Heterogeneous Catalysis and Catalytic Processes

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Lecture – 07

In the last lecture, we were talking about catalyst preparation and the various physical process parameters, which may affect the properties of the catalyst. Because, those steps are very crucial in terms of the preparation or developing a definite structure in a catalyst or crystal size.

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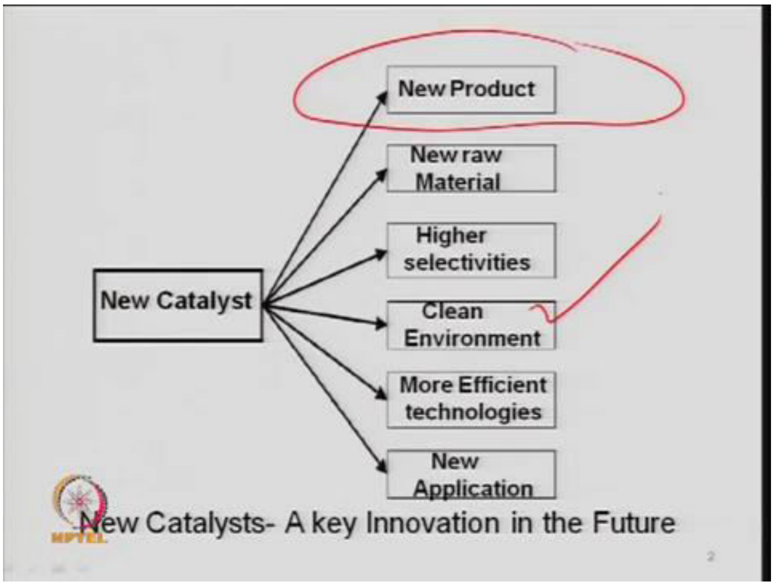

New Catalyst

New Product

New raw Material

Higher selectivities

Clean Environment

More Efficient technologies

New Application

New Catalysts- A key Innovation in the Future

So, if you look at a new catalyst development, where lot of R and D is being done as of today and need to be done, so this can be for the new product. So, variety of new process in terms of the green chemistry concept, as I said last time also, so this can be now there is a need in terms of the form green process on new kind of raw metals and transform into products. So, lot of new catalyst and need to be develop to develop a new product, it can be a different raw material.

Selectivity is one of the important issue even for the existence process, so higher selectivity is desired as I discussed before. Green process, so clean environment say just as an example, carbon dioxide sequestration, everybody is talking in clean cold technologies CCT. So, new techniques are to be developed for utilizing the coal, a large amount of biomass, coal which may be available and that can be used as a source of energy.

So, that can be converted into liquid or into hydrogen CTH, but the important thing is that, a novel catalyst which should reduce the carbon dioxide into the environment, sulphadioxide into the environment. So, this is very important in terms of the green catalysis or green catalytic process and then, more efficient technology, the existing process may not be efficient.

As an example, just as I said for fertilizer industry hydrogen production process, where the nickel or alumina catalyst is used, but since the mass transfer is the controlling step, so effectiveness factor is very very low, 0.001 of that order. So, how to improve the catalyst performance, so ruthenium may be one of the active material for the convergence of naphtha to hydrogen or natural gas to hydrogen, so depends on the process and no applications. So, these are the trends in terms of the catalyst development and which is the innovation need to be done.

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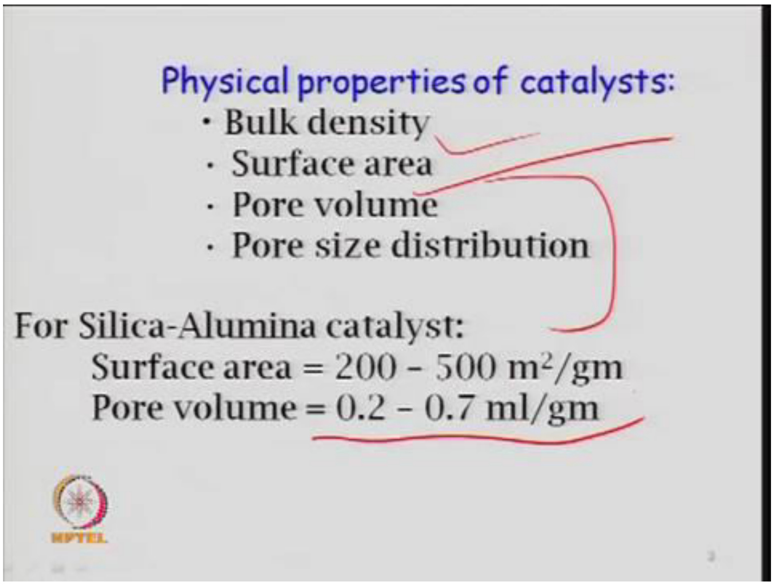

Physical properties of catalysts:

- Bulk density
- Surface area
- Pore volume
- Pore size distribution

For Silica-Alumina catalyst:

Surface area = 200 - 500 m^2/gm

Pore volume = 0.2 - 0.7 ml/gm

If you look at the characterization of the catalyst or a physiochemical properties of the catalyst, which are generally produced or developed during the catalyst preparation. So, this is also very important issue that, bulk density, that density of the pallet, density of the powered particle, density of the powdered material and when you made a tablet from that then, what is the density.

So, different kind of density, solid material, apparent bulk density and when you put it in the bed depending upon the shape and size, so the bed density, so different kind of density. So, the bulk density is very important in that case, when you look at the catalytic property in terms of the catalyst, depending upon the pressure which you applied when you make the tablet.

Surface area, I have said that, the most of the time rate of reaction depends on the surface area and a larger surface area may be recommended. So, that is very important and depending upon the pore volume, pore size distribution, you will have a definite pore structure, which is related to the surface area of the catalyst. So, this is important just for example, if you take silica alumina catalyst, the surface area may vary from 200 to 500 meter square per gram.

Same thing, activated carbon may have surface area of 100 meters square per gram or also 1000 meter square per gram, depending upon how the pores structure is developed. Because, the porosity or pores structure of the catalyst is very important, if you look at the internal surface area of the catalyst. Same thing for the pore volume also, so you can have a highly pores material with low mechanical strength or a less pores material with high mechanical strength.

So, you have to tune them in terms of the properties and the strength of the catalyst, so the pore volume may vary from 0.2 to 0.7 or even higher. So, everybody looks for a larger pore volume or larger porosity of bed, catalyst are the not the bed, so in order to get a definite catalytic reaction inside the pores structure of the catalyst. So, as I said earlier that, the calcination or sintering, so that becomes a crucialist, because when you have a nitrite salt or is oxide that is, chloride and converted it to be to the oxide. So, in the presence of ambient tire or oxygen, you hit the sample at a certain temperature and may be the time. So, the temperature time is very important and this is what you called calcination and discussed last time.

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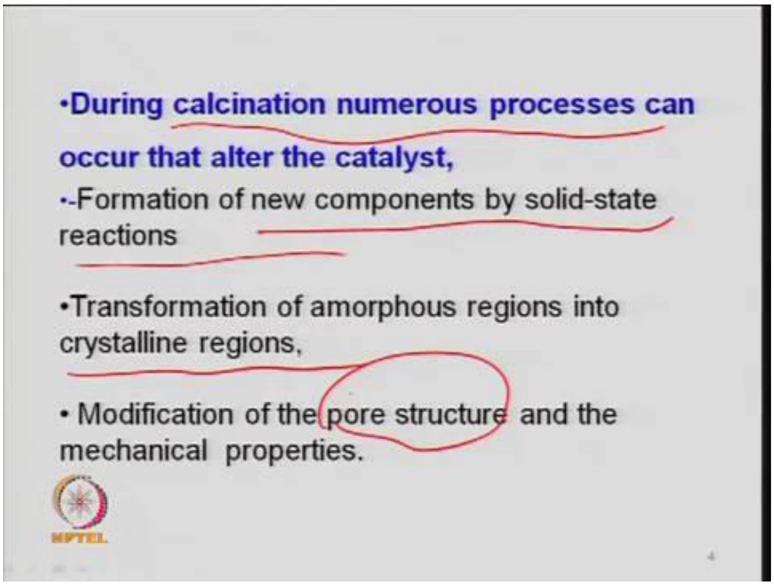

- **During calcination numerous processes can occur that alter the catalyst,**
- -Formation of new components by solid-state reactions
- Transformation of amorphous regions into crystalline regions,
- Modification of the pore structure and the mechanical properties.

So, why do that step is very crucial, because you get definite poll porous structure in that, so the formation of new component by solid state reactions, so this we were discussing yesterday. So, there is a diffusion between one species to other or it may be the reverse also, that is a multi component which may be diffusing in one to each other. And that time, you have a definite concentration in a pores structure that is one thing and simultaneously as I said that, nickel oxide and aluminum oxide, they are reacting during that sintering process and you get different phase, which may be nickel aluminide.

So, that is again important, because sometimes the nickel aluminide may be good and similarly in the calcium aluminide I told, 12 C O 7 ((Refer Time: 06:15)) may be a desired phase, when you have taken calcium oxide and aluminum oxide and centered it to certain temperature and time. So, this happens during that formation of new component, so new phase what I am saying, it is entirely a different chemical composition and that may have a different activity in terms of adsorption of a gaseous molecule.

Then, transformation of amorphous regions into the crystallized region, so as I said this is the difference between zeolite and a simple clay mode material. So, when you give a proper treatment say PHZ is your factor as I said, because nuclide formation crystal grow. So, a definite crystal may be desired, when you prepare the micro crystalline materials, MCM type catalyst, SAPO catalyst, so a definite crystal structure is desired.

