# Heterogeneous Catalysis and Catalytic Processes
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## Lecture – 03

In last lecture, we were discussing about homogeneous and heterogeneous catalysis different type of catalysis which are used. So, depending upon the reaction type of reaction where the catalysts are used; they are broadly classified as homogeneous and heterogeneous catalysis. So, this is the broader classification.

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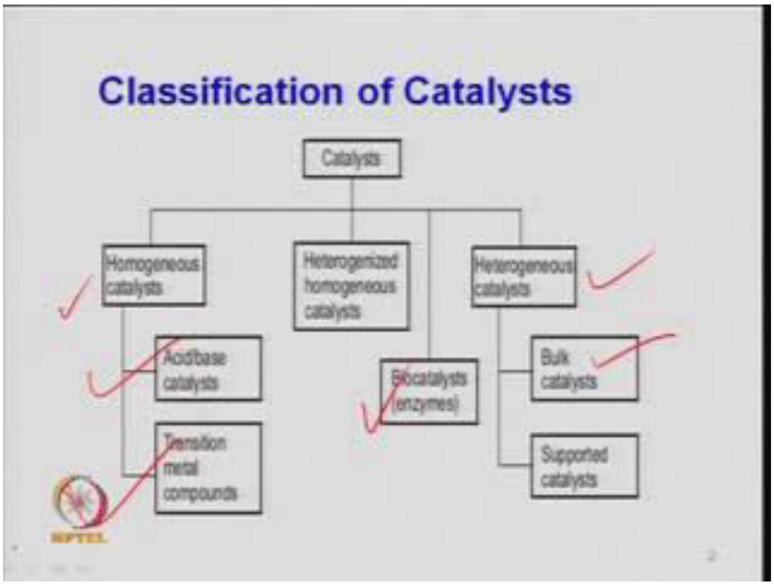

Classification of Catalysts

- Catalysts
  - Homogeneous catalysts
    - Acid/base catalysts
    - Transition metal compounds
  - Heterogenized homogeneous catalysts
  - Biocatalysts (enzymes)
  - Heterogeneous catalysts
    - Bulk catalysts
    - Supported catalysts

And, sometimes in between we can have a combination of hetero-homogenous like organo metallic complexes which can have some solid particles or small particles. And, partly dissolute into the liquid something like biocatalysts or enzymes; they are also amino acids high molecular weight acids amino acids. And, they when you have the reaction during the reaction and bio enzymatic reactions the part of these dissolutes and acts like an homogeneous catalyst. And, in the rest acts as a heterogeneous catalyst.

So, sometime these are also categorized as a heterogenide homogenize catalyst. So, broadly if you look at it is homogeneous and heterogeneous. So, if you look at your sulphuric acid alkylation and right or H F alkylation or $H_3PO_4$ that is phosphoric acid polymerization. So, these are homogeneous reaction in petrochemical industry and still they are being used although the acid concentration is very high. And, a different kind of material or construction is required for these kind of reaction. So, if you look at homogeneous catalyst; we have acid base catalyst; so as I said that biodiesel formation. So, trans astrification reaction where methanol is used along with the esters or long chain methyl esters or fatty acid methyl esters are the product which are known as biodiesel; and mainly form from the triangle sights.

So, fats oils, fats these can be converted into biodiesel; that is fatty acid methyl ester in the presence of some catalyst which can be a heterogeneous catalyst which is being tried now a days or it can be a homogeneous catalyst like sulphuric acid or caustic KOH, NaoH. So, these are example of acid catalyst and same thing I think I gave the example of HF alkylation which is again a homogeneous reaction system.

And, now in new concept which is being used for the homogeneous catalyst because the activity of your homogeneous catalyst is very high. So, everybody is looking for the homogeneous system and ionic liquid is also one of the examples of homogeneous catalytic reaction. So, transition metal complex which are organo-metallic complex; generally again in the form of the same metal which is used in the heterogeneous catalyst over some support.

Now, it can be in terms of something like a ligands like EDTA and over that have a metal complex which can form some organo-metallic complexes. So, these can be have a kind of homogeneous structure or gel type structure during the liquid phase reaction. And, can be used widely as a homogeneous catalyst; which has higher activity compared to the heterogeneous catalytic reaction. In heterogeneous catalyst we have the bulk catalyst we discussed last time also that the entire material itself acts as a catalyst, right.

So, just like if I use alumina for the dehydration reaction or geolide ZSM 5; normally they are used as a support but this can be used as a catalyst also. So, that is known as a bulk catalyst and supported catalyst sometimes or in more many cases; we would like to have the active metal deposited on some large surface area. And, there the active metal concentration is low.

But the support has a very high surface area and the idea is that the support can provides sometimes a different kind of sight also that is the acidic sight. And, metal function have may have some different kind of these are different kind of activity and they can be called as a bi-functional catalyst also. So, metal function and support so specially if you look at your reforming reacting plate; forming reaction in the presence of platinum alumina catalyst. So, it has dual sight or metal sight and acid sight.

So, parts of this activate the hydrogenation reaction; parts of the acid sights activate the isomerisation activity. So, these are the examples of the supportive catalyst. So, this is one broader classification of the catalyst but there can be the specific name the catalyst also say alkylated catalyst; which are used for alkylation reaction, hydrogenation catalyst, nickel, platinum, palladium, tiscon act as a acting as a hydrogenation catalyst. And, similarly for different reaction; sometimes we call it acid catalyst, sometimes we call it as a base catalyst. So, there can be other classifications of the catalyst.

