then, there will be a question that whether, the metal is dispersed or not which is the dispersed wave. So, this applicant is applicable to 24 percent. So, it is just a typical result.

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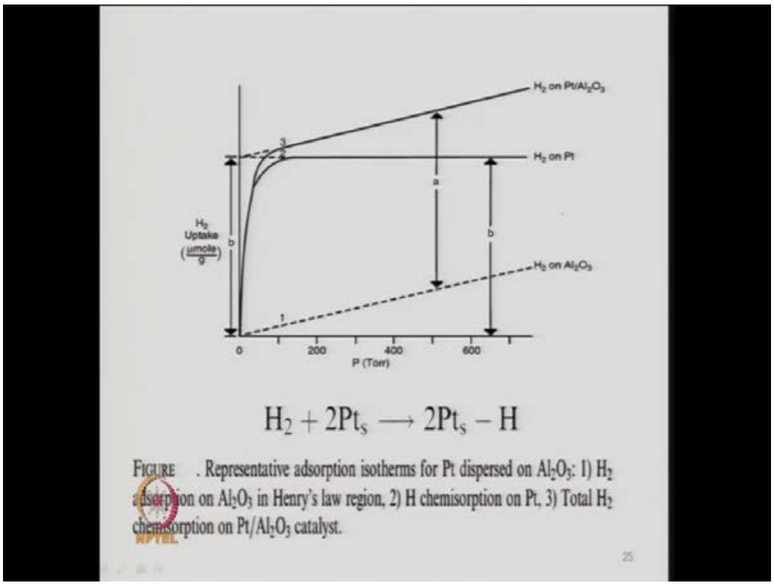

$$H_2 + 2Pt_s \longrightarrow 2Pt_s - H$$

FIGURE . Representative adsorption isotherms for Pt dispersed on Al_2O_3: 1) H_2 adsorption on Al_2O_3 in Henry's law region, 2) H chemisorption on Pt, 3) Total H_2 chemisorption on Pt/Al_2O_3 catalyst.

How to find out? Because, sometime the question will come that your support may also absorb some of the gas catalytic platinum on alumina. So, platinum alumina. So, there may be chemisorptions. So, the calculations we will discuss next time, I stop here today.

Thank you.