Heterogeneous Catalysis and Catalytic Processes

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Lecture – 05

Today, we will talk on catalyst preparation. See the basics of the catalyst as I told when we are talking a heterogeneous solid catalyst system, So, we are looking in terms of that deposition of some active metal on the porous structure of a catalyst on some support or carrier.

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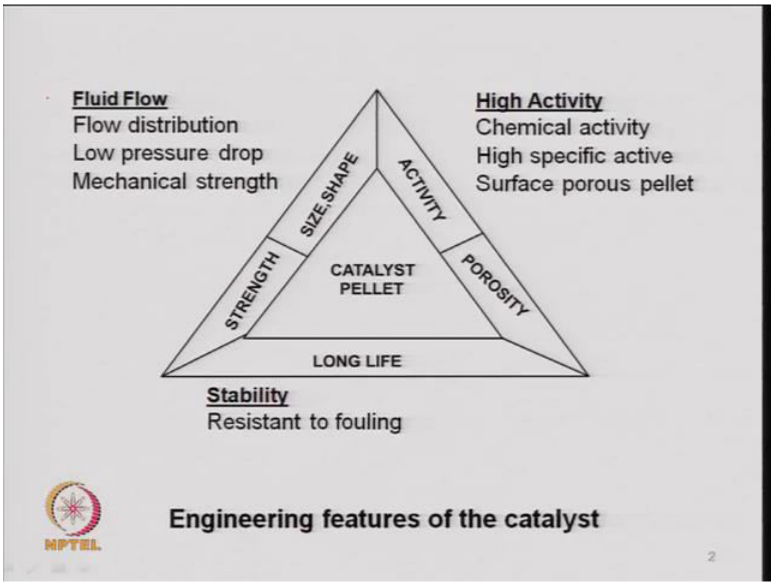

Fluid Flow
Flow distribution
Low pressure drop
Mechanical strength

High Activity
Chemical activity
High specific active
Surface porous pellet

Stability
Resistant to fouling

Engineering features of the catalyst

So, if you look at this triangle the catalyst pellet we need the desired that is a kind of good activity, ability to transform the reactant into product, which will depend on the porous structure of the catalyst and the concentration of the active metal and its type. So, type of metal, type of support that is the first thing to decide for a catalyst for a given reaction.

Because we have seen that, there is a kind of coordination or there is a kind of interaction between a reactant gas species with the metal, which will depend on the electronic configuration of the metal as well as the configuration of the reactant present or gas molecule. So, this is the first thing to get a desired activity the catalyst should have high activity. So, we are taking in terms of chemical activity which will depend on the metal adsorption that is weak or strong metal adsorption of the gas molecule, which is kind of chemical adsorption.

Then it should be highly specific in its activity so that also we have seen that we talk in terms of turn over frequency or turn over number. Surface should be porous because the porous structure provides a large internal surface area. And when you have a large internal surface area then you will have larger dispersion. So, large number larger number of active sides will be available on the catalyst surface. So, your total rate or if you calculate your turn over number, that will be higher or rate of reaction will be higher.

The other side if you look at the fluid flow or hydrodynamic condition so this is your activity part, which is actually required for the catalyst ability to transform it into product. This side is related to your hydrodynamic property, which is related to flow distribution so mollified distribution that is known ideal characteristic that is in the pellet or catalyst. So, that is also equally important because this decrease the efficiency for the convergent.

So, this may have a pressure drop so we do not want a very high pressure drop in the reactor, so a low pressure drop is desired good kind of flow distribution. So, to avoid the channeling, to avoid a kind of back mixing, if you are looking a pluck flow reactor so there are several known ideal parameters, which need to be studied for a given catalyst under given conditions. So, that part we will see later.

And simultaneously the catalyst should have sufficient mechanical strength because as I said that if you having a moving bed reactor or a fix bed reactor at high pressure, the particles may have a kind of attrition. So, they may crumble during the reaction or operation or during loading inside. So, fines will form and when the particles are very fine and you are using it in a prudised bed reactor the particles may leave the bed, illustration.

So, all these things should be avoided. So, strength should be sufficient, size and shape will decide pressure drop large particle may not be good white fraction in the bed will be different, but a smaller particles the pressure drop will be high. So, larger particle will create more diffusion limitation, more mass transfer resistant will come in your reactor.

So, transport limitation when you look at in terms of mass transfer or the diffusion resistance in a catalyst, you need a definite size of the catalyst particle.

So, that also we will see later, but larger particle will have low pressure drop but, a smaller particle will have the higher pressure drop, but they are good in terms of the transport property. So, we have to tune the particle size also. Same thing is related to shape the especially the mass transfer control reaction. So, a larger external surface area per unit volume is desired. Small a, which you write in your k g into a, for mass transfer area and mass transfer coefficient. So, this is small a, which is surface area per unit volume.

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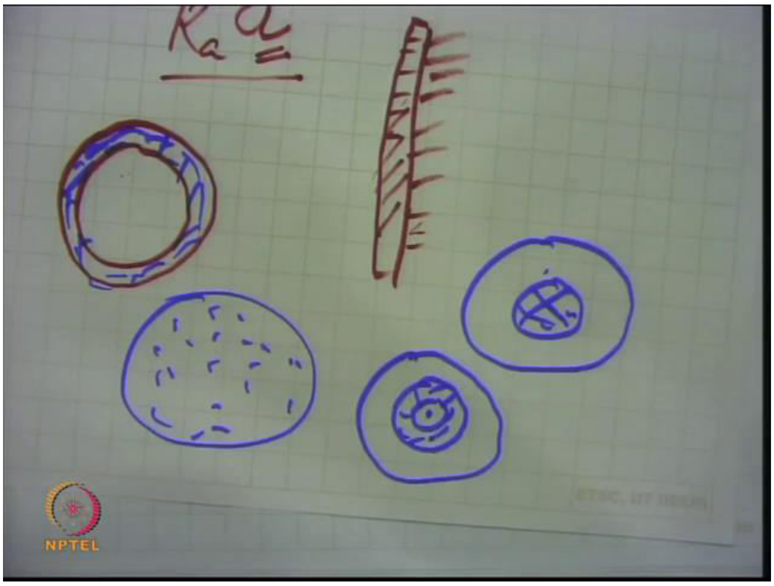

So, basically we talk in terms of this kind of interface. So, there is a solid if I just draw the geometry like this and this is this may be a liquid interface, this may be a gas interface. So, when you have a mass transfer reactions especially when we see monoliths or when you have an automatic exhaust catalyst, the pallet in non porous. So, there the reaction may be a mass transfer control reaction. So, that time this thickness of this one becomes important.

So, the surface area that is the mass transfer depends on the velocity linear velocity of the gas so that should be sufficient in order to avoid the mass transfer resistance. And also because the interfacial area surface area per unit volume is the desire property in that case. So, smaller pallet will have larger surface area per unit volume, but simultaneously the pressure drop is also high, so you have to tune that. And once this two satisfied and the most important factor or another important factor is stability of the catalyst for deactivation.

So, the life of catalyst in terms of the ion resistance so that should also be equally checked when you look at a good catalyst. So, that may also depend on your distribution of the metal in a poor geometry. So, something like a shell where everything is deposited on the uniformly on to the throughout the support or a pore or sometime it may be just like pore mouth like egg cell type catalyst we call and yolk type catalyst we call. So, it means how your active metal is deposited on a support.

So, it can be in the form, this is supposing my support. So, active metal can be deposited just like in the form of ring so, that that may be a kind of excel catalyst something like this. This may be good for some when the selective poisons are the pickers for the reaction and you want to avoid that kind of reaction. And this sometime most of the time we look at uniform distribution of the catalyst throughout the pallet or support. Sometime we look a catalyst where it just like here the active metal is deposited in the core of that, what you call at egg yolk catalyst.

And sometimes we need a distribution, which is something like annular ring somewhere at distance delta so like this. So, this what you call direct delta, there may be different kind of distribution, which may be decide for a suitable reaction especially when you look at the exothermic reactions or socks nocks removals. So, this is what called optimal distribution of catalyst in a pellet and that can be done by optimization technique. You can find what should be the thickness for this layer delta, a direct delta function where the concentration of the poison pickers are can be kept at a minimum.

So, lots of the studies have been done in this area also for the optimal distribution of the catalyst in a petal. So, there is a book by Markedly and Arvind Verma. So, that gives the details of this mathematical tools or mathematical design for selection of the optimal distribution. So, especially when the catalyst deactivation is significant then this kind of distribution may also be a factor. So, we have to look at a good kind of stability in the catalyst in order to avoid the coke or in order to avoid the poison.

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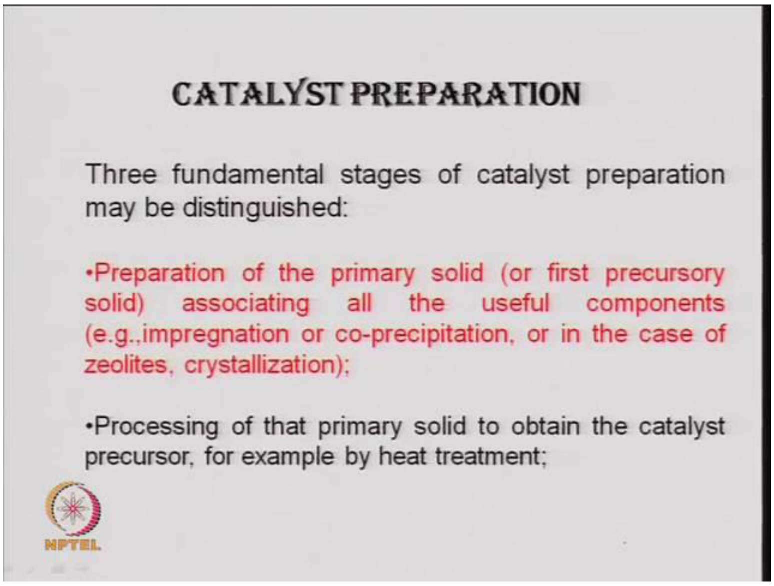

CATALYST PREPARATION

Three fundamental stages of catalyst preparation may be distinguished:

- Preparation of the primary solid (or first precursory solid) associating all the useful components (e.g.,impregnation or co-precipitation, or in the case of zeolites, crystallization);
- Processing of that primary solid to obtain the catalyst precursor, for example by heat treatment;

So, this is known as engineering features of the catalyst. So, we have to keep this things in mind while catalyst preparation. So, catalyst preparation is an art as well as a science as I said earlier also lot of chemistry involved here. The fundamentals of your heat transfer, mass transfer, diffusion and adsorption so, they are also associated. And then you have to look at the Leigh hunt base theory so it may be a polymer complex, it may be a precipitated agent.

So, pH may be a decisive factor because you are just decreasing the solubility of one component from the solution. So, this will get precipitated. So, depending upon this, there may be a variety of the methods for catalyst preparation. And one can have own method also in terms of the novelty, a combination of the several process. So, the fundamental if you look at here, the three fundamentally stages of catalyst preparation. So, the first one is that the preparation of the primary solid, which is just nothing but a kind of initial support or carrier on to which the active material is to be deposited.