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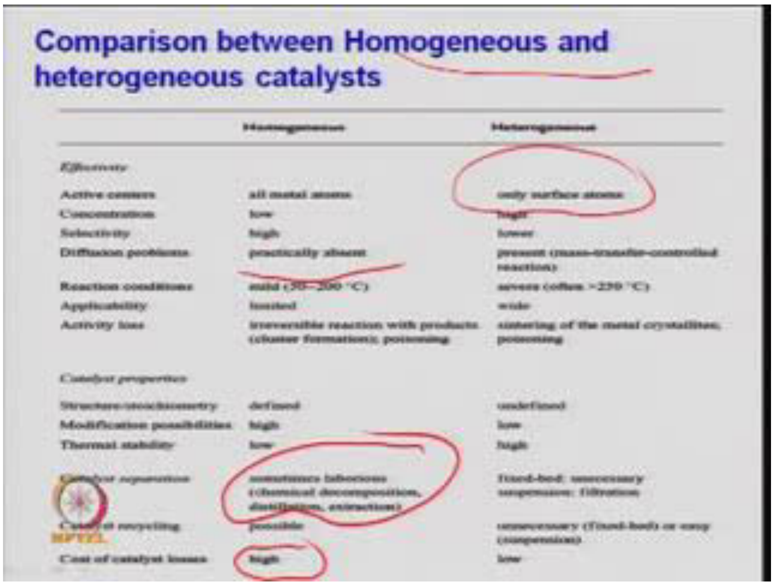

Comparison between Homogeneous and heterogeneous catalysts

There are advantages of homogeneous catalyst as well as for the heterogeneous also. So, just I have given here a comparison between homogeneous and heterogeneous catalysis. So, activity centers if you look at the homogeneous because it is the kind of nucleates or micro emulsions catalyst is in homogeneous solution, homogenide. So, it may micro structures or nano particles of the active material. So, the low concentration efficient in that way right. So, all type of metals will be there in the homogeneous solution. And, when you look at here the only surface atoms are active for the reaction, right.

So, which are the concentrations even may be high; but if the catalyst is not well prepared then the effective concentration may be too low. So, here in terms of concentration low concentration can be designed. But in the case of heterogeneous you may need high concentration; because total amount of material which is adsorbed on the support may not be active for the reaction; selectivity in homogeneous catalyst the selectivity is very high right or we call relatively high.

So, I that is why new trends are also looking for the development of homogeneous catalyst for the system; if other problems are resolved. So, here the selectivity is relatively lower compared to the homogeneous catalyst diffusion problems. Because the mass transfer, heat transfer these are the severe problems in heterogeneous catalytic reaction; when you have a solid and over that the gas or the liquid is adsorbing.

So, there may be a layers of the gas or liquid and creating a large amount of resistance for the mass transfer. So, mass transfer resistance is very common in heterogeneous catalytic reaction but in the case of homogeneous this diffusion problem is avoided. So, practically absent; same thing for the reaction conditions generally these are carried out at low reaction conditions.

But heterogeneous can be carried out at high reaction condition high temperatures. Applicability for the homogeneous because of that temperature limitation right they are very sensitive to temperature. So, it is limited where as in the case of heterogeneous catalyst they can be widely used. So, we still now heterogeneous catalyst are widely used in process industry because of the limitations of the homogeneous catalyst.

And, activity loss those most of the cases it is irreversible reaction with product. Whereas, in the heterogeneous catalyst the activity loss because of the sintering problem because of it is high temperature reaction condition. So, sintering may be a problem concentration of the active metal is large. So, it gets agguluramated in a reaction; properties wise if you look at catalyst properties the structure or stoichiometric it is well defined. Whereas, in the case of heterogeneous no clear cut definition is available in terms of structure of texture property, morphology, pore size pore size structure. So, many complicated structures are geometrical pictures may come when you look at a heterogeneous catalyst. So, sometime they are beneficial also in terms of the texture property if you have some kind of defects; the atomic defect electronic structure and there are certain kind of foreign elements.

And, that can provide you different kind of activity for a given reaction. So, sometime it may be good also. Thermal stability as I said earlier also homogeneous catalyst has lower stability compared to the heterogeneous catalyst. And, catalyst separation this is the big problem in fact in the case of homogeneous catalyst; the separation of the catalyst from the product or reactant mixture. So, sometimes it becomes a laborious or costliest of here where in heterogeneous this is not required.

Because all the time it is a solid catalyst and you can filter it easily. And, the cycling is possible if you can separate the catalyst from the system; then in homogeneous case the catalyst can be recycled. In fix bed also since the its not required; only regeneration is required when the catalyst activity draw faster; the cost of catalyst here because the preparation problem is severe. And, technology needs to be developed. So, cost of catalyst loses in this case is high compared to the heterogeneous catalysis.

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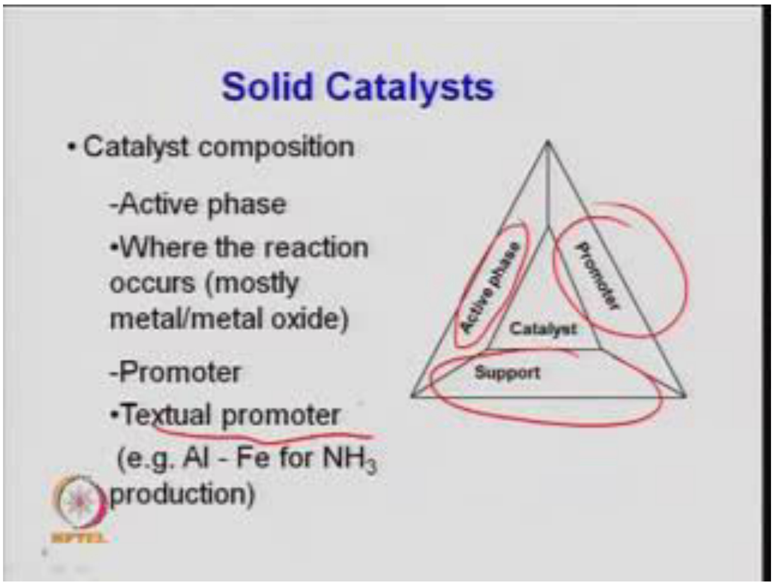

## Solid Catalysts

- Catalyst composition
  - -Active phase
  - •Where the reaction occurs (mostly metal/metal oxide)
  - -Promoter
  - •Textual promoter (e.g. Al - Fe for $NH_3$ production)

The solid catalyst what we are discussing is this course structure that in any catalyst you will have an active phase. But we are talking either a metal; then you will have a support on which you are depositing this metal. So, generally we need a high surface area. So, to provide a better dispersion and good kind of properties for the metal though good electronic structure. So, that is important and beside these two; that is the part of the catalyst to enhance the activity of the catalyst or to reduce the deactivation in the catalyst; we add promoters which may not have a catalytic activity. But it supports the main catalyst; in order to enhance the activity of some reaction or in it can suppress the activity of the undesired reaction also.