So, same thing in ZSM 5 hydro thermal synthesize you do, so a definite crystal structure is desired and this is happening during this heat treatment condition, so very important and modification of pores structure and the mechanical property. So, as I said that, depending upon temperature and time, there may be a solid solid reaction and the pores may get narrow down.

So, your porosity in one way is decreasing, but mechanical structure may be improving, so you have to tune these two in terms of a structure, when the pore structure is highly pores then, strength is poor. The particle make crumble during the handling, so you do not need those kind of pallets, because that do these becomes very difficult to handle during a catalytic reaction.

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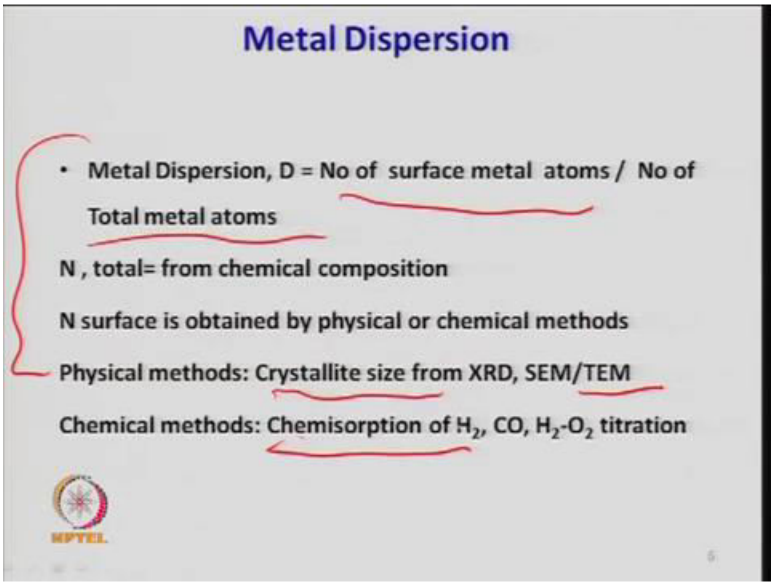

Metal Dispersion

- Metal Dispersion, D = No of surface metal atoms / No of Total metal atoms

N , total= from chemical composition

N surface is obtained by physical or chemical methods

Physical methods: Crystallite size from XRD, SEM/TEM

Chemical methods: Chemisorption of H_2, CO, H_2-O_2 titration

So, dispersion another important factor, which you get during the catalyst preparation, so dispersion definition we have already discussed earlier, that the number of metal or active metals which are exposed to the surface and we talk it in terms of the fractional dispersion. So, fractional dispersion when I am saying, that available surface atom divide by the total number of surface, total number of atoms which you have taken in the beginning.

Because, that is what you get from your ICP studies or some atomic absorption spectroscopy. So, you can determine the total concentration of the metal by extraction, you extracted from the catalyst and then, do the absorption in a definite wave length. At a definite wave length you will get the peak and you can find out the concentration or ICP can do that job or some idiots can also, although it gives certain line spectra. But, that can also be used, if you take the average at different points and that is just calculate, just take the average through all the surfaces and so on the surface.

So, it can be measured, but I mean to say for number of surface metal atoms divide by the total number of that metal atom and multiply by 100 you will report it percentage this, so very important domain. And when you have a nano particle, it can go to order of 50 percent, 60 percent or even the larger of it, but in most of the catalytic reaction when you prepare it like a incipient wetness or wet integration method, the dispersion may not be very high.

But, if you even if you get 15 percent or 20 percent for those kind of metals, it is a good number, so this is what the important property which you get during the incipient wetness technique or wet impetration technique. When you look at the precious metal or PGM what we say, platinum group metals, noble metals. Physical methods, as I said to measure this, so crystallized size you can calculate from x ray diffraction, we will talk on that later.

Similarly, scanning electron micrograph, you can take the pictures of that metal surface and you can see the crystal size morphology, topology of the surface. Similarly, that transmission electron microscopic, which also gives the image at high density or high resolution, so that time we can have 3D picture structures also and you can determine the crystal size very clearly from using this transmission electron microscope. And the same another high resolution transmission electron microscope, where you can count the particles also and you can compare your dispersion which can be determine by chemisorption study as well as from this study.

So, chemical methods are available which I said you know that chemisorption by using hydrogen, carbon monoxide or hydrogen oxide titration. So, basically it is a kind of titration, but sophisticated or computational methods are available to evaluate this parameters or dispersion or whatever the surface crystal size or metal crystal size number of particles, so all these can be determine in the catalyst.

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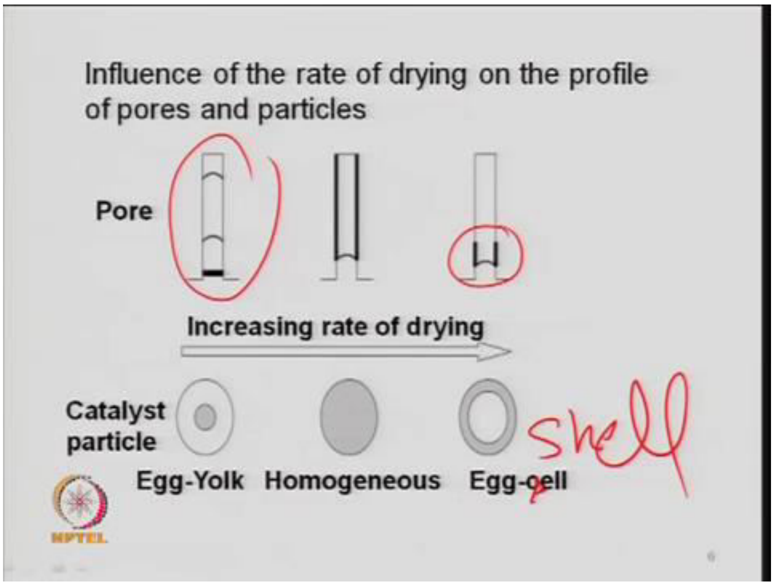

Influence of the rate of drying on the profile of pores and particles

So, this what I was talking that, what happens or what are the process parameters which may affect the catalytic property is something like that, so rate of drying. So, drying is a also important, how fast you are drying, at what temperature you are drying, so it is a kind of aging effect, so you can see here this is a pore of a catalyst. So, with time when you have increase the rate, so the metal or solution diffuse into the pore of the catalyst. So, at a given rate it may be very high or it may be intermediate or it may be low slow, so this is something like whether uniformly the metal had been deposited throughout the pore surface. And this if you do the very high rate of drying, so what happen everything just deposits at a local points something like on a shell, basically s h e l l at shell.

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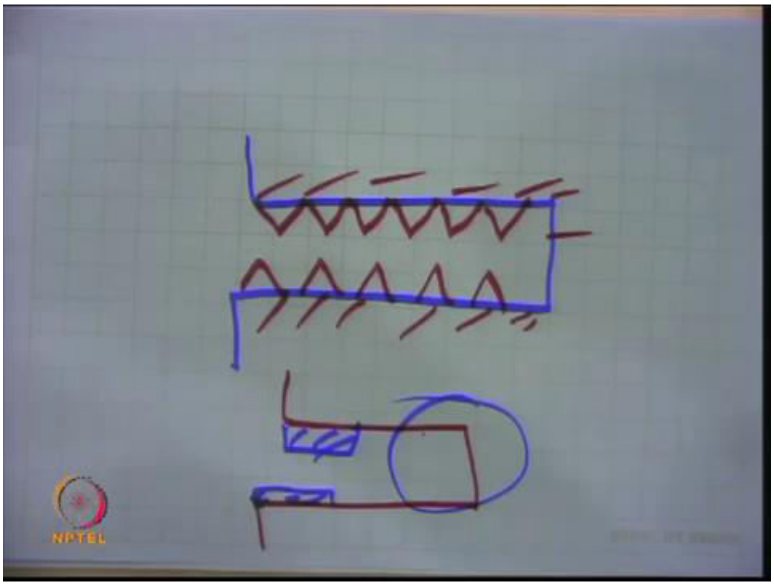

So, this what I mean to say that rate of drying can give you a pores material, where the metal may be deposited uniformly like this in the pore, so this is one pore in a solid like this, there are millions of the pores. So, active metal is deposited like this on the surface, the second case may be it is deposited just on the outer periphery, say only this surface is covered, at low drying rate and then it is extreme everything may go on this side at the pore head.

So, depending upon that you can have that the active metal may be deposited just at the outer mouth of the pore, it may deposited at the end of the pore or it may be uniformly distributed, so that is depending or rate of drying is one of the factor, which decides this. Another, thing that is the same thing in the pallet also, if you have a complete particle or pallet then also, so we define it egg yolk type, where everything is deposited on this side here. The second one is the uniform homogenous, so similar to this, so homogeneous throughout the pallet and when they say then it can just everything pore outer shell, so penetrated outside when the rate is very high.