So, this is associating all the useful components like impregnation. So, we talk it just now we are the low loading is desired we use the impregnation tackling low concentration, if high concentration is desired we talk in terms of co-precipitation. So, if you look at the co-precipitation or lot of complex mechanism of complexation formation is involved because the precipitation will take place under certain condition. Same thing in case of impregnation a kind of capillary action, some kind of force at adsorption forces may be desired.

So, we have to look at those when you are looking a impregnation tackling and that may be the different methods impregnation also, we will talk on that. So, Zeolites cation exchange, anion exchange because zeolites, you can have the proponent zeolites and then replace the hydrogen ion by the metal species. So, cation exchange or ion exchange may be involved and zeolites are very narrow or selective pore size. So, the diffusion may be the important phenomena and again because the molecule may be larger.

So, what is the mechanism of this transport that becomes important so the very selective? So, for Zeolite we will talk separately and then the crystallization of the material because when you are preparing the MCM type catalyst or Sapo or molecular C, what zeolite catalyst then, you have to be well specific for a particular phase. The first transformation step becomes very important. So, these are kind of hydrothermal reaction where you have the reaction takes place in the presence of water under certain pressure and large amount of time.

Some kind of ion exchange is taking place, formation of the complex and then it definite crystal forms and that formation of the crystal of via, what you call the nucleation jury that is very crucial. So, you have to look at different time intervals and then identify the phases or look at the crystal. So, you need a very specific type whatever the requirement depending up on the reaction. So, that that becomes a very complicated phenomenon here when you look at the crystallization showed you itself, which is base on nucleation.

So, this is the first fundamental thing and the second is the processing of that primary solid, which has been obtain from here to obtain a catalyst precursor. This may be just by your aging, but you call firing calcinations. So, there again you are getting developing some force and some pager. So, that becomes again important aspects during a catalyst preparation.

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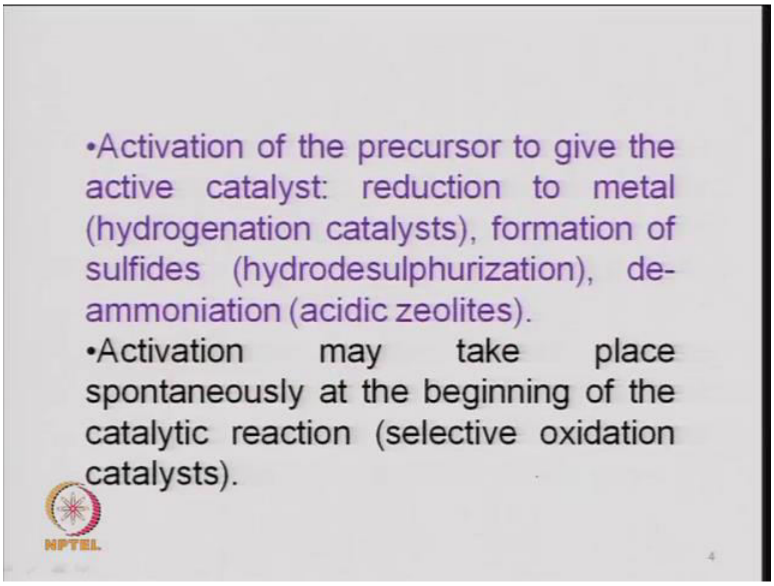

- Activation of the precursor to give the active catalyst: reduction to metal (hydrogenation catalysts), formation of sulfides (hydrodesulphurization), de-ammoniation (acidic zeolites).
- Activation may take place spontaneously at the beginning of the catalytic reaction (selective oxidation catalysts).

So, then activation, activation it can be a reduction type thing. You are treating the catalyst in the presence of hydrogen under certain condition, the refusing gas may be hydrogen it can be carbon monoxide. So, it depends on the type of the recursion required for catalytic reaction so, activation of the precursor to get the active catalyst.

So, this is deduction of the metal which may be hydrogenation that as I said the hydrogen is generally used to reduce to gas and formation of the sulfide. Sometime you pre-sulfide the catalyst as I said when the poisoning is faster because of the high activity of the catalyst when it is stress catalyst. So, you have to passivate the activity of the catalyst to certain extent also, it is not a severe passivation. Only at PPM level, the hydrogen sulfide treatment or Carbon-di sulfide treatment or any Sulphur precursors may be allowed to be in contact with that metal or catalytic species.

Same thing like de-ammoniation among removal of the ammonia so, when you did acidic zeolites because whenever we say the acid, it can be a different kind domestic type acidity or Louis type acidity. So, domestic type acidity means which can accept a proton and Louis type means which can donate an electron.

So, accept an electron donate a proton, so basically it is nothing but the formation of the species with a gaseous molecules. So, it can take a proton from the molecule and just get the proton at it and same thing again it can accept an electron and prompt the hydroxyl complex added almost. So that we will see later so, this activation species part is very crucial for a specific catalyst activity. For a specific catalytic activity you need to look at whether if carbide phase is important or just metallic phase is important, metal hydride phase is important, so it depends on the type of reaction.

So, the activation as I said depends on the temperature depends on the time, so pressure, time. So, it is a kind of exposure because during the activation it is a kind of time adsorption and says any oxide species. When it is in contact with some reducible species under certain condition of temperature and pressure make it because this is a Camay jobson, Camay jobson stable be related to the temperature a kind of activation required.

So, hydrogen cannot reduce platinum just at ambient condition. It need a certain condition of temperature so, you need to do temperature program reduction under a wide range of temperature and then check at what temperature the gas can reduce the metal oxide. So, that is the important and depending up on this condition, the size of the crystal is also that is metal dispersion, what I told last time and the growth of that crystal. Here also you can have because the metal oxide converts to the metallic form.

And you have to make insure or you have to make enough precautions in terms of that particle should not gets entered because otherwise agglomeration may be an issue. You have to develop some nano particle during your calcinations step, but when you reduce it in to reduction during the reaction because of the agglomeration the particle size may increase. So, activity may decrease so this these factors become very crucial in the catalyst preparation.

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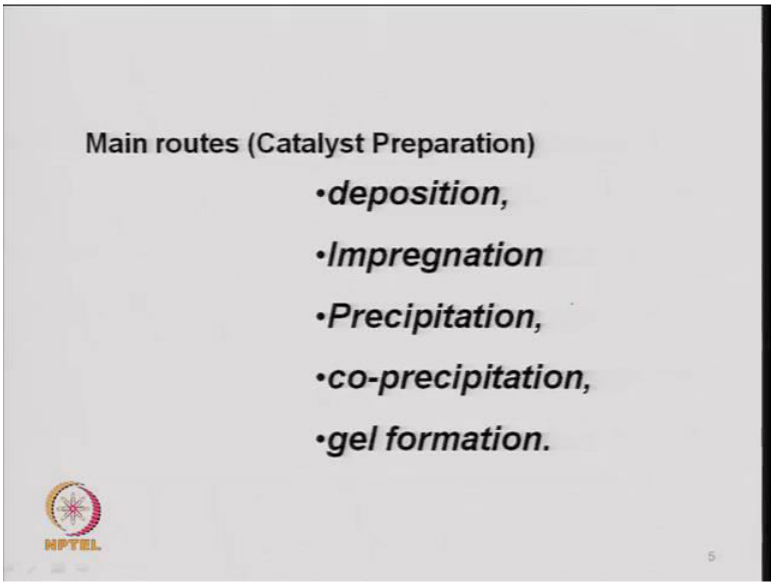

Main routes (Catalyst Preparation)

- deposition,
- Impregnation
- Precipitation,
- co-precipitation,
- gel formation.

So, in general say the catalyst preparation there can be the different methods or a combination, but it can be a deposition or some time we call it precipitation deposition also. So, the next one is the impregnation as I said that the where the low concentration is desired. Then again precipitation which is again based on the complexion theory very complex method, but you can have a well dispersed particle here. The large concentration of the metal can be used and the dispersal may be good particle size, may be uniform or it is it may be a smaller nano particles, but the preparation is very complex.

You need to tune the conditions in terms of temperature in terms of agitation in terms of the PH, which is very control or very decisive factor here. And same thing the co-precipitation you take two components to make two solutions and then co-precipitate them just like magnesium carbonate and nickel nitrate you take and make nickel carbonate and then these two are precipitated. A solution, B solution add them mix them and then control the pH at sodium carbonate or ammonium hydroxide to take the precipitate. So, you can have a mixture of two components and then you calcine it. So, basically sometimes the approached may be different as I said here that sometime we take the dry mixing also which is not been send here.

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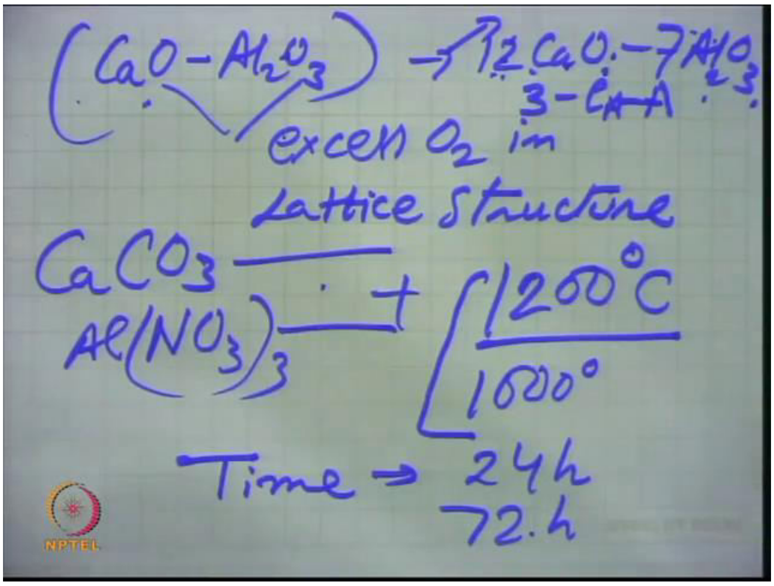

$(CaO-Al_2O_3) \rightarrow 12CaO-7Al_2O_3$

3-CaA

excess O_2 in lattice structure

$CaCO_3$

$Al(NO_3)_3$

1200°C

1600°

Time → 24h

72.h

So, suppose you have a calcium alumina, it is very simple example of catalyst preparation but, gives a very good catalyst here also. Sometimes these kind of catalysts are desired calcium oxide, aluminum oxide something like that. So, this type of catalyst they have a sufficient amount of basicity and also they provide the sufficient excess oxygen in their lattice structure. So, because of this these are good for poke removal.

So, the carbon which forms because of this oxygen, excess oxygen is present in the lattice structure. It reacts with that and then you can have the low deactivation and simultaneously they are providing a kind of basic sides. So, these kind of catalysts I have also been tested for reforming reactions or they can also be used where you need a kind of non porous or you do not need a very high surface area catalyst.

So, the basic idea is that here, you take the precursor, suppose you take calcium carbonate there can be surface system you take some salt of this, so it can be aluminum nitrate also something like this. Now, what about a composition you need because the component depending up on the temperature and time, it may present in different phases. It is not a component like calcium oxide and aluminum oxide, rather it is a phase definite phase and there can be different phases. So, it can be just like 12 Ca O-7Al 2 O 3, which has been tested so many times for paralyses reaction of hydrocarbons.