So, that that combination makes a complete catalyst that active phase what is active phase which may be metal right, inorganic metal. And, most of the time promoter may be some kind of which can have the texture promoter, which can have some kind of chemical strength provider right. So, all these kind of active metals like potassium can be a promoter for some of the reaction.

And, there can be iron just like ammonia you at the small concentration for the ammonia synthesis. So, that is a kind of promoter to enhance the or to support the main catalyst. So, will just talk on that. So, promoter is basically textual promoter. Textual promoter means, it is the its not providing anything to the catalyst but it provide some strength to the support. Because when you look at a f c c reactor just like fruit catalytic cracking; you have the jolted catalyst right in the since you are using food bed type reactor.

So, you need to have the smaller particles right. So, the particles are moving in the raiser which is of some cylindrical tube small diameter tube at certain velocity; along with the hydrocarbon vapors. So, these particles are just colliding among themselves. So, it should have enough mechanical strength right. So, in that case you need to provide a sufficient mechanical strength to the catalyst. So, textual promoters it can be a material which provides the strength to the catalyst or simultaneously it avoids the sintering of the material particle. How does it avoid the sintering?

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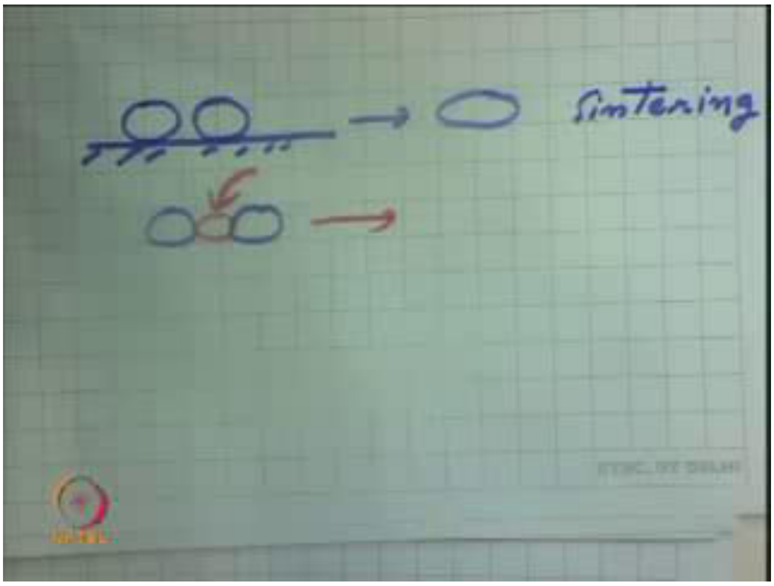

Just if you look at here suppose we have the metal particles here and another metal particle here which are and these two are separated on some support, right. So, what happens as I discuss last time that during the course of reaction or high temperature which will aggulumerate. And, it may become a larger particle which you call sintering right. So, this is the measure cause of catalyst deactivation because of sintering high temperature operation. But if you at some promoter in between; suppose if I have this particle, this is another catalyst particle.

And, in between you make some a bridging of some third element or third metal which sheets in between and a stable molecule. Now, this will not allow the metals to come together to come closer. So, this is a kind of textual promoter here right. And, this especially in this case of Fischer Trop reaction if you look at then the catalyst can or life of the catalyst can be prolonged during the reaction. So, this is what we were talking about the operation in terms of the sintering.

So, for the similarly for the if you look at here for ammonia; the aluminum iron generally they are used for the production; and they act as a textual promoter. Active sight what we discussed here active phase, right. So, it is basically the active phase which you are calling is the catalyst, right. So, catalyst it can be any metal but we have discussed earlier also. So, generally the good kind of metal; how to select the details of the that we will take later. But the most important thing is that the catalyst for a good catalyst activity the metal should have some unpaired d electrons or d orbitals per atom, right. So, number of d orbitals which are available in a metal depending upon that the catalyst will have activity for adsorption of say hydrogen any gas or carbon monoxide, right.

So, if more d orbitals are present then the binding will be stronger. So, it say strong biding because number of metals the d orbitals per atoms are more. So, as I said that the strong biding is also not desired. Because if there is strongly binded metal and the hydrocarbon species or the gas species strongly binded. Then, it will not allow the metal or metal will not allow the gas species to leave it.

Because ultimately it is something like that there should be a binding; then there may be a kind of transformation into some form of transition complex right or intermediate. And, which transforms to a adsorb product and that product desorbs. So, for having a good catalytic activity the interaction between these metal species is on the support; as well as interaction for a gas molecule onto a metal should be a controlled one.

So, that is it should neither be too strong or nor it should be too weak. So, if it is too weak the gas will leave the surface area right without converting into the product. So, this is very important when you select. So, generally is group 8 metal like all this platinum, palladium, cobalt, nickel; so they have 1 d orbital per atom. So, it has sufficient or reasonably good activity for adsorbing hydrogen.

So, they are good for hydrogenation or some. So, they can adsorb hydrogen easily and sufficiently bind it. But if you look at some of the metals which have large number of d orbitals niobium or even sorry molybdenum. So, they have the large number of d orbital in the metal form; they strongly binds the hydrogen or carbon monoxide on its surface. So, the activity for reaction will be poor.

So, you while selecting a matter or a support same thing for the support also the metal should not strongly binded with the support. And, also the when you have kind of say oxidation reaction; so silver can take oxygen easily. So, it may not be good catalyst for that. So, for some time to select a definite combination of metal support for a given reaction. So, it will depend on the type of the gas species also the type of metal and on the support where it is deposited. So, normally some time you taking support as an inert material but how this metal has been interacted with that support; that is also equally important for a chemical reaction.