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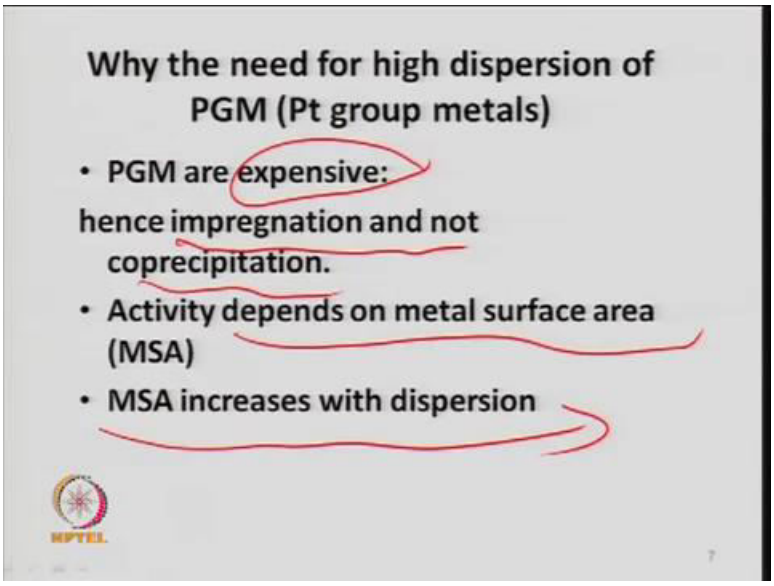

Why the need for high dispersion of PGM (Pt group metals)

- PGM are expensive:

hence impregnation and not coprecipitation.

- Activity depends on metal surface area (MSA)
- MSA increases with dispersion

So, if you look at the precious metals, so I told when the incipient wetness or wet integration method generally we use, so platinum group metals or platinum, when you use, so you need a high dispersion. The reason is that, they are very expensive, the cost is very high, so only a small concentration of these active metal should be used and that should be properly utilized, without wasting any concentration of that active metal.

And this will happen only when you have uniformly distributed it throughout the surface, so this is one impregnation method is referred for this kind of material, platinum material. Not the co precipitation, where you take the solutions and then precipitated, so most of the part there may be a possibility is that it is not precipitated completely, some may left in the solution.

And when it gets precipitated it may happen that, the every particle is not properly utilized or metal species properly utilized, because it is in the form of precipitation, it may have a clusters of that. So, that time, because the concentration is low, it is advised to use the impugnation technique or especially incipient wetness technique. So, active activity of these kind of metal will depend on the metal surface, I am not talking that total surface area, it is the surface area of the active metal and this can also be determined from the chemisorption study.

So, you can do the hydrogen chemisorption and you can find out the dispersion and since you know that how many molecules have adsorbed on the surface say any reactive gas and whether it is associative or dissociative, so you can find out that. And then you know that what is the surface area of that one gas molecule and that can be collated with the surface area of that matter.

Because, the gas species will chemisorbed only on the active metal surface and that fundamental thing you use for determination of the dispersion also and same thing can extended to determine the crystallize size. So, we will talk on that later, so metal surface area increase with dispersion, so when dispersion is high, your surface area of the active metal I am talking. So, because when you define the turn over number, you define the rate per unit area of the active metal or in other words either it is a permit area of the active metal or in terms of the per unit mass of those active metals. So, you will multiply by some time dispersion also, so that gives you the fraction of the material which is available on the surface.

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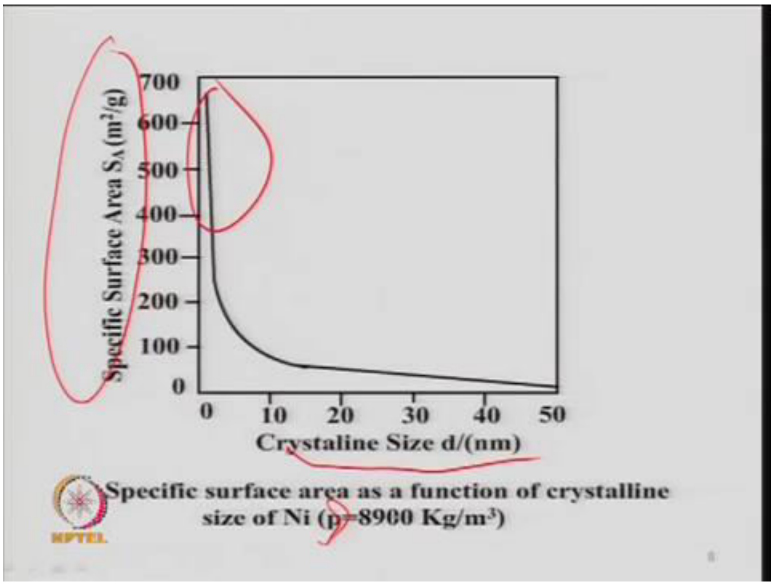

Specific surface area as a function of crystalline size of Ni (ρ=8900 Kg/m^3)

Is just an example if you look at here, the specific surface area, I am talking S 2 metal not be it is surface area here and this is a crystalline size or crystallized size of the metal. So, this is given for a nickel just, you can see here that as the crystal size increase surface area decrease, so surface area inversely proportional to the crystallized size. So, that is why we talk nano particles, smaller particle you have the larger surface area of this order, so this is nickel, for nickel which have density of roughly, this a density of the nickel 8900 kg per meter cube or 8.9 gram per meter cube.

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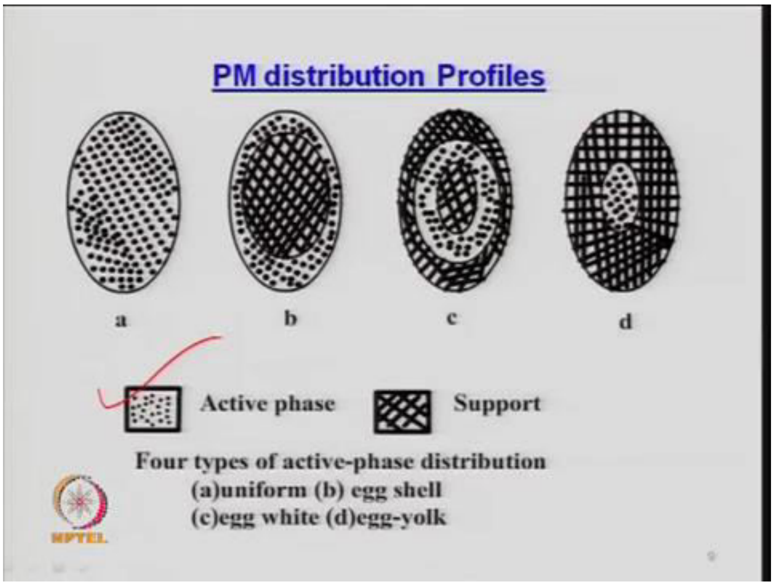

PM distribution Profiles

Active phase Support

Four types of active-phase distribution
(a)uniform (b) egg shell
(c)egg white (d)egg-yolk

And this example which I have correlated here earlier in terms of the egg shell or egg yolk, so similar thing that this precious metal or platinum metal distribution profiles has been shown a typical profile. So, these dots represents the active phase and this is representing the support, cross or this shaded silent lines or the support power pore. So, you can see here that we were talked 4 type of active phase distribution, so uniform type, so everything is distributed uniformly on the surface.

So, most of the time we will look at this kind of structure or this type of catalyst, that the complete surface of the supports should be utilized, dispersion will be better in this case. But, sometimes when the reaction may have a more of poison precursor, different type of rate of reaction, very fast, very slow, then we can have the distribution like this also.

So, this is another one, where you can see the egg shell type, so active metal is just on the outer shell of that kind, so this is something like that you have a hole support or surface of the solid and on that the active metal is deposited in this form like this. So, this surface is not being used now, only outer surface of the catalyst is being used and same thing you can correlated with the pore also as I said, at everything is deposited on here.

So, rest of the pore is waist physically and this is something like when you look at a monoliths, so on that also we just look at a small theta. So, when the diffusion may be a problem or diffusion resistance is high, then you can look at this kind of deposition, because they have the diffusion length will be low, so your resistance for diffusion will be low, so your rate will be high.

So, diffusion resistance is can be minimized by taking this kind of design, there are another one which we call is egg white, where you can see it is a kind of ring structure somewhere in between and that is known as direct delta distribution. So, when you look at there are lot of computations techniques are available, in order to identify the position at which or the location where the catalyst concentration should be kept highest.

So, this kind of distribution may be a direct delta of the incant, where the everything is deposited in this zone only, in a definite say which may be at distance r and r plus delta r and you call it direct delta once on. So, this is one kind of distribution and you call it egg white and this is egg yolk, where everything is deposited at the central portion or core of the catalyst. At the center, where I said that earlier it is a waist, but now it may be a useful or that is what the rate of drying as I said may be one, the concentration of the acid with may be another sometime we call it a pressure also. So, you give certain concentration of acid, so acid will allow it to penetrate inside, to diffuse inside the surface of the solid.

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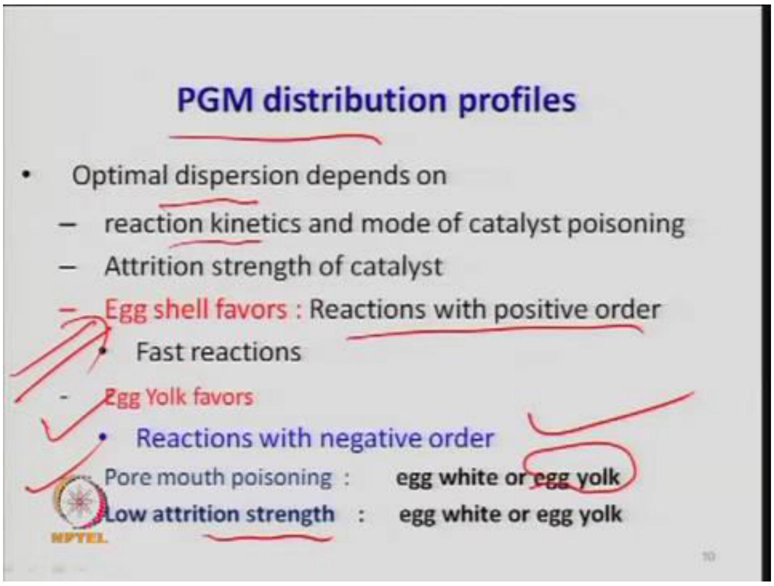

PGM distribution profiles

- Optimal dispersion depends on
  - reaction kinetics and mode of catalyst poisoning
  - Attrition strength of catalyst
  - Egg shell favors : Reactions with positive order
    - Fast reactions
  - Egg Yolk favors
    - Reactions with negative order
  - Pore mouth poisoning : egg white or egg yolk
  - Low attrition strength : egg white or egg yolk

So, the distribution profile for this platinum group metal, if you look at the optimal dispersion depends on the kinetics of the reaction and mode of catalyst poison. So, the poison pick that is a especially, when you have a naphtha or hydro carbon fraction which contain the sulphur and you need to avoid those transformation or transformation of those precursor into the catalyst pore. So, then you need to look at definite distribution or what you call optimal distribution of the metal, in a catalyst pore or support and also have a high dispersion.