So, 12 Ca O-7Al 2 O 3 it can be 3 Ca O like this 3Ca-A I will write like this so C a 1 it can be just like this. So, there can be different so if you see here this has more oxygen in its lattice structure because it will be O 12 basically Ca 12 O 12 here and then Al 14 and 21 Oxygen. So, large amount of oxygen is present in these kind of and simultaneously they are providing of certain kind of basicity also.

And this is the preparation of one kind of support species also you can call, over which another matter like nickel can be impregnated and that can also be tested for reforming type of reaction. Because it has a kind of basicity alumina is amphoteric calcium oxide is basic, so you can have and now how this force have been developed. So, you can make a dry mixing of these two in definite ratio, suppose you need 12 is to 7. So, you can take a definite ratio of these two and then heat treated to say may be 1200 degree centigrade and this is very important.

So, 1200 is a kind of now solid reaction, but you are using chemical reaction between calcium oxide and aluminum oxide. So, they are not in the physical form now after the sintering, it is a kind of sintering. So, definitely since the treatment is at high temperature so surface area will be low because the porous porosity will reduce in this case. So, it can be done at 1000 degrees centigrade and so this is what the temperature. Same thing is for time also, so time may be your 24 hours, it can be 72 hours to get a definite crystal.

So, the some little bit of trial and hit and trial is also involved here that which time is more suitable. And simultaneously lot of metal science is also important, but how these crystals grow during the reaction and so at what time the crystal will reach to a certain size or to get a desired stage. So, once you have identified that then, the preparation becomes easier. So, this is an example of dry mixing, which has not been shown here.

So, you have just mix the min a form of slurry and dried it and then given a heat treatment or calcinations at 1200 or 1000 for a period of 24 hour or 72 hour. So, different time and then you check the phases, which have been obtained during the treatment condition. So, this is another method of catalyst preparation. So, co-precipitation sol gel process, which is known as gel formation and there is another in the same continuously micro emulsion.

So, two time micro emulsion solutions like urea. So, they have a kind of some suspension, they can make a suspension that the particles their metal particles can be finely distributed or well dispersed. And when you rupture the emulsion and then finally, they will come in the small particles form. So, that is known as micro emulsion technique, which is similar to your gel formation technique.

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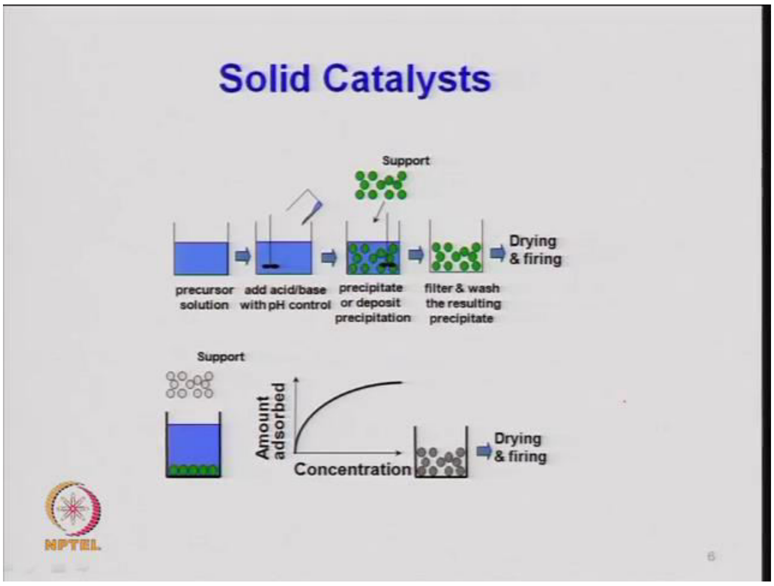

Solid Catalysts

This is just a crucial or typical step for that you have a precursor solution, precursor I am saying the metal precursor, it can be in the form of say nickel nitrate. Generally we avoid the chlorides and sulfide because the sulfur goes in the final catalyst even at some PPM level it may disturb the catalytic activity because of the poisoning. So, generally nitrates are preferred in that case, but in certain cases the sulfides may also be taken.

So, this is a precursor solution which can be your metal, metal precursor and where the solution can be depending upon, you have the complex which you have taken or the metallic complexes like what I said they may be soluble in alcohol also. And certain sometimes it dissolves in alcohols also, but water is the best one. It can be used as a solvent in many cases for the inorganic solid. So, this is the precursor solution and then you have acid, add acid or the base that will depend on the PH, small concentration say ammonia hydroxide sometime we add or acidic acid we some kind of buffers.

So, to adjust or to control the pH because pH is a decisive factor in all these reactions so, I will talk on that later. And then you have a support precursor, the support may be a readymade support just like alumina, silica. All these supports can be made when you have something like a method co-precipitation technique or sol gel; there you get the support also during the preparation.

So, it means you can control there that actual property of the support also. So, that will become a more crucial step or what I said the formation of the complex, which is again dependent on so many factors, which are taking part during the reaction or formation of that complex. So, that time the impregnation step is little bit easier or easier compared to your co-precipitation or sol gel method because there are support is also being prepared during the hydro gel formation or xero gel formation.

And then finally, you are calcining or drying that. So, you have a metal you have a support so, this is a kind of a just the co-precipitation technique. If you are not making a precipitate then, you can have just the impregnation technique also here. And then drop by drop you add take the support in a different vessel and then add drop by drop with a known volume of that solution and known mass of the support, depending up on the initial or final concentration of the catalyst which is desired.

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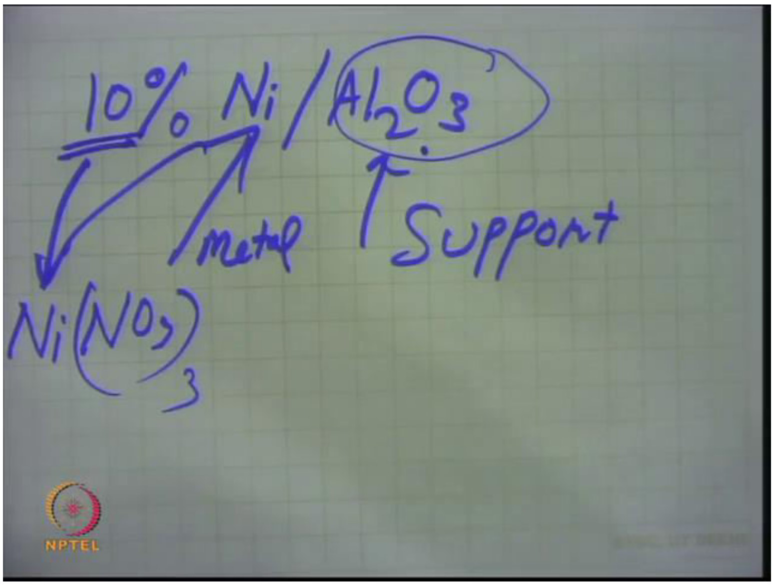

So, when we say we report the catalyst property like this, suppose 10 percent Nickel on alumina. If I write like this, this means that this is your support and this is your metal. So, the meaning of this if I say like this, so 10 percent nickel of alumina means that in 100 gram of the catalyst, there is 10 gram of the Nickel and remaining 90 is the aluminum oxide. So, this is a final catalyst, but precursors will be a Nickel nitrate, so whatever the solid nickel nitrate you have taken, this may be aluminum nitrate, but if it is an impregnation technique, so alumina support may directly be taken from some commercial vendor and then metal can be deposited.

So, you need not to worry about this part because its texture property everything are already well defined. And here you have to focus that in order to get this 10 percent, how much this will be required then, it will convert to nickel oxide and then finally, when you reduce you get nickel. So, the material balance or mass balance is very important in order to calculate the final mass of the metal desired in a given composition of the catalyst. So, this is just written one mono metal, there can be bimetallic there can be multi metallic also.

And same thing for the support also especially, when you are looking co-precipitation method, so you will take a solution of the aluminum nitrate say tersely betide aluminum hydroxide. So, these kinds of complexes you can take, which will decompose during our gel formation step, so that depends. So, here if you look at the support which is mixed here where, this during the pH adjustment you will get it precipitated and then the support is added and the metal will deposit on this.

So, you just filter and wash the resulting precipitate and then dry it at ambient temperature. And then followed by oven drying say around 105 degrees centigrade over night and then you fire it, firing means calcinating, which may be at 500 degree centigrade for 5 hour. It may be 600 degree centigrade for 7 hour something like this. So, the calcinations temperature is basically the conversion of the nitrate salt of the metal into its oxide form.

So, what is the temperature required either it is known as a priory or you just do some thermogrammatic analysis. So, take some nickel nitrate small concentration and put it in your thermogrammatic analysis and just check the weight loss. So, you can have the idea that what will be the most suitable temperature for calcinations, you can get idea. So, this is what happens that your amount adsorbed at different concentration will be different so, initial concentration is important.

So, that is how much metal concentration can be adsorbed on the surface of a solid because once you have a kind of impregnation technique, it is the adsorption base principle. So, there are kind of binding between the metal and support it is not the just like the physical. So, the adsorption will depend on the initial concentration of the metal.

So, that you have to calculate and accordingly you take a decision for preparing. And finally, again so this is a kind of impregnation technique, this is a kind of co-precipitation fact.

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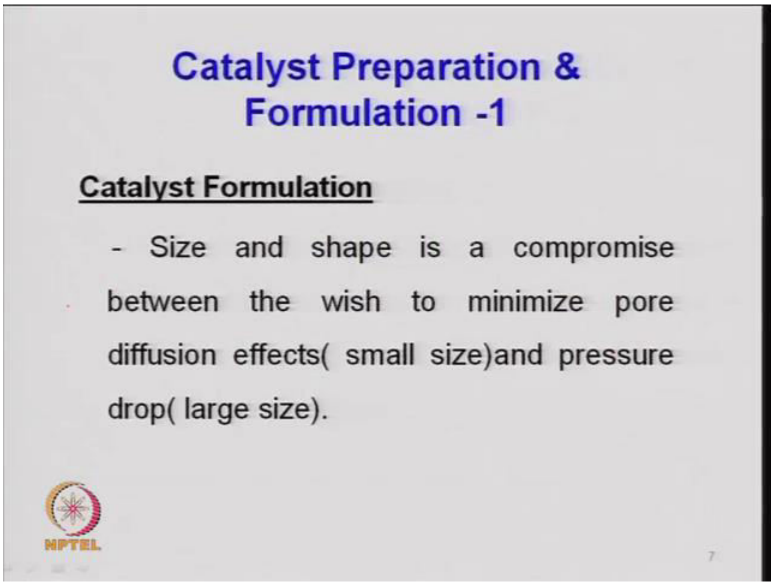

Catalyst Preparation & Formulation -1

Catalyst Formulation

- Size and shape is a compromise between the wish to minimize pore diffusion effects(small size)and pressure drop(large size).

So, catalyst formation, the funda is that the size and shape what I said this is the compromise between the wish to minimize the pore diffusion effect. So, smaller the size the pore diffusion effects will be minimum. That is pore diffusion resistance will be minimum when your particles are smaller in size. So, crystal particles I am talking, metal particles I am talking and funnel is the catalyst pellet size I am talking.