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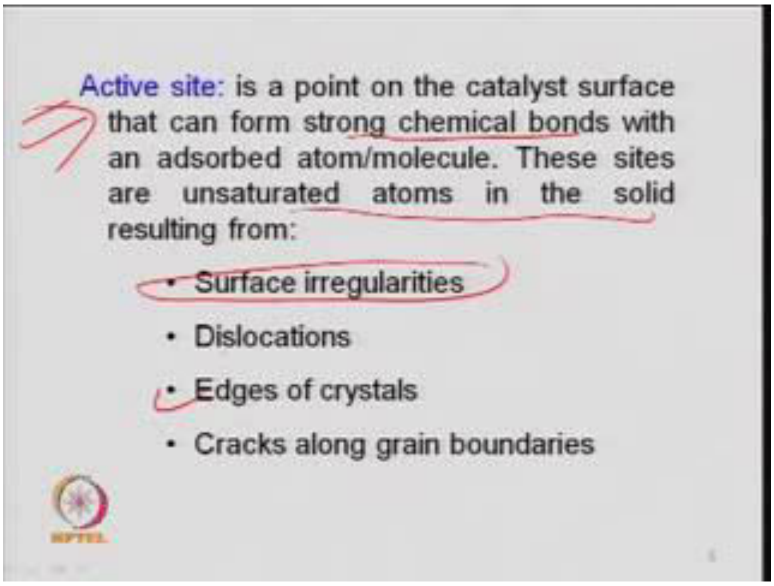

**Active site:** is a point on the catalyst surface that can form strong chemical bonds with an adsorbed atom/molecule. These sites are unsaturated atoms in the solid resulting from:

- Surface irregularities
- Dislocations
- Edges of crystals
- Cracks along grain boundaries

So, that is what I am talking here the active sight; which is more crucial that you have given the enough number of metal concentrations on your support. But it may not be active right. So, that is related to some number which is dispersion we will talk on that later. But basically the active sight is a point on the catalyst surface that can form strong chemical bond within adsorbed atom or molecule. So, this is the definition of active sight that it should take the gaseous species or reactant species. And, this definition will be used throughout the course.

Because whenever you have a catalytic reaction you talk in terms of adsorption of species a surface reaction and chemical that is surface reaction then chemical reaction. And, then transformation of the product final desorbs. And, that will happen on the active sight which is available on the surface. So, the active sights which is basically bonding of the metal; but if you look at the any unsaturated atom in the solid the active sight can come because of the surface irregularities. So, kind of defects, right.

So, in the metal generally or in a support also itself we talk in terms a structure a case how the metal is attached to a support and what is their electronic configuration? So, yesterday I was talking about f c c face centered cubic structure right; b c c body centered cubic structure. So, and it may be third one in h c c hexagonal cubic structure. So, idea is that whether they are in the form a cuboids and where these metals are attached to that cuboids. And, it and what is their orientation if I just look at talk x y z plane. So, 1 0 0 like that which has everything in terms of suppose; if I will say one is my x coordinate. So, everything is coordinate to directing towards x right; same thing it can be 0 0 1 also right everything is directed towards z coordinate system. So, how the molecules are or atoms are attached in the structure; that is known as the orientation of these. So, orientation of these metal on the support as well as orientation of the gas molecule which is along coming to this.

And, that is related to our sticking probability or sticking coefficient. So, sticking coefficient is something which is related to your original factor or rate constant used in the reaction. So, because it is the actual number of molecules which have interacted with the support. And, the finally they have they have been able to transform into some useful products right; they are able to convert to some intermediate which is for reaction. So, all the molecules gas molecules may not be active for the chemical reaction.

So, it means the surface to have some activity thus there should be some edges some defects. So, that is why when you look at a metal on a support you just look at it shape of the metal. So, spherical shaped, it may be just like a prismoid shape, it may be some kind of say ellipsoid shape. So different kinds of shape may be available and depending upon that the reaction activity.

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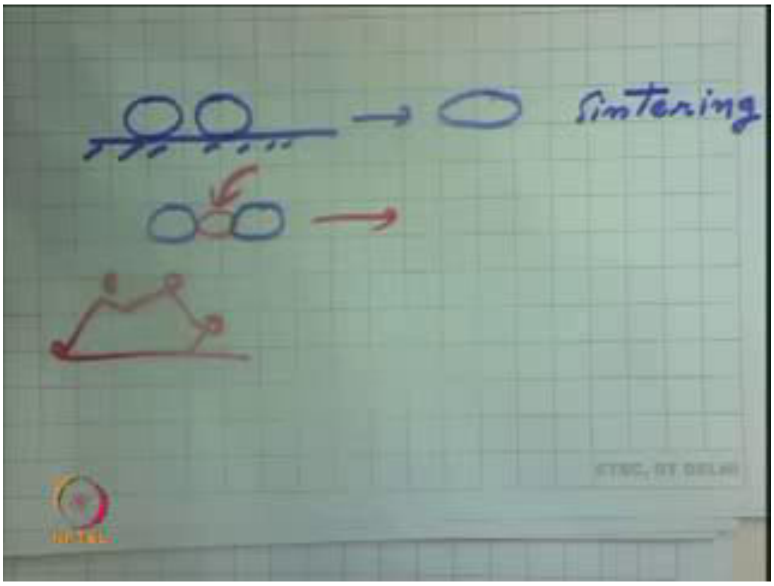

So, sometime we talk in terms of an edge which is something like this in structure something like this more and more edges; there you have the ability of a gaseous species;

which can come and attach on to this surface. So, these are some kind of defects or edges or electronic structure of the molecule; everything is important here in the case of catalyst. So, same thing for dislocation cracks along the boundaries. So, a certain kind of defect should be there in if you look at in totality we want to have some kind of defects; in a crystal to have a good kind of catalytic activity.