So, that is optimal dispersion which will depend on the kinetics of the reaction, fast reaction, slow reaction, first order reaction, negative order reaction, positive order reaction, so that is one factor attrition strength of that catalyst. So, when the catalyst strength is poor, then you would not like to deposit it on the outer surface, because what will have happen, during the attrition like this, the outer skin being gambled, so particles will fall down from here.

So, in that case if the active metal is deposited on the outer surface, then this will loss, especially when you have a platinum group metal or precious metal. So, generally this is some rule of term or guideline that egg shell if you take, egg shell I said something like this distribution like this on the outer surface. So, egg shell if you generally favors the reaction with the positive order and fast reactions, so the reaction is positive, so egg shell is desired.

So, concentration because positive order reaction, you know the rate R a proportional to the concentration to the power n, so higher the concentration lower will be rate. So, you would like to have to complete the reaction in the small zone, because as a diffuse inside the concentration will decrease down the length, so there the rate will be low, because concentration is low. So, for generally positive order reaction you prefer egg shell and if you look at other side egg yolk, which is on the center of the catalyst, so negative order, because you need a low concentration higher will be that.

So, similarly the other basic I am not saying it is it is a very important con consideration, but sometimes when you design the catalyst, depending upon the type of the reaction and type of the feed stock, we look at a design proper selection of the catalyst. But, most of the time you select the uniform catalyst and you try to control the poison or increase the rate by some other design factor. There are several other parameters also by which you can enhance the rate, or you can reduce the diffusion resistance, we will talk on that later.

So, pore mouth poisoning, pore mouth poisoning means the precursor deposits on the outer surface of that, so that time it is advisable to take either egg yolk or egg white. So, because you do not want to allow poison precursor to reach to the platinum surface, because your catalyst is very precious and the poison deposits on those surface, your activity becomes zero or negative very low, so that to be avoided. So, that time you prefer something like egg white or egg yolk, but not the where the catalyst is deposited on the outer surface egg shell. Same thing for the attrition resistance, as I said when the attrition strength is poor, then do not take egg shell, so you prefer the egg white or the egg yolk.

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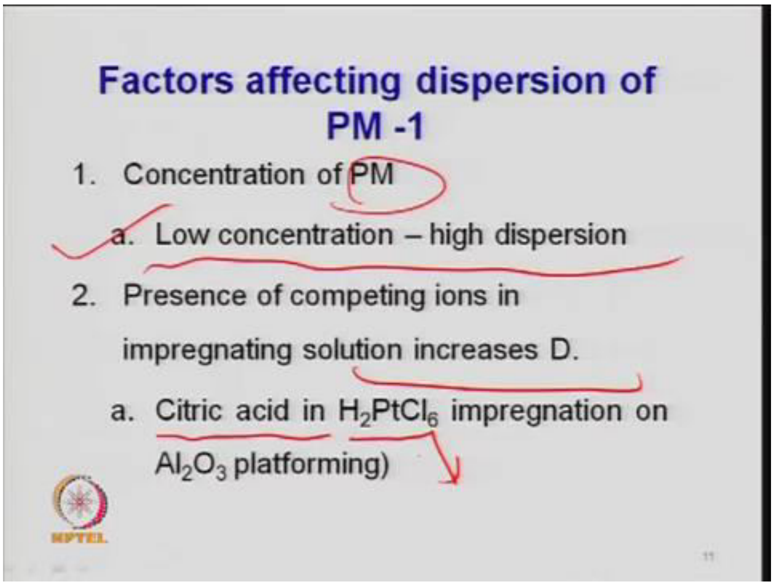

Factors affecting dispersion of PM -1

1. Concentration of PM
   a. Low concentration – high dispersion
2. Presence of competing ions in impregnating solution increases D.
   a. Citric acid in H_2PtCl_6 impregnation on Al_2O_3 platforming)

So, there are several factors for which may affect the dispersion on the platinum metals or platinum group metals, so the concentration of the platinum metal, so I have taken platinum on alumina as a base, but it can be for ruthenium it can be for rhodium, so in general we said platinum group metal. So, if you look at this, that the concentration is very important, so that is why the incipient wetness technique or wet impregnation technique, you take the low concentration.

Because, they are costly that is one reason, second thing is that the high dispersion or which metals are highly active, so a small concentration just like 1 percent or 0.1 percent, may be effective for the catalytic activity. So, why did you have designed in such a way that this dispersion is high, so it may be 40 percent, 50 percent, 60 percent so; that means, just all those 40 percent sides are active and available for reaction, that is sufficient for chemical reaction.

There are large number of atoms which are available in that much mass of the catalyst, that you should understand, so the concentration is very important, so when the concentration is low, dispersion will be good, so sometimes you diluted, it the fundamental thing of Ostwald dilution law. Then presence of competing ions, sometime you add the third component, in order to enhance the either dispersion or in order to enhance the diffusion rate in the surface of a catalyst.

So, this competing ions in impregnating solution that may increase the dispersion, just like for example, you can have any acid, a small concentration very dilute acid or you can take HCl also. But, only just one drop of the HCl, dilute HCl and one drop is sufficient for catalytic activity. So, if you look at this the citric acid is 1, and if you take this is the chloroplatinic acid, as a platinum precursor which is to be deposited on alumina.

So, you are using either impregnation technique, wet impregnation technique or incipient wetness technique, so a small concentration of this citric acid will push the material inside, but if you have a high concentration, what will happen everything will go to the egg yolk type catalyst. So, you have and if you take a definite it can give you the egg white also or egg shell, when you have a very dilute if you do not take then everything will be deposited uniformly on the surface. So, this is very important, that how to deposit this active metal, under the presence or in the presence of some third, which may called a active material or which can enhance the dispersion of the metal.

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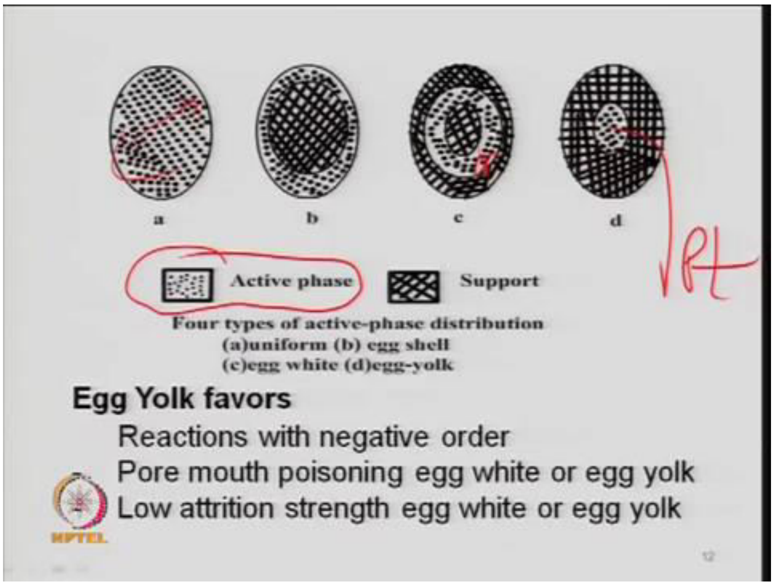

▨ Active phase ▩ Support

Four types of active-phase distribution
(a)uniform (b) egg shell
(c)egg white (d)egg-yolk

Egg Yolk favors

Reactions with negative order
Pore mouth poisoning egg white or egg yolk
Low attrition strength egg white or egg yolk

So, this is just if you look at here a, b, c, d what we have discussed again earlier also, and this is the active phase which is platinum or taken from H 2 P 2 Cl 6 chloroplatinic acid, this is your support, which is here like this all the sided portion is your support. So, is this is my platinum here basically inside, here it is in this core zone platinum, here this is uniformly distributed, so this is the same slide earlier as when discussed.

So, that is what I told that depending upon the concentration, so one thing is the rate of drying, that time I was talking just rate of drying, but same thing can be controlled by selecting a proper concentration of the acid. So, HCl or citric acid and you can have high concentration of the HCl or citric acid, then you will get the phase like this or like this, everything is going inside. So, it will make just a thin layer inside, so when it is in thin layer then again your dispersion will go down. So, high dispersion may be this case, because here it is uniformly distributed, but in this case it is just deposited in a thin layer, so problem may be that dispersion may be low, this may be 1 consequence of this acid concentration.