So, all these are equally important and same thing that when you have a smaller particles size than pressure drop will be large. So, you have to tune this two in terms of the size and shape of the pellet because shape is also equally important. So, that is the first thing that smaller crystal sizes are always better because you have a larger dispersal for this crystal size. So, that is the first thing that nano catalyses the catalyses in nano catalyses. So, how to develop this kind of crystals, you take the weather ethanol will be used as a solvent instead of water or some other heat treatment condition, some novelty in the process which can give you finely disperse metal particles on a support. So, that becomes very important in terms of the catalyst development and design.

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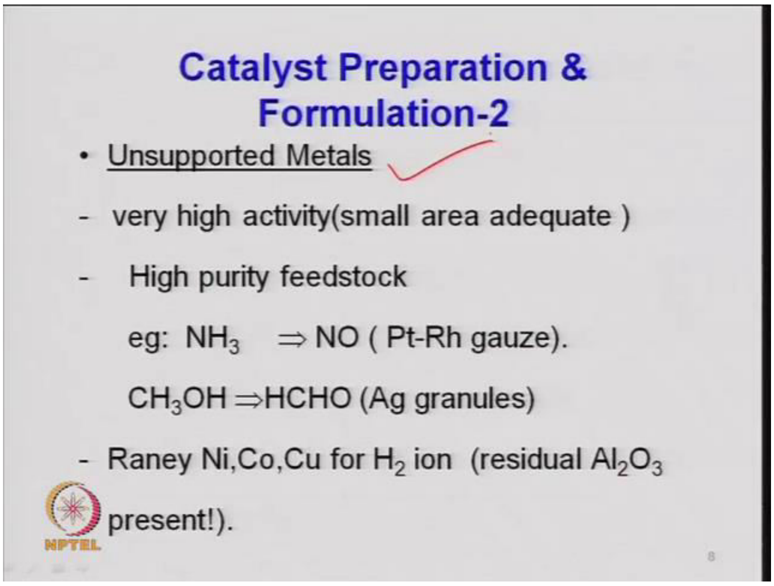

Catalyst Preparation & Formulation-2

- Unsupported Metals

- very high activity(small area adequate)
- High purity feedstock

eg: $NH_3 \Rightarrow NO$ (Pt-Rh gauze).

$CH_3OH \Rightarrow HCHO$ (Ag granules)

- Raney Ni,Co,Cu for H_2 ion (residual Al_2O_3 present!).

The second funda is that when you have unsupported metals sometimes we use directly the complete metal as a catalyst just like the wire gauge catalyst, which were use for the automatic exhauster. Absorb oxidation that is socks, nocks, cocks are sometime c way catalyst, which are monolith types. So, in this case very high activity because they are just like a small area is sufficient because they are activity very high. So, they are itself a total matter just like in the case ammonia oxidation small process.

So, oxidation ammonia to get nitric oxide the platinum rhodium gauze is used as a catalyst. Now no support so, this is a complete the entire material is used as a catalyst, so, this are known as unsupported. So, same thing when I say that germanium five is used as a catalyst or alumina is used as a catalyst of some of the reaction. So, there is no support for this itself the entire the metal is being is used as a catalyst. Same thing if you look at this, all convergent to formal dihyde, this is also over a silver ganguals.

So, that is also, but now a days the research being done to have the support also because the surface area agglomeration is the problem. But otherwise if you have silver nano particles, the formation of silver nano particle is little bit difficult, but they have very high activity. Same thing I told that for co oxidation also that is lot of research has been done; just to give they are using the platinum nano particles.

The oxidation can be done at room temperature you need not to go to high temperature if you have a nano particle of platinum. So, and production of this kind of nano particle is not difficult, sometime produce this nano particles, which is similarly just you take the salts and then just decompose it under certain organic complex and make a organovetlic complex of that and then rupture the gel. And then you give some kind of bombardment if you need to deposit on them some support separately.

So, the process that is how this nano particle will attach to the support, after once you prepared the nano particles separately and then you are attaching to the support. So, that is again is separate science and very difficult when it is not easy to prepare this kind of error. What can be done and same thing that sometime you use the oregano metallic complexes of this or gel, which is just like your hetero homogenous catalyst, so that is the concept.

So, that is another important concept because this homogeneous catalyst has very high activity for a given reaction. So, homogenous catalyst have been developed or tested for the process provided, if your sufficient technology for separation and purification and reuse them in the process, that is very important. So, this can be separated by centrifugation, there is separate technique available for the separation of the homogenous catalyst also.

On the other side if you look at Nickel, Cobalt, Copper, Hydrogen ion, they may be on alumina also, sometimes Raney, nickel itself acts as a catalyst. Although par ferric, it is very difficult to control it because it becomes the bio ferric atom condition, but for methane decomposition reaction Raney, nickel have been tested as a catalyst. So, you have to put them in alcohol solution otherwise, they will just explore when you have kept it in the oxygen. So, this can also be as a added used it as a catalyst cobalt, but some time many time the cobalt copper they are just deposited on some support.

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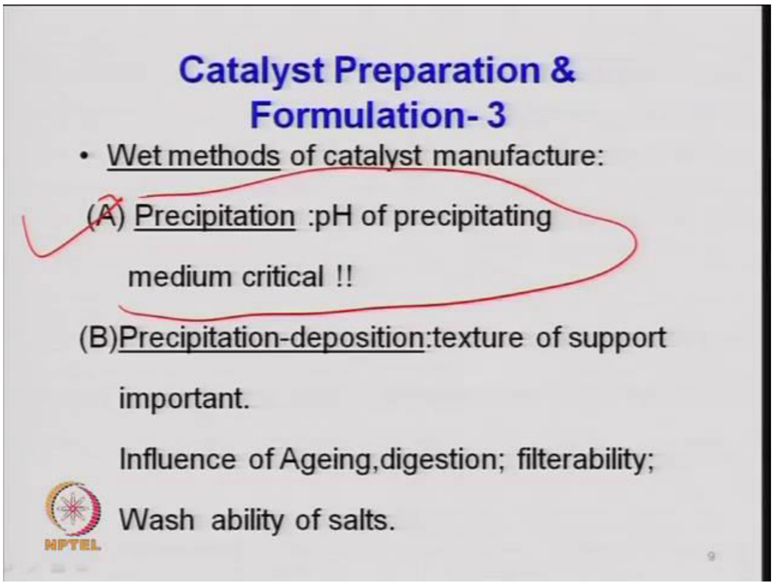

Catalyst Preparation & Formulation- 3

- Wet methods of catalyst manufacture:

(A) Precipitation :pH of precipitating medium critical !!

(B)Precipitation-deposition:texture of support important.

Influence of Ageing,digestion; filterability; Wash ability of salts.

So, the preparation part which we are talking is that the precipitation method. So, precipitation method the pH of the precipitating medium is very critical because you are just decreasing the solubility. The precipitation means you are precipitating one component that can be done, when you decrease the solubility. And here pH this is a factor which is nothing but the hydrogen ion concentration.

So, depending up on this because the complexation formation is the function of PH, so what kind of complex you are forming or whether on oxide support, the cation will come or anion will come. So, that is again the pH factor so, that will depend on point of zero charge, so we will talk on that. So, same thing for precipitation deposition method that you have a texture of the support, which is very important because what kind of support is being used, because that will come during precipitation and deposition texture.

So, similar to pro precipitation technique, but slide the pH becomes a very important in both cases in fact. When you look at the deposition or and development of this particle because it is a complexation formation, and growth of nucleate formation for a definite crystal. So, here the ageing is very important that for how much time you are keeping digestion process, but kind of organic precursors or solvent has been taken then filtration, washing and all the whatever the type of salts. So, how fast they can just go and precipitate and then can be washed and then take it dry it and age it. So, this depends on the type of salts.

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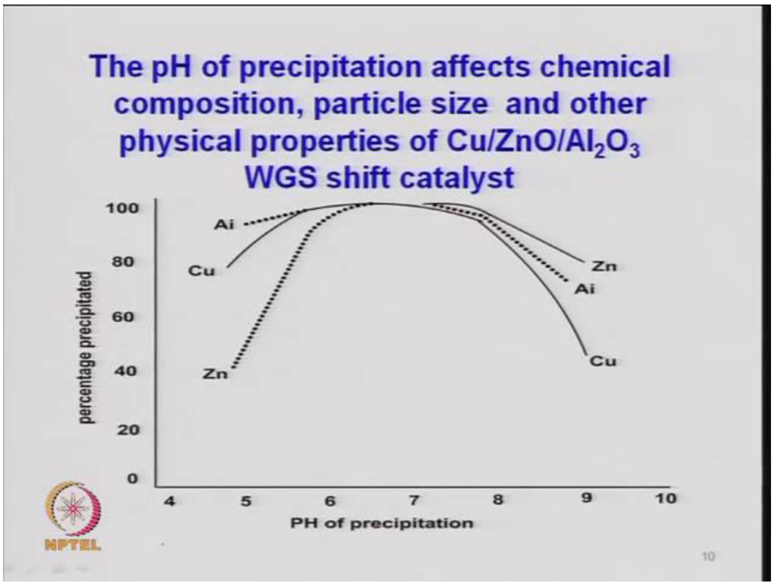

The pH of precipitation affects chemical composition, particle size and other physical properties of $Cu/ZnO/Al_2O_3$ WGS shift catalyst

So, I was talking that pH is very important or this is an example for water gas shift where, you have CO plus H 2 O gives you CO2 plus H2. So, this Copper, Zinc, Alumina catalyst can be used, they are affective for that, but there are other catalyst also in novel metal platinum group metal, they have also have been trusted for water gas. So, just as a example that when you prepare this kind of catalyst for WGS reaction, the pH of the precipitation affects the chemical composition, particle side and other physical property.

So, not only in terms of that decreasing the solubility, but also it concludes the nucleation size. So, growth of the particles at one points the growth because it is a function of super saturation. So, when this growth stops or you get a good kind of crystal or definite shape of the crystal that becomes very crucial and pH pressure is very important role. So, here you can see that for Zinc this is the curve for this dotted line, the zinc line and this is for copper and then this is for aluminum here.

So, for different metals you will have a different PH, so pH5 to 9 if you look at here and between 7 and 8 your maximum percentage precipitated here somewhere. So, this becomes very crucial factor in terms of the growth or in terms of deposition of this three. Suppose, you have taken the salts of all these different components in a solution and then you had adjusted the PH.

So, each component will precipitate depending up on its PH, that is a point of zero charge and then accordingly the growth will take place, the particles as well increase like that. So, the final catalyst or final solid material, which you get at the bottom that will have a property in terms of the particle size, shape and what about the concentration that is, how much particle of particular component have been precipitated or has been precipitated.