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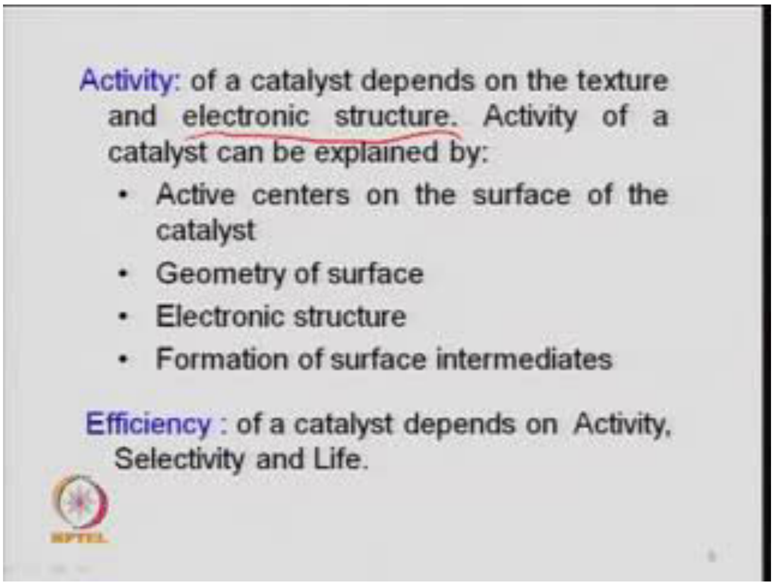

**Activity:** of a catalyst depends on the texture and electronic structure. Activity of a catalyst can be explained by:

- Active centers on the surface of the catalyst
- Geometry of surface
- Electronic structure
- Formation of surface intermediates

**Efficiency :** of a catalyst depends on Activity, Selectivity and Life.

So, activity we are defining in just because it depends on the ability of a catalyst to transform a reactant into product. And, which will depend again on textual as well as the electronic structure which is coming. Because how the metal has been deposited on the support? So, it means the catalyst preparation is very crucial right; the temperature which you are giving for heat treatment or aging are ((Refer Time: 21:10)) the p H; if it is requiring the p H definite p H the or hydrogen and concentration or acidity or basicity the definite kind of active centers may develop.

And, when you do the calcination then you are getting different kind of phases during the reaction. And, heat treatment step that is depend which may dependent on the temperature as well as it may depend on the time of sintering. So, that is basically called calcination system. So, during calcinations system also you are activating a metal and a support structure and generating the different kind of phases. So, any activity of a catalyst if you look at any types of activity the active centers on the surface of the catalyst.

So, how do you develop these active centers on the surface that is a first thing? And, techniques are available to characterize them; then geometry of the surface. So, that is as I said shape and the shape size of the crystal morphology of that crystal. So, everything is important when you look at a catalytic activity, electronic structure, the configuration of the electrons.

So, how they are able to transform because the electronic configuration is again important. Because the metals will whatever the metal which is deposited; it will exchange the electron from the gaseous species or reactant. So, the carbonium ion which you say that in the case of acid base catalysis. So, the so you will have that kind of adsorption on the surface. So, this is important; then formation of the intermediates because that intermediate will convert finally into the product.

So, how these forms on the surface that is again important. So, efficiency if you look at here of a catalyst depends on activity, selectivity and life. So, in general when you characterize a catalyst; you have to finally look at in terms of its activity that is ability to transform a reactant into a product. And, when we say product then we say a desired product; so selectivity is important. And, of course at the end you have to look at the turnover number for how much time the catalyst can be used effectively. So, that is very important. So, that is what the life of a catalyst.

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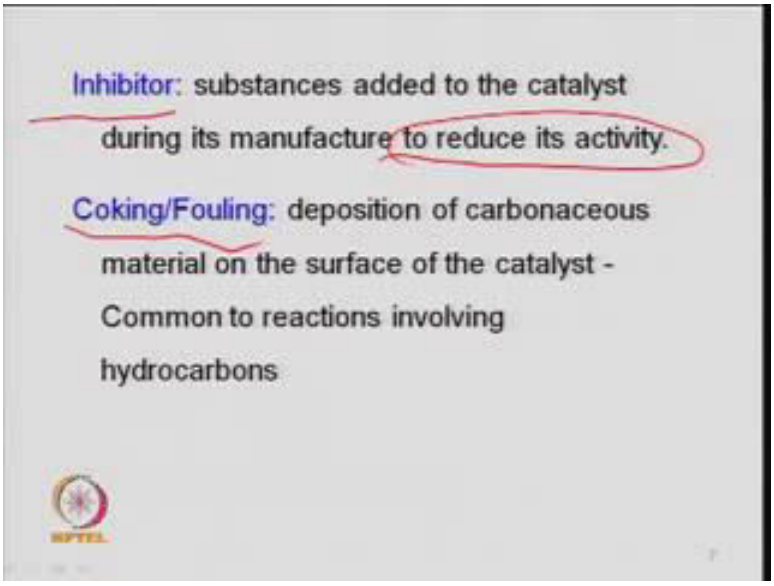

**Inhibitor:** substances added to the catalyst during its manufacture to reduce its activity.

**Coking/Fouling:** deposition of carbonaceous material on the surface of the catalyst - Common to reactions involving hydrocarbons

Sometimes we add a promoter which instead of enhancing the activity of catalyst it suppress the activity catalyst; that is also desired in many cases. Because you have seen from the thermodynamics or principle of micro reversibility we says that if the reaction is increasing in the forward direction; the similar thing will happen in the reverse direction also. So, it means when you have added a catalyst and if you the catalyst which can have the activity for hydrogenation reaction; the same catalyst may have activity for dehydrogenation reaction also.

So, it means a forward reaction rate is increasing then reverse reaction rate may also increase. So, in that case it becomes very important that; sometimes we add a passivator which suppresses the activity of a catalyst. And, this generally we do especially where the poison precursors are present in the feed stop like say hydro desulphurization reaction. So, you know that the in hydro desulphurization generally we use cobalt molybdenum type like we call commox or knemox.