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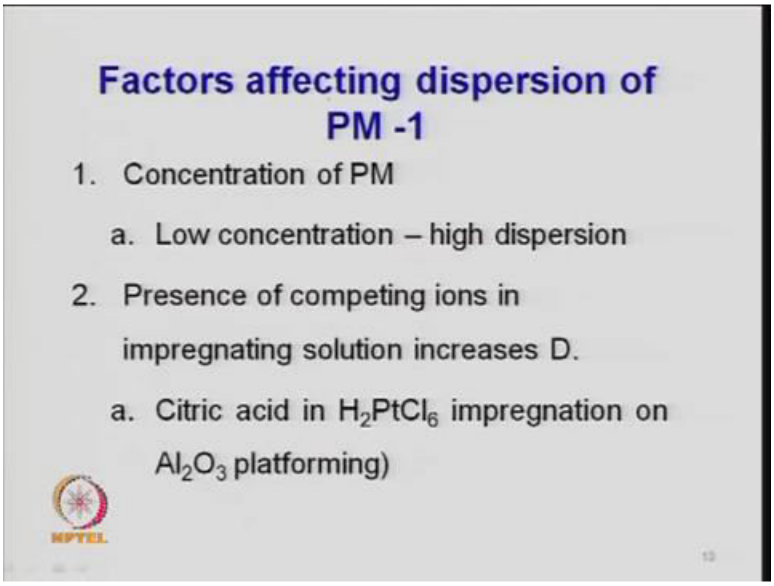

Factors affecting dispersion of PM -1

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So, concentration as I discussed last earlier and then, these are important and this is what, so we have the increasing concentration of the citric acid.

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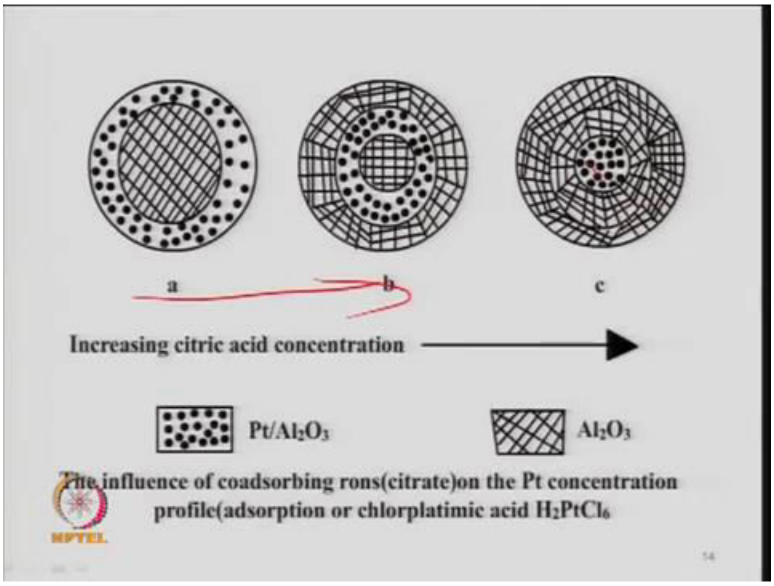

The influence of coadsorbing rons(citrate)on the Pt concentration profile(adsorption or chlorplatimic acid H_2PtCl_6

So, as you increase the concentration, so finally you reach to this level, so this is your active platinum alumina inside, which will happen when you have a high concentration of the citric acid. And this is the case when you have a low concentration of the citric acid and this may be changing like this, if you do not have any concentration, it will give you a kind of uniform distribution. So, regions of small concentration of these acids, resource is or increase the rate of diffusion of the solution into the pore of a solid or particle.

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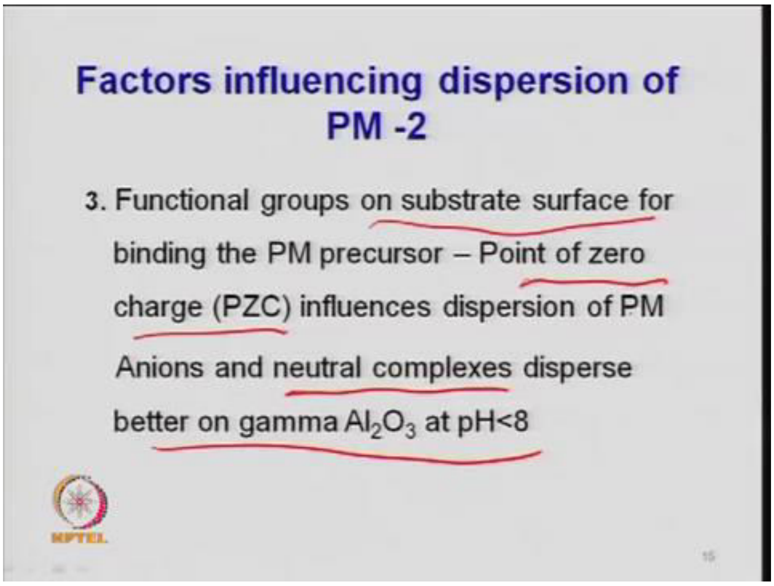

Factors influencing dispersion of PM -2

3. Functional groups on substrate surface for binding the PM precursor – Point of zero charge (PZC) influences dispersion of PM

   Anions and neutral complexes disperse better on gamma Al_2O_3 at pH<8

So, you can have a different kind of distribution in the pallet and these information you can get by transmission electron micrograph or the scanning electron micrograph, you slice the surface and take the picture or just by optical microscope also you can take that. The another function is the functional group, so that in the beginning we were talking about point of zero charge, when the surface has no charge.

So, that also becomes very important, because you are adding acid, you are changing the when you are adjusting the ph, so you are changing it is point of that is the pH is less then PZC or high higher than the PZC. So, you are changing the concentration of the act ion, positivity or the negativity on the surface, so that is the functional group on substrate surface for binding a precious metal or platinum group metal precursor, that will depend on the point of zero charge, so this is important that first study what is the PZC of that metal.

So, point of zero charge influence the dispersion of platinum metal, anions and neutral complexes disperse better on gamma alumina at pH less than 8. This is just an example that the how is PZC is important, which will take the concentration of the cat ions or anions on the surface of the catalyst.

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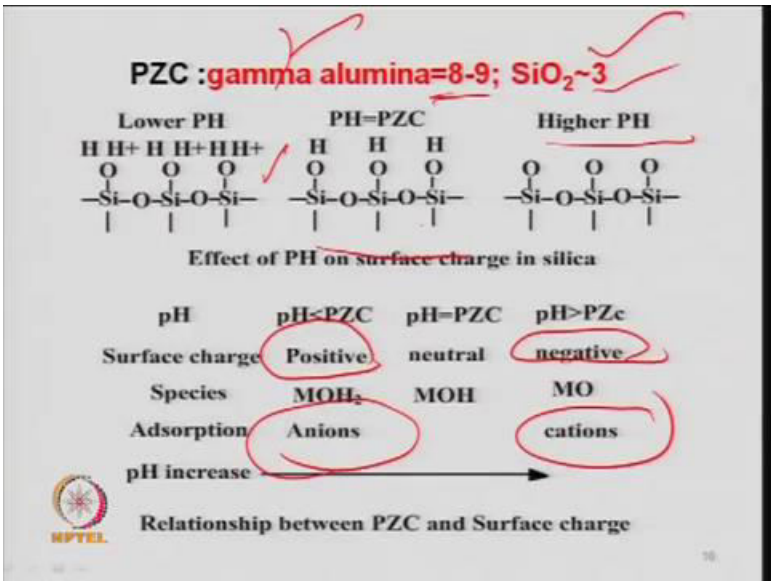

PZC :gamma alumina=8-9; SiO_2~3

Effect of PH on surface charge in silica

pH	pH<PZC	pH=PZC	pH>PZc
Surface charge	Positive	neutral	negative
Species	MOH_2	MOH	MO
Adsorption	Anions		cations

pH increase →

Relationship between PZC and Surface charge

So, this I have shown here if you look at here, that for your example for gamma alumina the PZC is between 8 and 9, and if you look at silica then it is 3, so it means for gamma alumina at 8 or 9, there is no charge on the surface, when you have taken the pH 8 or 9. Same thing for silica a pH is 3 the surface has no charge, but if you look at here for the silica we have taken the different case, so this is at lower ph, at lower pH the surface will have a positive charge.

PH less than PZC, because here PZC is 3, so at less than this the surface will have positive charge like this, all this H positive will come here. And when you have extreme case pH which is higher than PZC, the surface will have a negative charge. So, what is the consequence of positive surface, it will take more and more anion and negative it will take more and more cat ions.

So, and when it is neutral then it will have just like the something like OH group some charge attached to the surface, so when you adjust the pH during the catalyst preparation, it may your changing the concentration of hydrogen ion or hydroxyl ion on the substrate surface. And accordingly it can take positive metal ions or negative metal ions, so whether it is alumina or silica your pH adjustment will be different, so for different support the idea is that depending upon the support and their PZC, you have to adjust the PH.

And simultaneously it will depend on the, when you are doing a co precipitation technique, then approach is that at what pH value, it gets precipitated that is solubility is another important issue. So, here we are talking impregnation technique, so you are just correlating at with respect to the PZC, so that is the surface concentration and pH effect and then crystal size of the substrate that is support which you are taking, but is the size of that.