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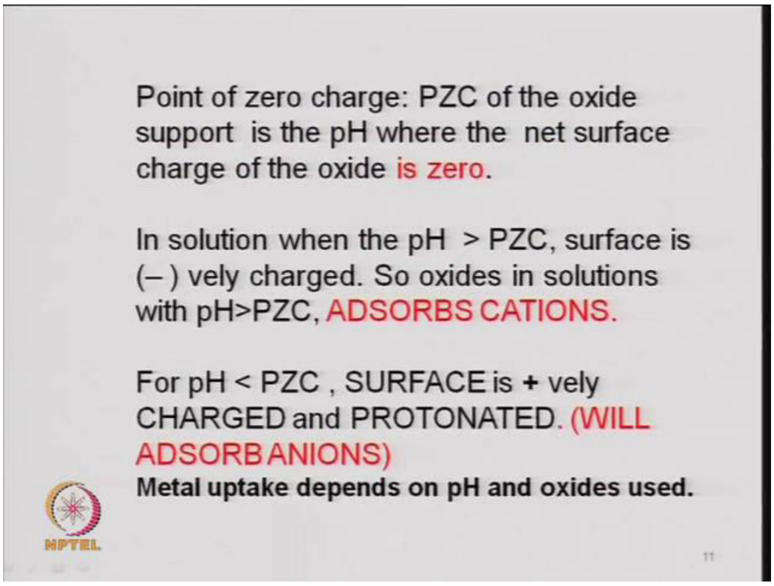

Point of zero charge: PZC of the oxide support is the pH where the net surface charge of the oxide is zero.

In solution when the pH > PZC, surface is (–) vely charged. So oxides in solutions with pH>PZC, ADSORBS CATIONS.

For pH < PZC , SURFACE is + vely CHARGED and PROTONATED. (WILL ADSORB ANIONS)

Metal uptake depends on pH and oxides used.

So, that becomes a very important point of zero charge, I was talking PZC very important because when you talk PH. So, with that it is an adsorptions phenomenon there also it may be a function of pH very important very crucial factor. So, point of zero charge of oxide support is the PH, where the net surface charge of the oxide is zero, so at that there is no charge, neither positive nor negative.

So, this can be PZ method, it is just nothing but a titration method or there are other PZ potential by which you can PZ. So, otherwise titration that the net charge on the surface or oxide is zero. For example, suppose the solution where the pH is above this PZC the surface is negatively charged. So, if the PZC of the oxide it is a suppose x and pH is suppose an acidic side.

So, when I am saying the pH is greater than the PZC, so suppose PZC 07 so, pH is eight solution pH is 8 like that 9 10. So, there this is the 8 and this 7 so, when pH is greater than PZC then the surface has negative charge hydroxyl ion concentration will be there. So, oxides in solution than pH are greater than PZC, they will adsorb cations. All the cations will come to the surface when your pH of the solution is greater than PZC. So, pH means 8 9 10 and PZC may be 5. So, that time your cations will adsorb on the surface that is very important to take pH.

And what is the most optimum pH for getting the precipitation especially, when you are preparing the pressure catalyst iron base cobalt base catalysts. So, the pH becomes very decisive when you look at the co-precipitation because when you are taking high concentration of this matter precursor, the co-precipitation method is better compare to wet impregnation or impregnation or incipient vectors method. In total they are known as impregnation method.

So, co-precipitation method is preferred or sol gel method is preferred because it may have a smaller particle size, it may have larger surface area of the support compared to whatever you have the protonated method. So, this is first then pH is less than PZC, so just I am saying PZC 7 so it is 2 3 4 acidic medium something like that. So, the surface is positively charged, the oxide surface will have a positive charge and this is known as surface is protonated and that time it will adsorb anions.

So, this fundamental thing is used for adsorption also, selection say removal of die organic metal or removal of nickel chromium, they all depend on the pH. So, which kind of adsorbent has to be selected that will depend on the PZC of that absorbent. So, whether your activated carbon is good for nickel removal or nickel adsorption chromium adsorption so, all it will depend of PZC of the adsorbent oxide support. So, so the same thing for the catalytic activity also, when you are looking at precipitation, you want more and more solution to get precipitated or metal precursors to get into the solid explicate.

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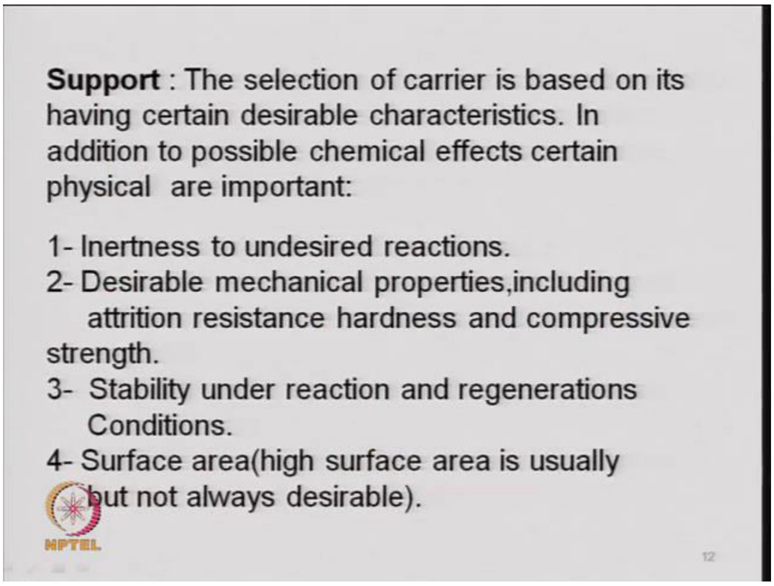

Support : The selection of carrier is based on its having certain desirable characteristics. In addition to possible chemical effects certain physical are important:

1- Inertness to undesired reactions.
2- Desirable mechanical properties,including attrition resistance hardness and compressive strength.
3- Stability under reaction and regenerations Conditions.
4- Surface area(high surface area is usually but not always desirable).

So, that time you have to check what is the PZC of that oxide support. Support we have already discussed so many time, either you say carrier or support. The selection of support is based on having certain desirable property. So, mainly see chemical effects we will see we have already done also, but physical properties are also important so, inertness to undesired reactions.

So, when you are saying that this is acting as a support and alumina support and portrait, so I am trying to take zeolite as a support acidic in nature. So, when you need feel that the carbon formation or core forming activity is more or tracking is the phenomena and you do not want the tracking during the main reaction, so, you should not take zeolite there because zeolite will promote the tracking reaction.

So, when you track you will have a smaller hydrocarbon. So, it means when you do not want the activity for a given undesired reaction so, the support should be such that it should act as an inert for that undesired reaction. That is the first basic thing that whether silica should be taken, alumina should be taken or any clay material zeolites so that depends on the activity for a given reaction, which may be undesired for a given.

If it is desired then it is good that select the support in which cures that and multiple reactions takes place. And desirable mechanical property as I said earlier it is very important, which include the attrition resistance, hardness and compressive strength. There should be enough strength because you make the tablet from the powder so, the porosity is important, but simultaneously the particles should not scramble, so that is again important.

So, in of my spherical distance is desired stability under reaction and regeneration condition. So, they should not sinker among itself the alumina particle as I just give the example, when you heat the aluminum oxide from say room temperature to 1000 degree centigrade, it converts to gamma aluminum converts to the alpha alumina. So, alpha alumina has very low surface area 2 meter square per gram, gamma alumina has 220 meter square per gram.

So, the because of the centering the particles size increase so, your over all crystal is growing basically. So, surface area will reduce poring to volume and also the porosity is decreasing because of the centering phenomena so, this should be avoided. When you are looking a repeated regeneration cycle or where the catalyst is used for large period of time. And same thing surface area so, generally we prefer high, but not all the time, just like as I said when the mass of a control reaction, the internal surface area may not be important.

The porosity may not be important; the important thing is the diffusion line that should be kept minimum in the case of monolith types of reaction mass transfer control reaction. So, that wires gauge which I am saying platinum wire gauge or silver so, they are essentially the mass transfer control reaction, no diffusion into the pore of a catalyst. So, we do not want that in fact because everything is taking place on the external surface of the sodium. So, that is what when I am saying the nonporous, that time it is just providing in the external surface. So, you should take care the in terms of the particle size and the porosity when you feel that during is no diffusion limitation, it should be avoided.

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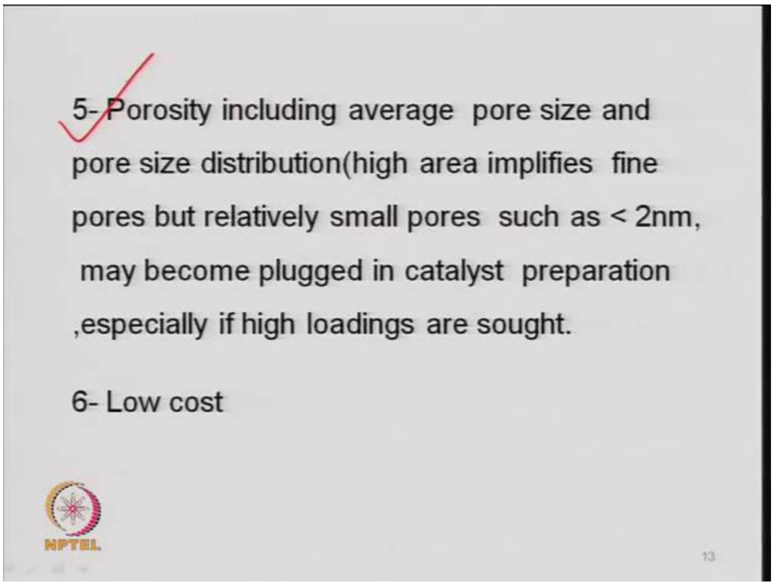

5- Porosity including average pore size and pore size distribution(high area implifies fine pores but relatively small pores such as < 2nm, may become plugged in catalyst preparation ,especially if high loadings are sought.

6- Low cost

So, porosity as I said earlier also, which includes the average pore size and pore size distribution. So, high area which implifies the fine pores, but relatively small pore such as 2 nano meter or less that, which are generally the micro pores. They become plugged in catalyst preparation especially at high loading are sought. So, when you need a high concentration of the metal and your catalyst is something like a micro porous material, so plugging may take place.

So, it means you have to take care, whether you are going with the ion exchange process. So, in the only we just replace the hydrogen ion by some gallium or platinum, ion exchange is more preferred because pores may block. So, in that case you have to look at a certain kind of anion or cation exchange process or ammonium forum of the zeolite, which may be converted to hydrogen form and then metal, can replace that. So, ion exchange process, which are slow generally, but this will be more effective for the preparation of this kind of value.

So, you have to just take care when you have a micro pore then, the plugging of these pores may be common because of the larger size of the crystal particle or the higher concentration of the metal. A smaller concentration is enough especially, as I said when the desired concentration is low, you go with the impregnation catalyst the cost of course, it should be low.