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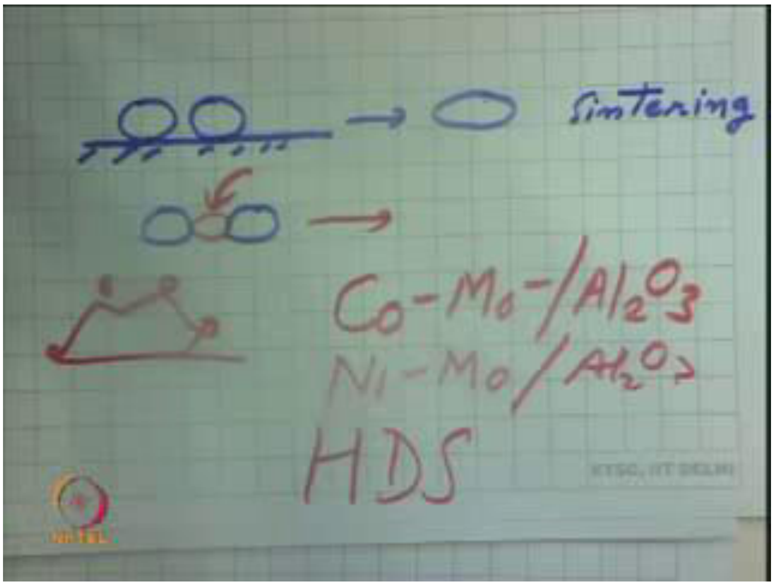

So, cobalt molybdenum on some alumina type support or nickel molybdenum on alumina support; they have a good hydrogenation activity. And, as well as they have good activity for the desulphurization reaction also alumina catalyst. So, these are used for hydro desulphurization reaction HDS or sometimes you call hydro treatment also. So, as I said that if the activity is enhancing. But the sulfur in this because you are working with sulfur here removing the sulfur from the petroleum feed stop. And, if the feed contained sulfur then the poisoning of these catalysts becomes faster. Because of the because the sulfur is a poison precursor right and see one type of deactivation where the catalyst can be regenerated. But when you say it is poisoned then the regeneration is very difficult because it is almost impossible.

Because it is irreversible chemisorption of the sulfur precursor on the active site of the metal. So, it blocks the site or it poisons the sites completely. So, your life of the catalyst will reduce faster. So, in order to passivate the activity of chemisorption of negative chemisorption I will say poisoning poison chemisorption the we at certain kind of passivators right; which can suppress the activity for the main reaction also. But also it will suppress the activity for the poisoning reaction also. So, the sometime we pre-supplied the catalyst just like in your reforming reaction also; we for the plate reforming the sulfur maybe a poison precursor because sulfur is present in feed stop. So, we add certain kind of sulfur passivator or sulfur precursor in the form of says hydrogen sulphide; we reduce the catalyst in the presence hydrogen sulphide.

So, when you have the sulfur precursor already in the catalyst then activity of the catalyst suppresses. So, the activity of main reaction also suppresses but activity of poison precursor is also suppressed. So, that is in terms of saving the life of the catalyst right. So, sometime when the reaction is highly active. So, we just try to suppress the catalyst; especially when you have a fresh catalyst it will be very active, right.

So, a small concentration of some poison precursor; it may be any sulfur precursor, carbon disulphide say or hydrogen sulphide treatment. So, it can suppress the activity of the catalyst in order to avoid the poisoning of the catalyst. So, these are known as inhibitor. So, inhibitors are the substances which are added to the catalyst during its manufacture; to reduce its activity that is partial reaction or reduction by a small fraction. Coking and fouling is again as I said the unwanted or undesired phenomenon the catalytic reaction or during the catalytic reaction. So, coke formation when you have a kind of hydrocarbon precursor and if you crack it.

So, the ultimate end is nothing but the coke. And, coke is nothing but poly-condense aromatic hydrocarbon. So, if you have a different benzene ring you heat treatment; so benzene ring will condense together right because of dehydrogenation reaction. And, then that condense polymeric is this will have something a structure like c x h y right enthocene large number of benzene is connected together. And, the large number of carbon and less number of hydrogen. So, that is nothing but the definition of coke which contains more than 90 percent carbon.

So, this coke is a product of severe cracking in the hydrocarbon. So, sometimes in order to avoid these phenomenon we avoid we add certain kind of precursors. So, coke which can be just the job is to reduce the coke; just like in the potassium is one of that compound. So, if you have a hydro cracking carbon cracking on silicon catalyst. And, if you add the small of potassium on that; then in the presence of steam the potassium reacts with the carbon of that catalyst.

So, whatever the carbon deposits in the presence of potassium which have some kind of oxidation reduction cycle a redox kind of behavior. So, this reduces the carbon on the catalyst. So, because basically it is a kind of gasification reaction. So, potassium is converting the carbon; so it acting basically catalyst for the gasification coke gasification but not for the main reaction.

So, sometimes we add the coke inhibitors also the this is one. And, the first example I gave that sulfur may be added; to reduce the main reaction cracking; sometime with the coke is forming you just add in terms of a gasifying agent. Same thing in the case of ceria also generally in reforming reaction over the main catalyst say the nickel, alumina generally these are the catalyst; but if you have a small concentration of cerium oxide.

So, this has the excess oxygen or it has good oxygen storage capacity. So, the oxygen and again this will a kind of redox cycle; that is it will convert in one form c u o x; then again it will come to the other form because of the oxidation reduction cycle. So, it takes the in the it will react with the carbon give it to the carbon dioxide convert into carbon dioxide. And, again take the oxygen and convert into the ceria. So, different types of chemical reactions are involved during this step; and that we will see depending upon the time. So, deposition of the carbonaceous material on the surface of the catalyst which is common during the reaction of the hydrocarbon. So, sometime we have to add the inhibitor in order to avoid these kind of reaction.