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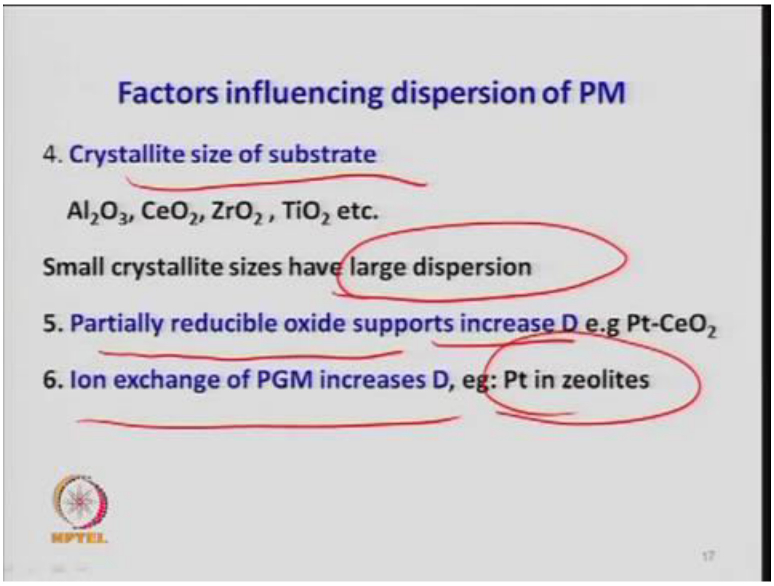

Factors influencing dispersion of PM

4. Crystallite size of substrate

Al_2O_3, CeO_2, ZrO_2 , TiO_2 etc.

Small crystallite sizes have large dispersion

5. Partially reducible oxide supports increase D e.g Pt-CeO_2

6. Ion exchange of PGM increases D, eg: Pt in zeolites

So, sometimes you reduce it to a size of the say 50 micron or say just 100 nanometer where you find powder, the idea is that the one thing in that you are increasing the surface area of those particles. Because, small and second thing that the particles when you have a smaller they can bind, because see the particles property change, when you change the particle size and when you go to the nano level.

So, especially when you look at that monoliths and that monolith when you deposit a kind of alumina powder say it is not easy to just deposit it on the surface or a substrate, when the particles are larger in size, but when the particles are smaller they can easily stick to the surface. So, these that is the particle size of the substrate also important, so when I am saying alumina, cilia, zirconia, titania all these support material, so crystalloid size will have large dispersion.

So, it means the particles support particle should be considered as a smaller or should be taken as a smallest possible, when you are impregnating it on to that some metal on to that. And same thing that this is partially reducible oxides upon, it also increase the dispersion like platinum or cilia, so it has the redox property of oxidation reduction, cilia on platinum and you have, so, because of that also the dispersion may be higher.

So, this is just depending upon the experimental and the catalyst preparation, you have to just check that and then, see the effect that, how much cilia concentration is desired how much platinum concentration is desired. And then look at the condition and controlled it and then you can have properties which you can develop in the catalyst. Then, ion exchange method is another one, which is generally used for this zeolites catalyst and where you have a act ion anion exchanger.

So, here you can have high dispersion. So, platinum group metals that is the dispersion increased, if you prepare it by ion exchange, so sometime we prepare these metals by ion exchange or catalyst by ion exchange method. So, for example, just platinum and zeolite if you want to give to better rather impregnation use the ion exchange, so you have H positive ion on the zeolite or ammonia you convert it into ammonium sulphide and replace that ammonia of zeolite by platinum. So, platinum, gallium, so these can be impregnated on to the zeolite catalyst by ion exchange procedure, but there should be a sufficient ion exchange capacity, so again the time pH particle size these will be crucial.

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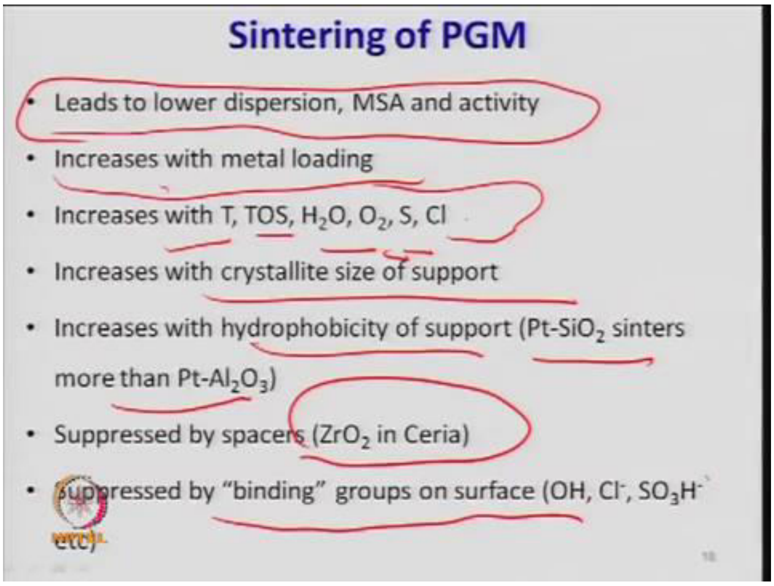

Sintering of PGM

- Leads to lower dispersion, MSA and activity
- Increases with metal loading
- Increases with T, TOS, H_2O, O_2, S, Cl
- Increases with crystallite size of support
- Increases with hydrophobicity of support (Pt-SiO_2 sinters more than Pt-Al_2O_3)
- Suppressed by spacers (ZrO_2 in Ceria)
- Suppressed by "binding" groups on surface (OH, Cl^-, SO_3H^- etc)

Sintering, so that is what you get during firing of a catalyst, so calcination, so it leads to a lower dispersion, so metal surface area and activity drops, so MSA refers to metal surface area. So, when you have a calcination conditions, so you have to do it in controlled way because that is the crucial step where you get different phase, but simultaneously since you are heating it to a time course given time, so the particles may come closer a kind of reaction.

So, you have made some nano particle during your aging or drying a step over co precipitation this step, but when you have given the heat treatment, then the particles make again collapse or become a larger, so this is the problem, as I said that was the nano particles of number of metal. So, when you give the heat treatment they may agglomerate and reduces the dispersion, because the crystal size now increased it grows, so metal loading if you have high then again the same problem.

So, because larger number of metal concentration on the surface and now, more reaction when you have high a temperature condition. Temperature time of a stream water, oxygen, sulphur, chloride they are also affecting the performance or the crystal size or dispersion, when you give the heat treatment, so this should be avoided. So, a definite temperature is desired, not more than certain level that you have to tune it or check it, same thing time, time on a stream water may be a problem, so give a sufficient aging or drying before calcination and same thing oxygen environment should be controlled.

Sulphur, chloride this should be avoided, so that this are the certain precursors which may affect the performance. So, increase with crystallize size of the support, if crystal size is high then also your sintering that is if you look at the reaction. So, sintering depends on the crystal size, so when you have a sintering then crystal size will increase, increase with hydrophobicity of the support, so support is hydrophobic or a hydrophilic.

So, again your metal surface an activity that becomes a crucial factor depending upon the surface, so you have to look at that the platinum silica, platinum alumina if you have, so platinum silica sinters more compared to platinum alumina. So, if you have platinum on silica, that may not be a good when you have a, because that the during the sintering the agglomeration will take place, so dispersion where platinum silica catalyst.

Yeah, definite this sinters more the dispersion is less here and dispersion is more in the platinum alumina catalyst, same thing some time we had the spacers, so zirconia in ceria to avoid the sintering phenomena. The crystal, so solid-solid reaction, I am saying that is to be avoided the sintering is to be avoided, suppressed by binding groups on the surface hydroxide, chlorides, sulphate like this what I said.

So, that they are present, so sometimes the chlorination is done during that sintering time, because the dispersion will improve in that case, so that avoids the sintering phenomena. So, we need to calcine the catalyst, but the sintering is undesired basically, because sintering is nothing but, the solid-solid agglomeration, so two small crystals comes closer, because of high temperature and time and becomes a larger.

So, surface area of the crystal decrease, dispersion decreases and these are the parameters which affect the sintering performance, so we try to avoid the sintering, so it means the temperature should be controlled, time of distance should be controlled. So, water should be avoided oxygen concentration should be kept low and same thing for sulphur and all these chlorides to use, so you have to control this poison precursors in the catalyst, so high purity metals are required when you prepare the catalyst.

So, the characterization what we are talking surface area, pore volume, pore size distribution all these things can be determined based on simple condensation of any inorganic gas on the surface of the solid. And we discussed physical adsorption and chemical adsorption, so chemical adsorption means you need a chemical reactive gas and physical adsorption means any gas which can be adsorbed on the gas surface, side below it is critical temperature.

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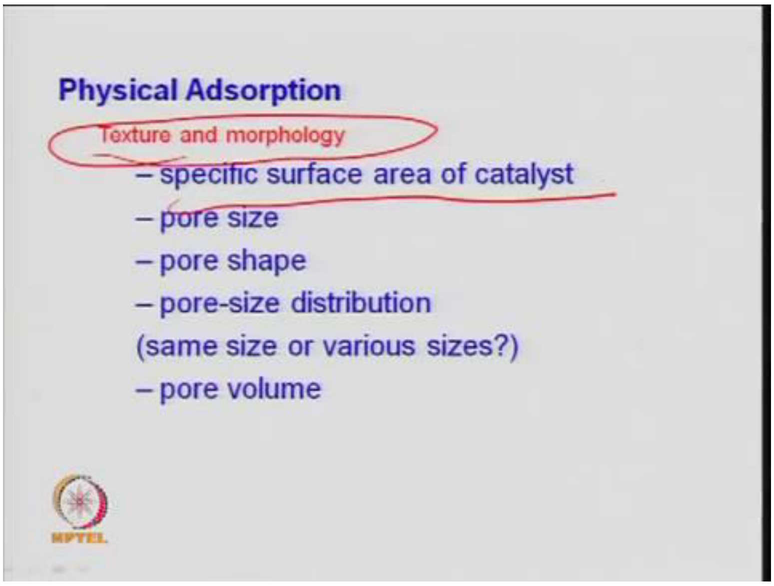

Physical Adsorption

Texture and morphology

- specific surface area of catalyst
- pore size
- pore shape
- pore-size distribution

(same size or various sizes?)