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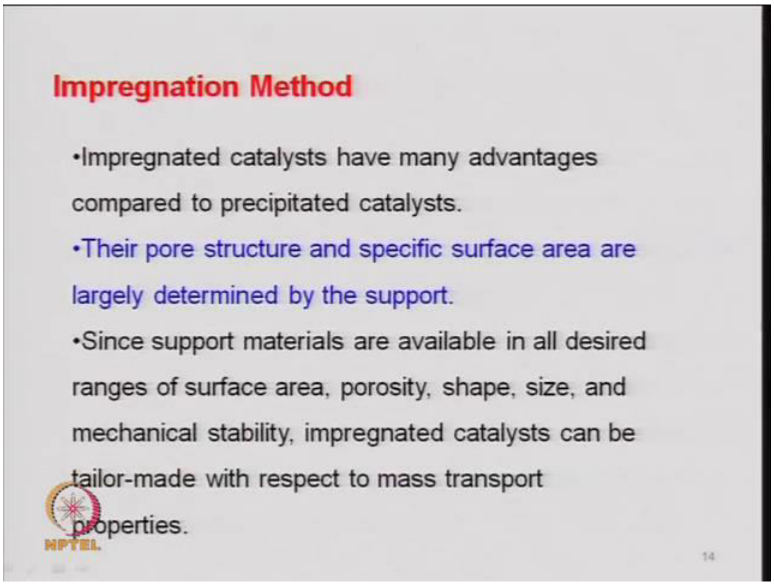

Impregnation Method

- Impregnated catalysts have many advantages compared to precipitated catalysts.
- Their pore structure and specific surface area are largely determined by the support.
- Since support materials are available in all desired ranges of surface area, porosity, shape, size, and mechanical stability, impregnated catalysts can be tailor-made with respect to mass transport properties.

Impregnation method we have already talked in brief, but it has advantage if you look at compared to the precipitated catalyst because it is not a very complex process. So, their pore structure and specific surface area are determined by the support. Because in impregnation method what you are doing, you are taking the metal in solution form and then drop by drop you are adding or dipping that solution in some vessel, where you have already the support or support has been dropped in that solution. So, generally we take that in one of the vessel something if you do the impregnation technique, so generally in one of the vessel you take your support like this.

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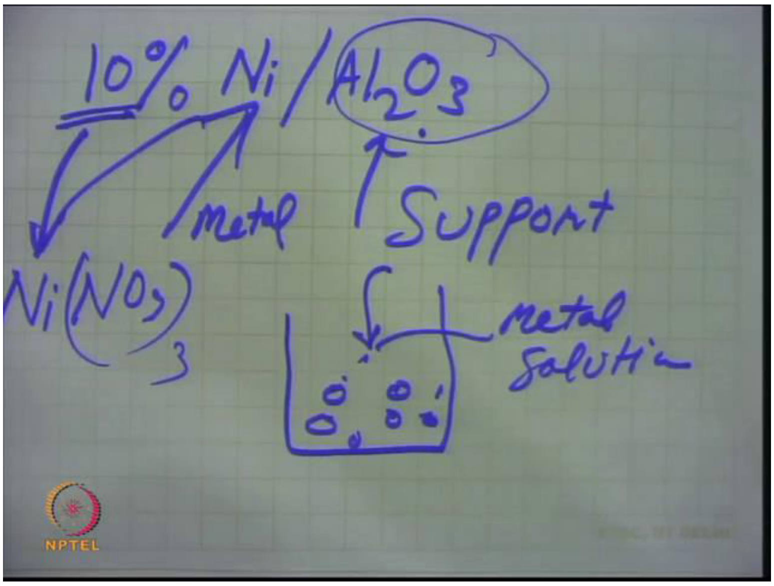

And then gradually add from the top throughout a micro pipette or pipette and add drop by drop the solution so, metal solution just as I said you in the picture earlier. So, supports are here and then shake it slowly or gradually and keep on adding it, till it becomes saturated and then dry it and calcine it. So, this supports are already available or already you have prepared it by co-precipitation and characterize them. So, surface area of the support you already defined, porosity of the support is already defined and that is why the concept of incipient wetness, the name indicates certain impregnation technique is known as incipient wetness.

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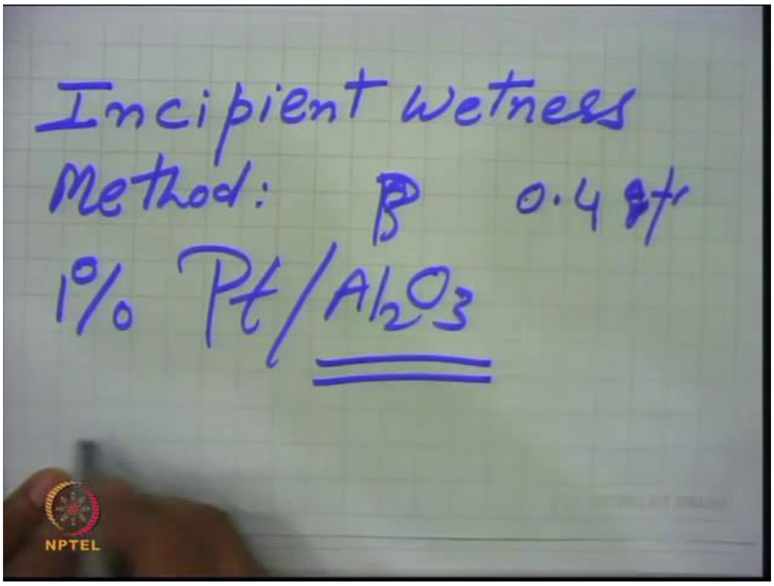

Incipient wetness
Method: β 0.4 [illegible]
1% $Pt/\underline{\underline{Al_2O_3}}$

So, this method meaning the pores are just filled so, this is generally used when a small concentration or the precious metal is to be deposited on some support, which has large area say platinum. So, if I write platinum on alumina where only 1 percent of platinum is to be deposited on alumina, it means for a 99 gram of alumina and 1 gram of platinum on the catalyst, this concentration because this is a dilute now. So, take say n, I am saying incipient wetness so, measure the surface area and pore volume of the support on a priory, so preformed support you call it. So, if I say that suppose the pore volume of this alumina is 0.4 centimeter cube per gram.

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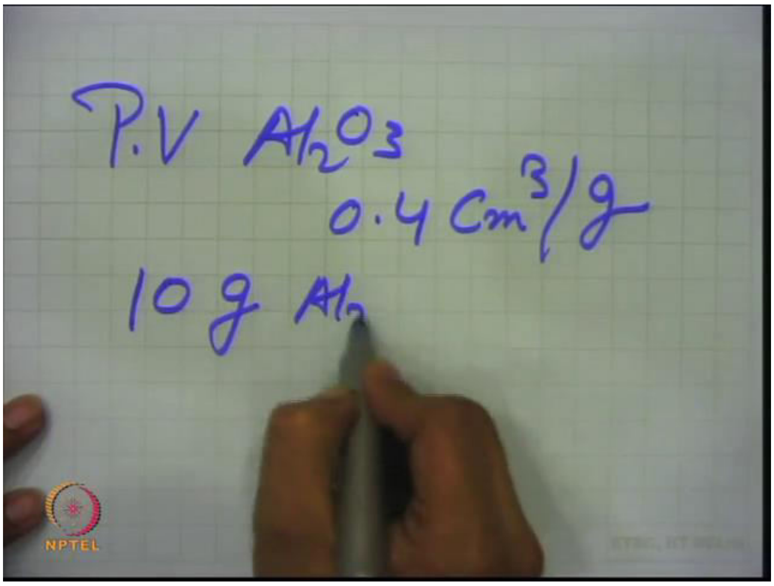

So, I will write it here pore volume alumina pore volume, which is already characterized is 0.4 centimeter cube per gram. So, this is the 1 gram of the alumina will have this much number of cavities or cylindrical pores.

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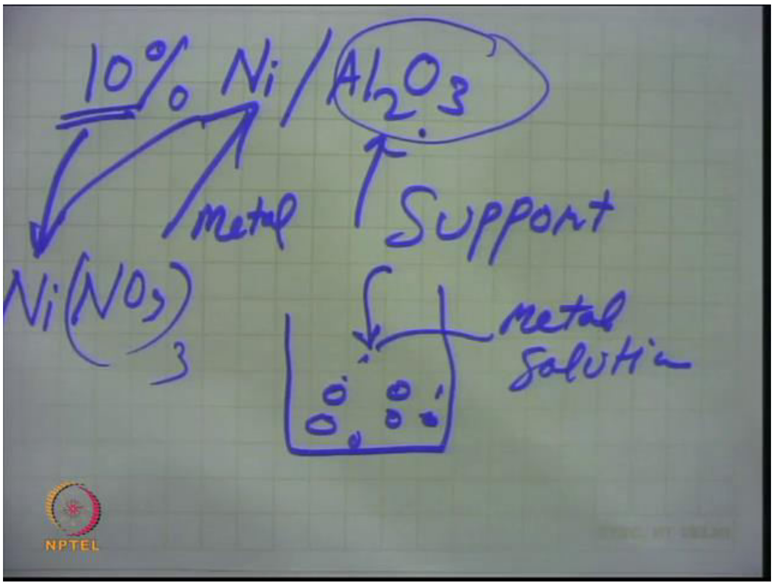

So, this much suppose you take 10 gram of alumina, I think if you do the impregnation technique so, generally in one of the vessel, you take your support like this. And then gradually add from the top through a micro pipette or pipette and add drop by drop the solution, metal solution just as I said you in the picture earlier. So, supports are here and then shake it slowly or gradually and keep on adding it, till it becomes saturated and then dry it and calcine it.

So, this supports are already available or already you have prepared it by co-precipitation and characterize them. So, surface area of the support is already defined, porosity of the support is already defined and that is why the concept of incipient wetness, the name in the case of impregnation technique is known as incipient wetness, so this method meaning the pores are just filled.

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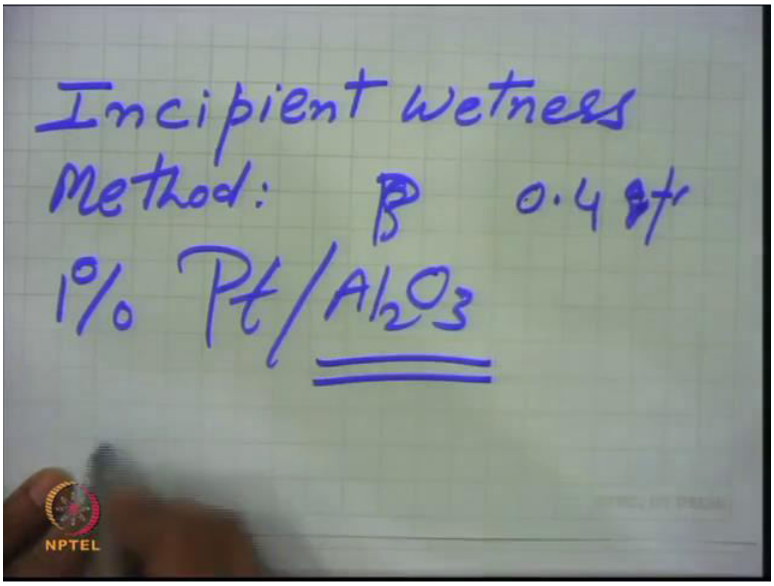

Incipient wetness
Method: β 0.4 g/r
1% Pt/Al_2O_3

So, this is generally used when a small concentration of the precious metal is to be deposited on some support, which has large area say platinum. So, if I write platinum on alumina where only 1 percent of platinum is to be deposited on alumina, it means you have 99 gram of alumina and 1 gram of platinum on the catalyst. So, this concentration, this is a dilute now, so you take say and I am saying incipient wetness. So, measure the surface area and pore volume of the support on a priory. So, preformed support you call it.