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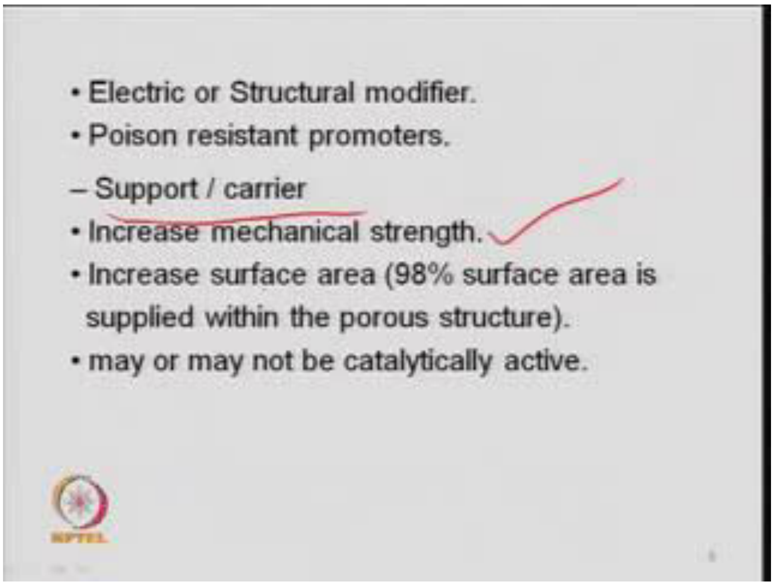

- Electric or Structural modifier.
- Poison resistant promoters.

– Support / carrier
- Increase mechanical strength.
- Increase surface area (98% surface area is supplied within the porous structure).
- may or may not be catalytically active.

And, beside that there are different kinds of other promoters also electric and structural modifier. So, sometime we add the to give a different kind of electric conductivity, heat conductivity during; because especially you are when your reaction the material say ceria, alumina when you need that the heat distribution is not proper. So, sometime we conductive material can be added in the catalyst. And, that can provide you the sufficient kind of heat transfer right or some kind of electronic transformation.

So, structural modifiers can be added like graphite is added when you prepare the catalyst small concentration of graphite or even a wood solid material if you add; then it is known as a pore former. So, if you need a highly porous catalyst. So, during calcinations this will gasify and you will have more over more number of pores or large size of pore. So, these are known as pore former in the catalyst.

So, graphite acts as a pore former. And, same thing for the sometime a poison resistant promoters we add as I discussed earlier also then support carrier. So, support we have already discussed again in the; main purpose of the support is the carrier that the support catalyst when I am saying it is a it may be just either you say support or carrier both are same meaning.

So, anything like alumina which I say that is that. So, these are acting as a support we generally provide the high surface area. But simultaneous in reactions the support itself maybe as a catalyst or it can be a bi-functional catalyst also. So, sometime we had two type of metals like cobalt, molybdenum. So, it is a bi-functional; cobalt will have one role; molybdenum will have another role right same thing nickel moly. So, nickel have one role, cobalt has another role. So, these are also known as bi-metallic catalysts and same thing for multi-metallic catalysts. So, different metals may have a different role during catalytic activity. So, we will look at those parts later. But right now I am saying the role of support is the main role is to increase surface area. And, to provide the sufficient strength or mechanical strength to the catalyst.

So, and these are main may not be catalytic active as I said that alumina it may act as a catalyst. Because it is amphoteric in nature; acid base both type of property sometime act ZSM 5 which have highly acidic property. So, it can provide the acid function, acid sites to the catalyst which helps in cracking reaction.

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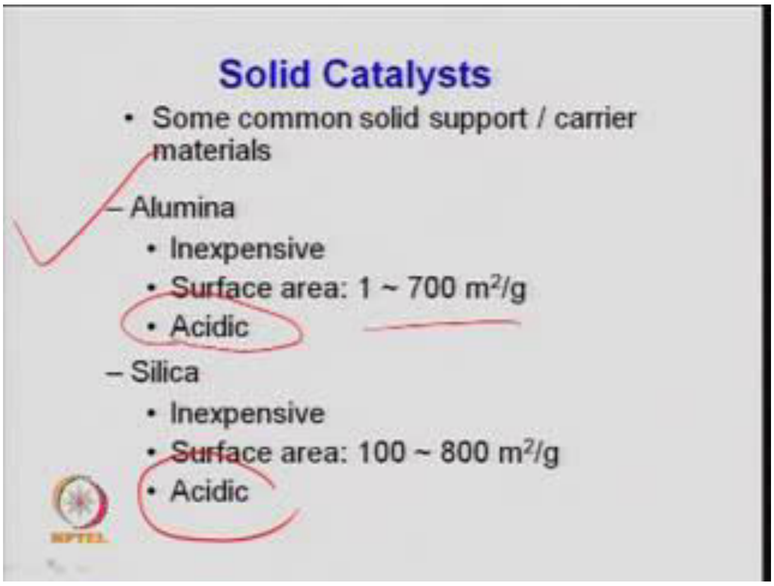

## Solid Catalysts

- Some common solid support / carrier materials
  - Alumina
    - Inexpensive
    - Surface area: 1 ~ 700 $m^2/g$
    - Acidic
  - Silica
    - Inexpensive
    - Surface area: 100 ~ 800 $m^2/g$
    - Acidic

So, in the solid catalyst we use different kind of support. So, alumina is one; which is the advantage as the most common support is alumina. Because it is inexpensive one also and surface area it has a wide range of surface area. So, 1 meter square per gram to 7 meters square per gram. So, you can see that a simple a single chemical is preside alumina A l 2O3 but the area wise if you look at that can be.