- pore volume

So, if you look at here the texture and morphology, that is the first important property of a catalyst, that texture the how does it look like morphology is spherical or what is the shape of that particle. And in depth if you look at how the cracks have been developed inside, pores structure has been developed in the in the catalyst. So, in that case the first thing is that the specific surface area of the catalyst, that is surface area of the catalyst per unit mass of that solid material, so that has to be identified or determined.

Then size of the pore that is important, because you have done all these preparation methods, you are by using them those method. You have prepared the catalyst and now, you would like to check the texture property of morphology of that solid material, so that is a kind of physical characterization of the catalyst. So, surface characterization in terms of the texture property or morphology of the catalyst, so pore size, pore shape, pore size distribution and pore volume, so these are the properties of the catalyst, which can be determined based on physical adsorption.

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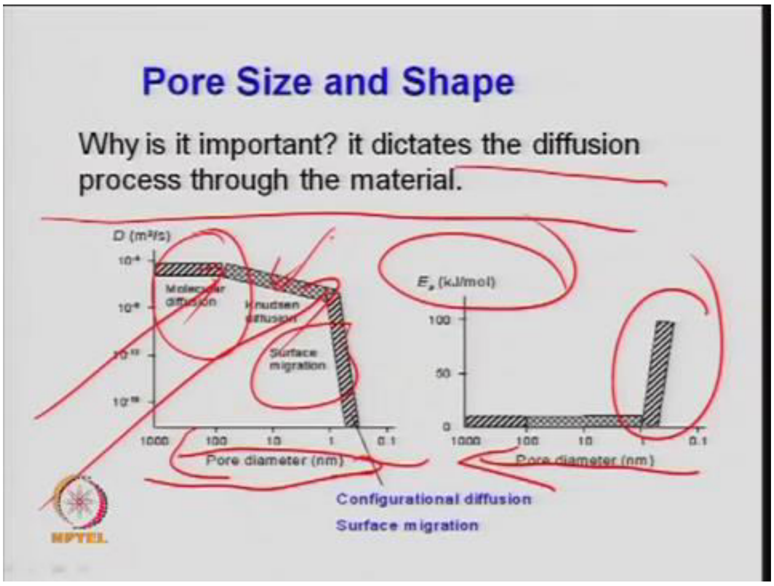

Pore Size and Shape

Why is it important? it dictates the diffusion process through the material.

So, why do you need that, why do you study this pore size distribution or pore size measurement the reason is here, that it dictates the diffusion process through the material, because you know larger pore, the gas methane can diffuse easily. A small pore methane may go, but aromatic may not go or bronze commands may not go, so the if they are difficult to penetrate inside, so it means the distribution resistance may be a dominating parameter.

So, basically in one way you are calculating the transport property or diffusion co efficient for that gases species into the pore, but you should know on a priory that what is your pore size, but kind of pores are available in that solid material. And based on that only, you can give your theory or postulate your chore or you can control suppose you want to minimize the diffusion resistance, so accordingly you can control it.

So, there can be the parameters, in terms of the temperature, in terms of particle size, or in terms of development of the catalyst itself, but once the catalyst size already been developed, then it will be the secondly parameter by, which you can control it to the certain level. But, when you are preparing a catalyst, then on a priory you should know your reaction for what type of reaction, you look those catalyst and then, depending upon the molecular property of those chemical species and then, you try to develop a definite kind of support.

So, that is why, the computational method may help you to develop a definite kind of structure and you try to reach to that type of structure experimentally, so this is, but the state of art and catalyst development and then, look at this property. So, in generally when you look at a solid material, there can be different type of diffusion phenomena, so one is known as the molecular diffusion.

So, molecular diffusion means nothing but, the kinetic based on the kinetic molecules are colliding and penetrating itself, so that is one thing, so there are different co relations by which you can find out the diffusion coefficients. And second thing your Wisden diffusion and generally, this happens in a small pores, so one thing is that the collision is between the molecules and the molecules are moving.

The another thing is that since the pores are narrow at the channel is the narrower, so what will happen, the molecule will collide among themselves, but also they will collide with technology wall of that, because it is a narrower lane and molecules are moving. So, when the molecules larger molecules move in a small lane, then the possibility of probability is that the molecule will strike with the wall more and then, they will move, so that is known as insertion diffusion.

Whereas, the molecules when they are colliding among themselves and moves, that is known as bulk diffusion or molecular diffusion, so bulk of the molecule they are moving, because they are colliding among themselves. And second is the molecules are colliding with the wall and then, penetrating itself and sometimes generally it is a very rare phenomena, the surface diffuse migration. The molecules are adsorbed on the surface and they are migrating because of the temperature phenomena, they leave the surface and move to the other side.

Surface, just like an a reaction on the surface, so it is a kind of diffusion on the surface on migration of the molecule from surface to surface, because of the temperature phenomena or surface property. So, these depends on the type of pore here, I am talking this thing for a molecule property of the gas or any reactant molecule which has come to the surface of the solid and planning to react, or penetrating inside and then, it will react transform into a product.

So, it means the first thing is that understand, how these molecules can go into the pore or can they go inside or not, because for a chemical reaction molecule has to go inside a pore of a catalyst. So, the first thing is that the depending upon the kinetic diameter of that molecule, depending upon the pore size, you have to take this understanding or phenomenon that which kind of diffusion is dominating, so molecular diffusion larger pores generally in the larger pores.

Knudsen diffusion a small pore, so diffusion will be difficult, so, but when it will dominate at high pressure or temperature, so again there are some factors like kinetic diameter as I said radius of the pore is important, molecular weight of the gas is important. So, if the molecular weight of the gas is high, that is related to the diameter of the molecule, so diffusion will be slow, so the read over the first one diffusion you know the kinetic diameter the molecules are colliding among themselves.

So, it will be function of temperature and more dependent on temperature, the ason pressure and like that. So, there are several phenomenon, so temperature, pressure everything and the diameter of the metal, so Knudsen diffusion bulk diffusion and surface diffusion this may happen. So, that is what the first understanding, that can a molecule penetrate if it penetrate then how, because of diffusion the convective term will be there, but generally that will be very, very small, because you are talking a surface of the solid.

So, the velocity becomes 0 and then, it is diffusing because of the concentration gradient, so you can see here the activation energy, which is required for these kind of pores, so pore is increasing in this side. That is why I said that in larger pore you will have molecular diffusion, with intermediate pores between 10 or 1 to 100 Angstrom that Knudsen diffusion a nanometer 1 to 100 nanometer Knudsen diffusion and then, at very small pore and high temperature surface diffusion.

This is the activation energy graph, so again you can see here the pores are increasing in this, so pores when they are larger, temperature the activation energy it is not a problem, because the molecule can go easily. And this is basically a fundamental thing pore surface diffusion, that is why i said that temperature phenomena very important, when the activation energy is very high, it means it will require high temperature for diffusion. Same fundamental thing that higher temperature will favor the transmission or transformation towards the higher activation energy.

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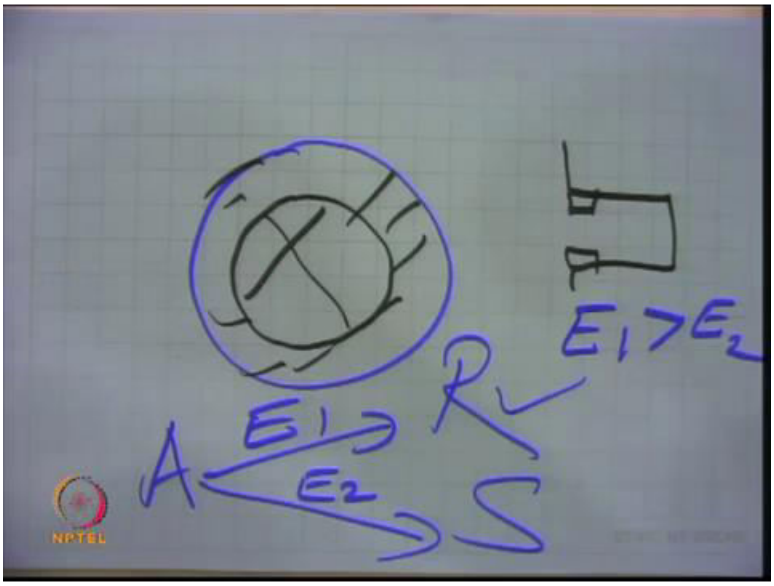

Suppose, you have a multiple reaction as I discussed earlier also, A goes to R and A goes to S, so depending upon the activation energy E 1 and E 2, the temperature will show it is direction. Suppose, if I say E 1 is greater than E 2, and if you increase the temperature then rate of formation of R will be more compared to S, that is what I am saying that higher temperature favors the reaction of higher activation energy. Same thing you have in the diffusion phenomena, the activation energy for surface diffusion is higher compared to the bulk and the kinetic. Because, I told you diffusion control reaction will have low activation energy, we will discuss that later, but rule of thumb kinetic control reaction will have higher activation energy.