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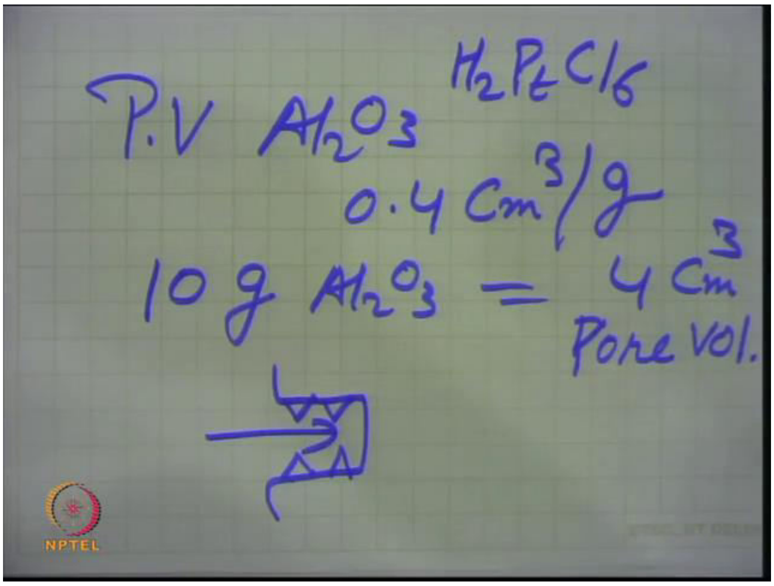

H_2PtCl_6

P.V Al_2O_3

$0.4\ Cm^3/g$

$10\ g\ Al_2O_3 = 4\ Cm^3$

Pore Vol.

So, if I say that suppose the pore volume of this alumina is 0.4 gram per centimeter cube per gram, so I will write it here pore volume alumina, pore volume, which is already characterized as 0.4 centimeter cube per gram. So, this is the 1 gram of the alumina will have this much number of cavities or cylindrical pores. So, suppose you take 10 gram of alumina so, the volume will be 4 centimeter cube total capillary volume.

So, it means the water, which will go into the capillary like this in a solid will go here, the solutions will diffuse inside and then the active side will deposit like this your platinum. So, solution is diffusing and how it is diffusing because of the capillary action. So, capillary forces are dominating here in the impregnation method or in what incipient vector. So, incipient vectors means pores are justified, so we do not give any larger volume of this solution, we take just which is equal to the pore volume or slightly higher than that. So, suppose you know the pore volume is 4 centimeter cube for 10 gram of alumina so, you just take this platinum, which may be in the form of H 2 P 2 C 1 6, chloro-platinic acid.

Generally this is a good precursor for platinum, you can take platinum chloride also, and you can take any other salt of the platinum also. So, H 2 P 2 C 1 6 a given mass to prepare this 0.1 gram or 1 percent of platinum, you have taken 10 gram so, it means in 10 gram it will be 0.1 gram. So, to have 0.1 gram of platinum how much of this H 2 P 2 C l

6 will be required, you can calculate from stoichiometric non priory. So, and that much mass of H 2 P 2 C l 6 will be dissolved in 4 centimeter cube of water very small.

You can just go slightly on a higher side because excess water will remain will come out, it will not go inside because once capillary is filled it will come out. So, it means the just this mass of the H 2 P 2 C l 6 will be dissolved in 4 centimeter cube of water or maybe you can take 6 centimeter cube of water and just shake it, it will dissolve easily in that. And then from micro pipette you add a drop by drop to this in a vessel, you take it in a vessel here. So, these are the alumina say and add drop by drop.

So, it will become saturated excess water will come out you can very clearly see it and then dry it in the oven over night and then take it out and then calcine it. So, calcination temperature roughly for this, it can be 550 degree centigrade and for 5 hour time or you can check it with different trials. So, you can have platinum on alumina by using incipient vector type.

Since platinum is very costly, it is much more costly than gold so, the cost of this is very crucial. So, the high dispersion of the platinum is desired on the support because the small concentration of platinum should be sufficient to give you enough catalytic activity. So, that is our aim and this platinum metals, they have stability also, their life is very high. So, they can be used as a catalyst.

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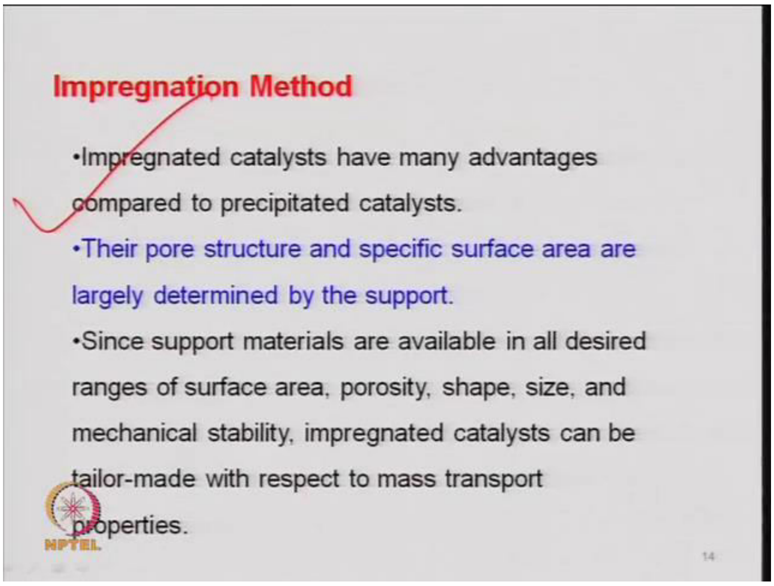

Impregnation Method

- Impregnated catalysts have many advantages compared to precipitated catalysts.
- Their pore structure and specific surface area are largely determined by the support.
- Since support materials are available in all desired ranges of surface area, porosity, shape, size, and mechanical stability, impregnated catalysts can be tailor-made with respect to mass transport properties.

So, that is why the novel metals are being looked into for the reforming reactions and the reactions where the deactivation or catalyst stability is an issue. So, impregnation plays a very crucial role in this case. So, pore structure of the support and surface area of the support should be well defined in this case.

So, since support materials are available in all desired range of surface area, porosity, shape, size and mechanical stability, the impregnated catalysts can be tailor-made with respect to mass transport properties. So, control is in your hand now because you know or a priory their properties so that is the advantage of impregnation method. So, you know what the pore size of this is, you know what the pore size distribution is, so for a given reaction suppose you are taking a sulfur aromatic ring. So, diffusion may be controlling for that, but suppose you have a methane smaller molecular or hydrogen so, diffusion may not control. So, kinetic diameter of the gas molecule and the pore diameter of the support, that will decide and you have already the idea for that.

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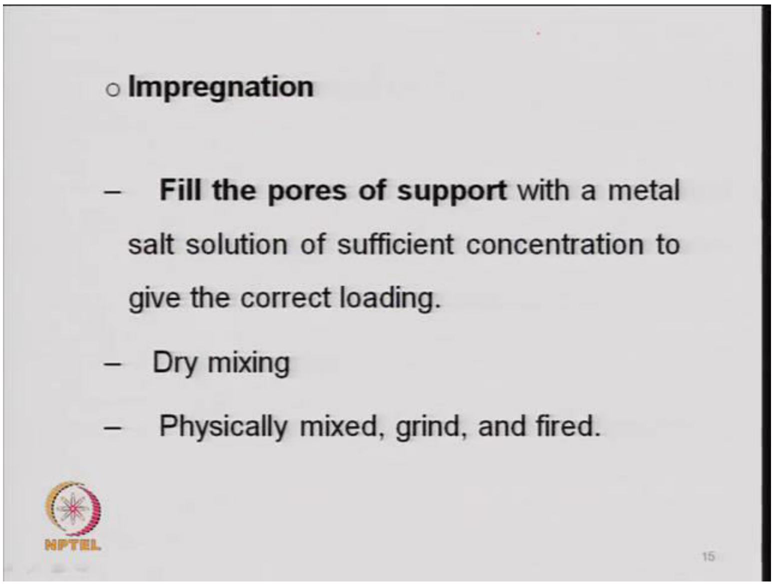

○ **Impregnation**

- **Fill the pores of support** with a metal salt solution of sufficient concentration to give the correct loading.
- Dry mixing
- Physically mixed, grind, and fired.

So, you can have that advantage once, you have this impregnation method because supporting already preclude from some other source and it is physical chemical property are known compared to co-precipitation method or other methods. The basic I have already talked that in the integration method you fill the pores of the support with the metal salt solution of sufficient concentration to give the correct loading. So, again here becomes a very decisive factor because of high loading low loading and point of zero charge what I discussed before. It can be dry, mixing also and physically, mixed, grind and calcine, so any method can be used here.

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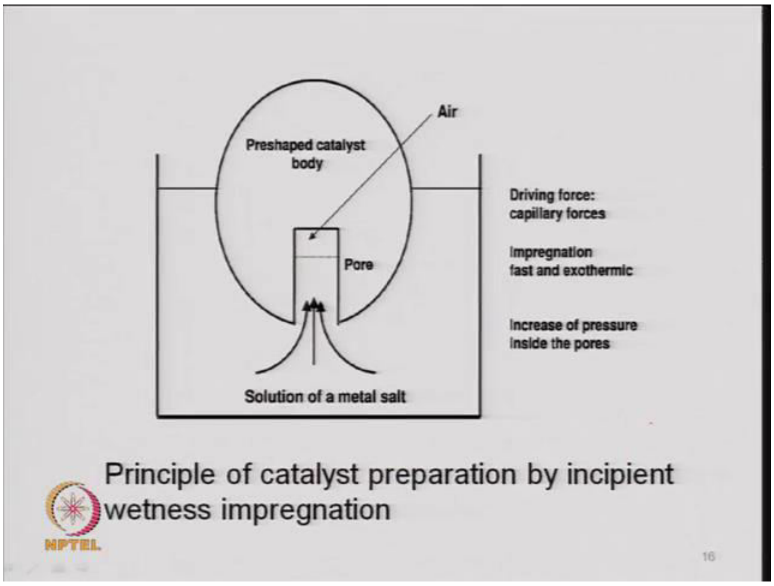

Driving force: capillary forces

Impregnation fast and exothermic

Increase of pressure inside the pores

Principle of catalyst preparation by incipient wetness impregnation

This is just an action of the capillary phenomena solution of the metal and this is going into the pore here like this, so this is one pore. So, please check the catalyst support you accurate it to remove the air if it is there. So, generally we connect it to the vacuum system to remove the air from or any gas, which is inside the pore and dry it over night before using so that all the moisture from the pore should be removed. And then we get a pore volume and then do this thing.

So, pores are filled with that and then they will adsorb on the surface, the metal is adsorbing on the surface of that. So, the driving force is capillary force as I said here. So, impregnation is very fast and exothermic because it is a kind of adsorption, so adsorption is exothermic. And increase of pressure inside the pores because the solution is diffusing inside so because of that they have displacement here. So there will be a kind of pressure phenomena which you see during the principle.