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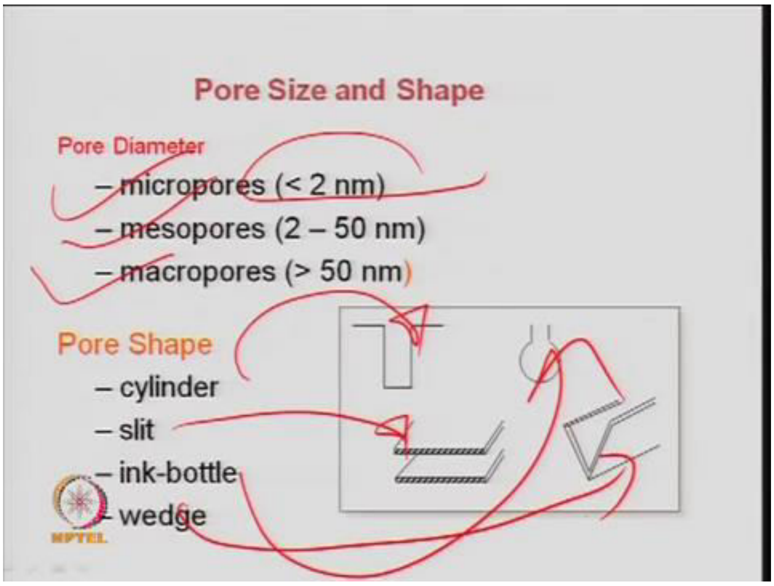

Pore Size and Shape

Pore Diameter
- micropores (< 2 nm)
- mesopores (2 – 50 nm)
- macropores (> 50 nm)

Pore Shape
- cylinder
- slit
- ink-bottle
- wedge

So, it means this is the fundamental here that surface diffusion will take place at high temperatures and here this is what the bulk lamp Knudsen diffusion, which has less effect on temperature, but other properties are very important, molecular dimension very important, pressure has a role graph. Of course, you can see that, so we just have discussed this slide earlier, that in a pore when you look at a catalyst geometry or pores structure.

There may be a micro pore mesopore and macro pore by definition we say a pore is less than 2 nanometer is the micro pores 2 and 50. So, between 2 and 50, these are our mesopore and more than 50 nanometer or some time you call it 100 also metropores, so that between the particle. And then also, shape of the pore it may be straight cylindrical, so most of the time we assume the pores size straight cylindrical, it may be closed from one end, it may be opened from both ends.

But, even the pore are not straight cylindrical, we take the average pore as a straight cylindrical by considering some non cylindrical parameters, so will talk on that later. It can be a slit type like this say alumina mainly lambda type structure slit type, it can be ink bottle type like this and it can be wedge type structures again in the most of the siliceous materials, it is calcium silicates and they can have either this type or that type structure.

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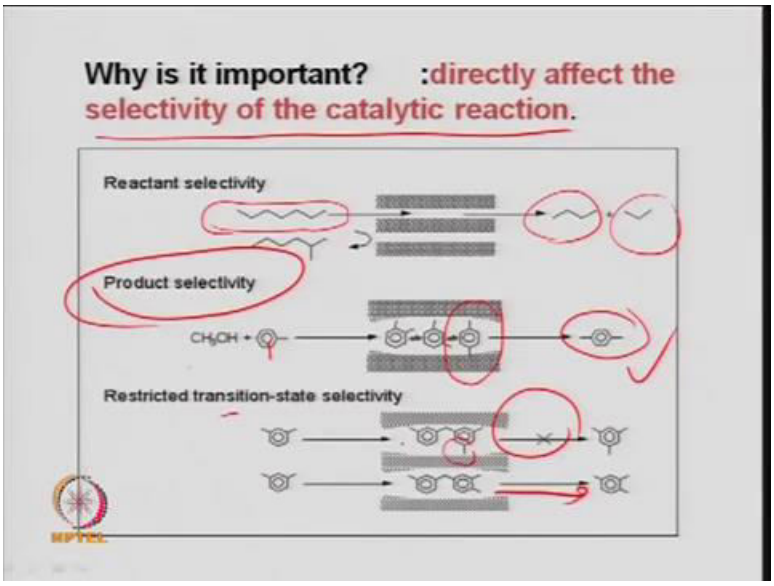

Why is it important? :directly affect the selectivity of the catalytic reaction.

Reactant selectivity

Product selectivity

CH_3OH +

Restricted transition-state selectivity

The selectivity is very important issue when you look at a pore size or pore size distribution, so this a just an example of zeolite type catalyst, if you look at or any pores structure material where a material al reactant specie which is a straight change like this. So, that is the selectivity term which we are defining, so this kind this straight hand molecule here, this can go easily into the pore and crack, smaller paraffin and one alpine like this or 2 smaller molecules.

It can easily go, but if you have some other molecule which is bronzed here or something like aromatic, so it cannot go inside the pore of a catalyst. So, it can be a poison precursor also, like sulphur species, cyclic sulphur compounds it can be aromatic, so this cannot go inside or that if it is a poison precursor, it will not damage the catalyst pore, so that is the meaning of selectivity. So, these is a reactant selectivity we call it, where only one type of reactant or one reactant can go inside, but not the other.

This can be a product selectivity also, because this is the what we are talking that the selectivity of the reaction can be affected depending upon the pore structure, so you can see here you have methanol, you have something like a cyclic compound may be a toluene, benzene. And they have gone, because it is a larger pore both of on inside and then, now here it is a larger arrow compound, it may be a 2 ring compound or it may be just like ortho xylene, meta xylene, paraxylene whatever.

So, this type of species may form, but this may it come here just like when you have a isoxylene or sorry this isoparaffin formation, in some other pores. A straight change for of an main form the isoparaffin, but which aromatic is formed it cannot come out, it will remain there same thing when you have a co precursor aromatics. So, dehydrogenation of aromatic and you get the product, but simultaneously you get the coke also, so coke may not come because coke is a poly condensed aromatic hydrocarbon.

So, that may be blocked inside or remain inside, this is now only this molecule is come out, but this structure cannot come out, it remain there inside. So, that is known as product selectivity, though selectivity of this kind of molecule will be now high, the only thing that your catalyst is being deactivated. So, you have to regenerate that or remove that time to time, but otherwise you are getting the whatever the ortho, meta, para type zerlines or desired component from that.

Sometime it can be restricted transition state selectivity, the meaning is that this kind of molecule orientation, because I said orientation of molecule is also equally important. So, this kind of molecule can go inside, the pore and then isomerizes or convert it into product, but very difficult because the molecule has this kind of transition state which is formed during the reaction.

So, this and this is the some types of alkalized if you look at ortho group like or meta group or para type, so para type, but here if you look at the ortho and meta connections are at this and this not at this. So, this structure can come out, but not this one, so this is that intermediate has formed during the reaction, so which kind of intermediate product has formed it is something like A goes to B and B goes to C.

Suppose, B is a larger molecule, so it will remain inside, so when you have a reaction like psychotrope synthesize, you get a series of the product, so that is the wax formation, so that is problem in the psychotrope, that large amount of wax formed. And that poison are catalyst, same thing when you look at the methane thermodant to liquid hydrocarbon you have to look at these kind of, because methane is converting into a larger molecules, so to what extent larger.

If coke is forming it will remain there or it will drop there, but if this is a kind of a structure a definite kind of pore state, it will continuously come out, but this will block of course. So, there can be a different kind of selectivity which may be good also, but some time most of the time they are good, but some time they may be a poison precursor and that deactivate the catalyst. So, now we are talking the activity of the catalyst, but this could be the consequence of catalyst deactivation, because of the undesired product species formed and it remain inside or deposited on the catalyst surface.

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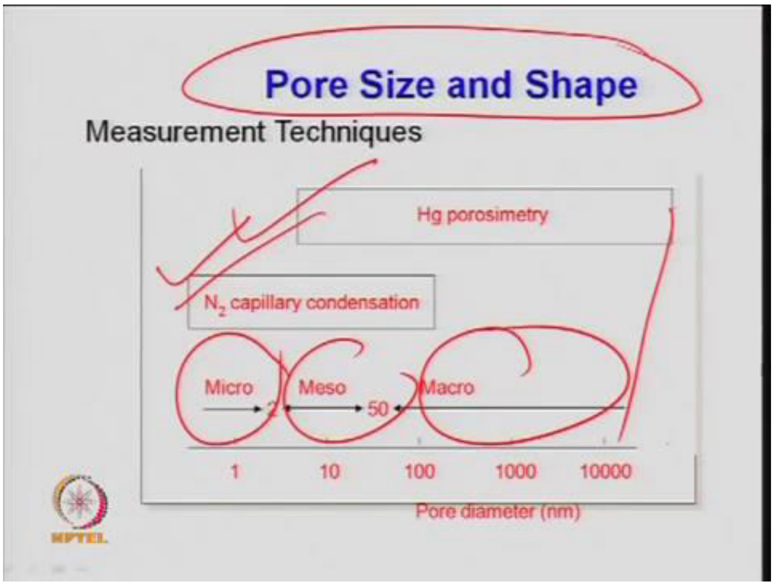

Pore Size and Shape

Measurement Techniques

So, If you look at the pore size, shape distribution of the pore, they are very important and need to be determine. So, we have several methods by which we can determine the pore size and shape of a catalyst, which are based on physical adsorption reaction, so one of the most important or commonly known is known as mercury porosimetry method. The second one is known as nitrogen adsorption desorption method capillary condensation, that is phenomenon which is based on capillary condensation.

And these can give you a wider range of pore size distribution, that is as I said micro pores macro pores and in between mesopores, so if you use this two together or combined then you can find out that complete pore size distribution. So, 1 to 10000 Angstrom 10000 may large number, 10000 nanometer here, so it is a very large pore, so these can be used to determine the catalyst property, so I stop here and will continue it next time ((Refer Time: 57:33)).