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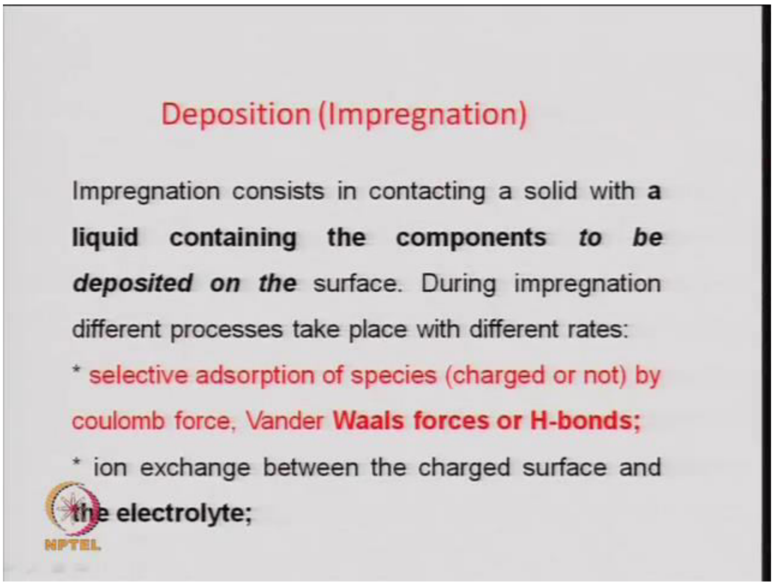

Deposition (Impregnation)

Impregnation consists in contacting a solid with **a liquid containing the components *to be deposited on the*** surface. During impregnation different processes take place with different rates:

* selective adsorption of species (charged or not) by coulomb force, Vander **Waals forces or H-bonds;**

* ion exchange between the charged surface and **the electrolyte;**

So, this is the principle of catalyst preparation by incipient wetness method. Another is again the deposition is same as impregnation point so, this consist of contacting a solid with a liquid containing the components to be deposited on the surface. So, same thing what I said that in the case of incipient wetness, you are taking the volume just equal to the pore volume, but this is similar to your excess solution method or you call it wet impregnation method also, where you do not bother about the pore volume.

So, means say I said that 4 centimeter cube was taken, but if excess solution method because you know the austral dilution low. So, dilute concentration means it has more and smaller particles, smaller ions. And the idea is that the particles are well dispersed in the solution and when you use your capillary force then, diffusion will be faster because it is a dilute solution, the gradient will be less in terms of the resistance for diffusion.

So, this is the advantage when you take a large excess of that solution in water. In incipient wetness the dispersion may be a problem because you have taken just equal to the pore volume. So, all the particles may agglomerate at some point because they are just in the small volume and whatever the calculation you have made 0.1 percent of that platinum or 0.1 gram of platinum salt was taken in that or platinum is pieces by taken.

So, that was dissolving just 4 m l of that so, it will become a concentrated solution. So, it may agglomerate when it adsorbs on the surface. So, particles may be larger that is the nano particle concept may not come here in the incipient method. But in this case because it is a kind of excess solution, we have large amount of water so, it is a kind of dilute. Now it will diffuse easily into the pore faster and then the since the concentration is solid is low so, it will adsorb on the surface and the chances are their probability is there.

Then the two particles may not sit on the same side or same place because it is in very dilute solution, but there may be some waste also because you have taken excess water. So, that is the drawback on the other side, so during the impregnation the different process take place at different rates. That is what I said the selective adsorption of the species whether it is charge or not by the Coulomb force Vander Waals force or hydrogen bonding because I said that it is a kind of adsorption now on the surface. So, all it will dependant up on the zero charge of the oxide in the pH of the solution. And accordingly the adsorption will take place and sometime the ion exchange between charged surface and the electrolyte is also important that may take place.

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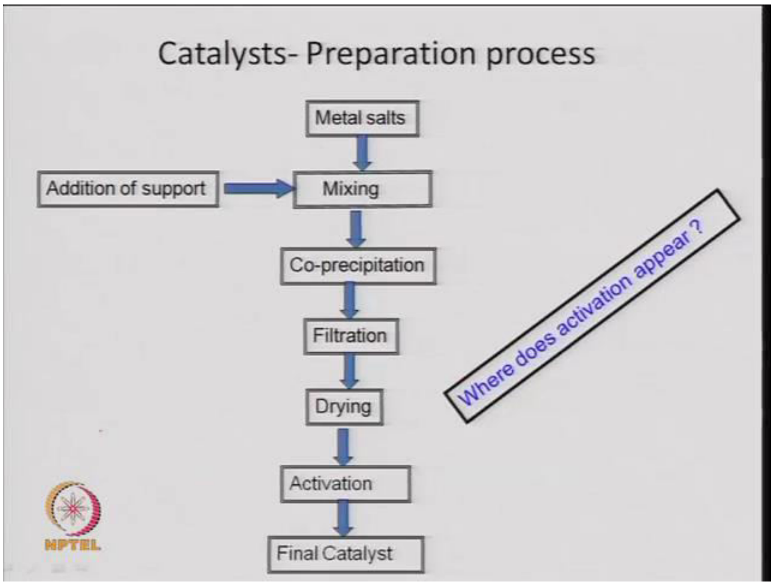

Catalysts- Preparation process

Metal salts

Addition of support

Mixing

Co-precipitation

Filtration

Drying

Activation

Final Catalyst

Where does activation appear ?

This is just a flow sheet if you look at the impregnation method, the metal salt you have taken you have added support, you have mixed it dry mixing what I have talking or you can have a solution of that, this is a co-precipitation method. Then you got it co-precipitated not the impregnation, co-precipitate it, then filter it then dry it then activation.

Activation means treatment in the presence of hydrogen or any reactive gas where you are converting the oxide phase into the magnitude or carbide phase or carbonyl phase, that depends on the reaction. So, which phase is important for your catalytic activity that should be known based on the reactant or that should based on the catalytic activity and then, finally you get the catalyst for the reaction.

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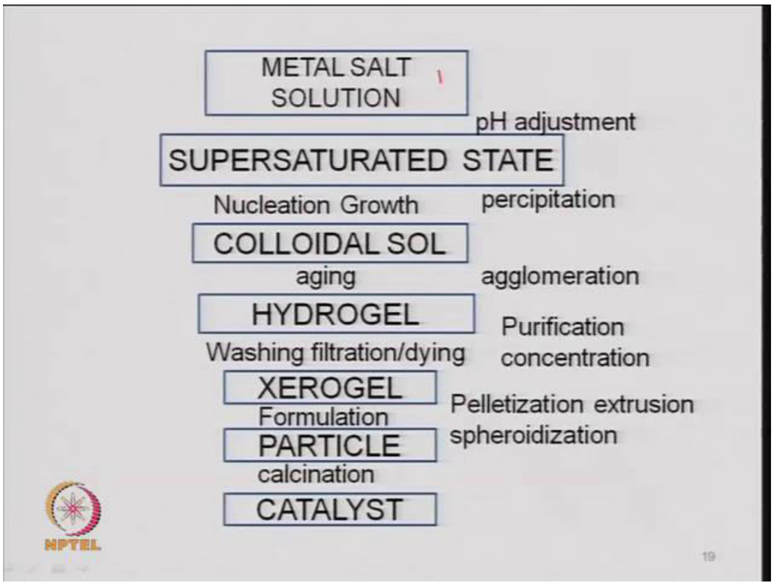

METAL SALT SOLUTION
pH adjustment
SUPERSATURATED STATE
Nucleation Growth
percipitation
COLLOIDAL SOL
aging
agglomeration
HYDROGEL
Purification
Washing filtration/dying
concentration
XEROGEL
Pelletization extrusion
Formulation
spheroidization
PARTICLE
calcination
CATALYST

Same thing we have for the metal salt solution, pH co-precipitation technique because this is another same flow sheet that is what you have seen before, the approach may be different in catalyst preparation, pH adjustment. So, you have super saturation state here and by adjusting the pH so, that means the maximum precipitation occurs. Then because you know the when the crystallization take place, the growth is done nucleation growth so, complexation formation basically and it increase in size and then settles down.

So, you will have a kind of colloidal gel, so this is a kid of sol gel method also where, you have a hydro gel or you have taken the organ of metallic complexes and adjusted the pH and then kept it under a state condition for a long period at certain temperature. So, you will have a formation of the gel where the particles are well disperse inside that hydro gel and then you have just a heat treatment. So, you will get a hydro gel and then you wash and dry it.

So, you call a dry powder zero gel and then finally, you just give the heat treatment or a calcine it, if required. Here you can make the pellet also, this powder can be taken to a die at a given size and you make the tablet from that powder and then you calcinate. So, by step that you can do the calcination before also you have the dry powder you calcine it and then make the tablet, but generally when you make the tablet you add certain kind of binders also say a poly vinyl alcohol 1 percent.

So, when you do that make the pellet then again you need to give the heat treatment to remove that binder. So, it is advisable that first to make the pellet then do the calcination. So, that during the calcination the binder will go out, but sometimes it happens that during calcinations you are make the pellet, after you have made the pellet and then calcine it, sometime the pellet may gamble also. So, you have to just check depending upon the particle size that is very crucial in the calcination step and when you make the tablet of that.

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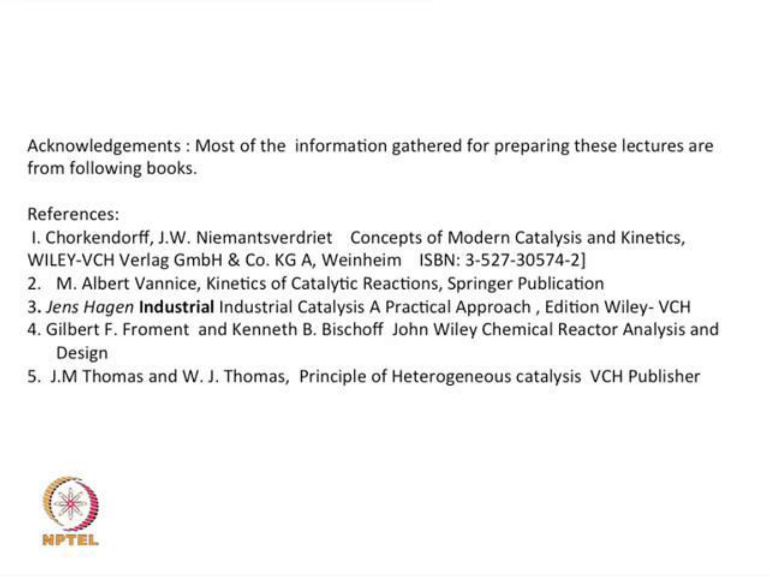

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References:
I. Chorkendorff, J.W. Niemantsverdriet Concepts of Modern Catalysis and Kinetics, WILEY-VCH Verlag GmbH & Co. KG A, Weinheim ISBN: 3-527-30574-2]
2. M. Albert Vannice, Kinetics of Catalytic Reactions, Springer Publication
3. *Jens Hagen* **Industrial** Industrial Catalysis A Practical Approach , Edition Wiley- VCH
4. Gilbert F. Froment and Kenneth B. Bischoff John Wiley Chemical Reactor Analysis and Design
5. J.M Thomas and W. J. Thomas, Principle of Heterogeneous catalysis VCH Publisher

So, these are very crucial step in this calcination step when you get a definite phase of that catalyst or powder definite size of the catalyst powder. So, particles calcine them and you get the catalyst. So, I stop here.