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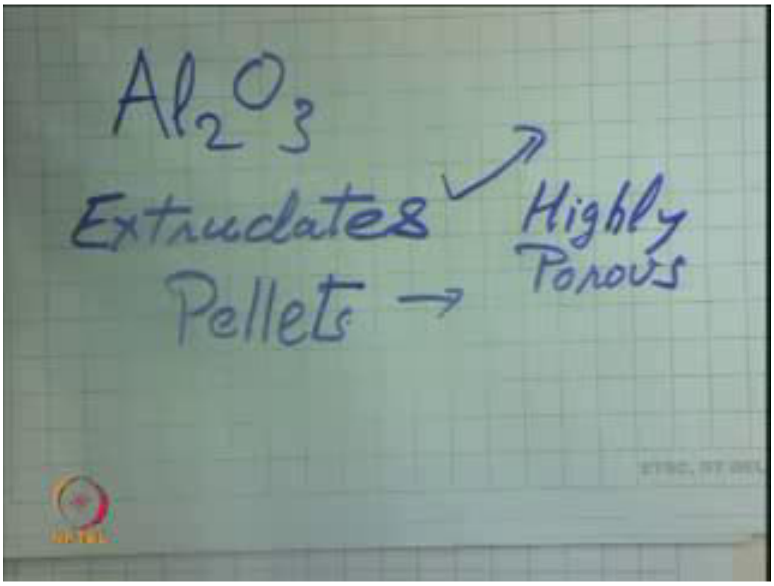

So, structure wise it is just like this one and amphoteric in nature. But the surface area is coming because of the pore structure. So, the pores which are present between the particle or within the particle. So, there can be different kind of pore; one is the pore between the particle of alumina, another is the pores which have you are made a pellet of several particles. So, space between the particles. So, that is a kind of pore structure which should develop; when you have give the sufficient compression. When you make a tablet then depending if you apply more stress. So, you are increasing the density right more force you are compressing it; so pellet density is increasing. And, that is required a tuning is required in terms of mechanical strength versus the pores structure.

So, extrudates versus pallets this is the only difference. So, extrudates and versus pellet right. So, extrudates where the exclaims poor right because you are not applying that much pressure and making a pellet. You are just passing through a dye right molding machine and dye and then you get the just like your noodles and you get. So, they are very soft material and but their porosity will be high because you are not compressed down.

So, the space between the particle will be more. So, but the mechanical strength is poor. So, when you handle it in fix by reactor and specially it high pressure. So, they will get crumbled a definite size of the catalyst is also required. Because when in the fix by reactor when is use the powdered catalyst the pressure will increase right. And, pressure increasing means you are giving more energy for the conversion. So, energy consumption will be more.

So, we have to tune that in terms of mass transfer resistance also as well as in terms of the mechanical operation. So, when you are giving a pellet with sufficient the strength the problem is that you have reduced the porosity. Because when you apply by making a pellet you are compressing it. And, by compression the density can be increased 3 times in a pellet you can have 3 times more than pellet from the same powdered. Because you are compressing it to a level; but when you compressed it highly then the porosity will go down. So, most of the time we the desired thing is that because we want highly porous material. So, we want a highly porous material for the chemical reaction because the catalytic reaction is inside the porous structure not on the external surface; and internal surface is more important.

So, extrudates are better in terms of providing the large surface area but the mechanical strength of the extruder will be poor. So, it in case you are using extruder you need to provide sufficient mechanical strength. So, additives need to be added. So, sometime in the f c c catalysts we add the additive to improve the mechanical strength of the catalyst sufficient binding is required.

So, different kind of catalytic supports can be used in for silica also. Why surface area just I will discuss in that part that why surface area is changing it is because of the heat treatment. When you calcine it you get a different phageginal. So, galima alumina surface area like your 220 to 500 meter square per gram but when you heat it continuously you get alpha alumina right.

So, alpha alumina is almost non-porous material almost sintled alumina gamma alumina. And, this is happening when you have a phase transformation during the heat treatment. So, you should take alumina particle or gamma alumina heat it from 25 degree centigrade to a 1000 degree centigrade. So, at 1000 degree centigrade you have almost the alpha alumina, almost non-porous which is equivalent to 1 meter square per gram catalyst. So, the basic idea is that here what I am talking is that surface area of the catalyst change depending upon the heat treatment conditions used. So, in deforming if you look at your fertilization industry or forming catalyst these are generally nickel on alpha alumina. Because the forming reaction takes place at high temperature 800 or 1000 degree centigrade.

So, at that condition you may not have the galima alumina rather it will be a kind of alpha alumina low surface area material. So, it can be a mass transfer control reaction there. So, that is why the new concept in the reformer is that you go with a micro reformers system via channel type reactors; what you call monoliths. So, different kind of channel structures can be used for these; where the reaction mass transfer controlled. Because the diffusion resistance is more in those kinds of pellets right; the length of diffusion is increasing. So, you give a vast coating or give a special coating to this kind of material. So, that the diffusion length is minimized, right. So, these are the challenges for the future. And, support can also provides alumina is also acidic in nature, silica is also acidic in nature. So, sometime they provide you the acidic sites required for the catalytic reaction.

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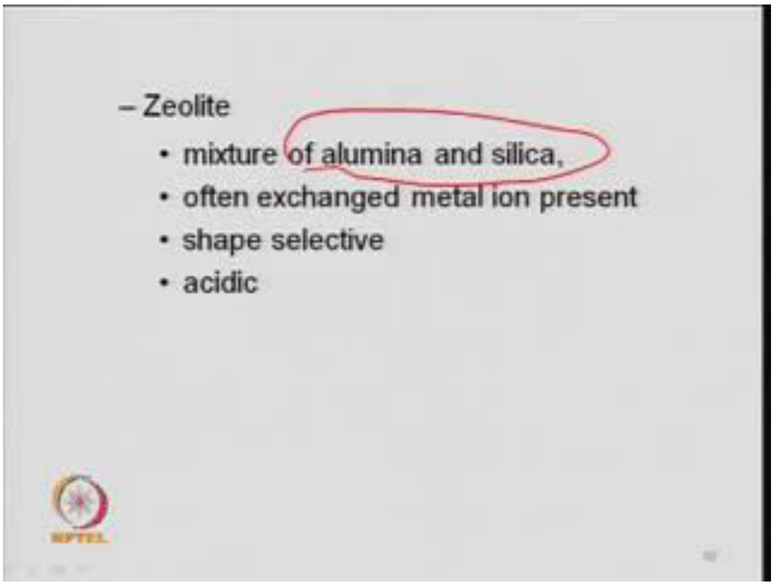

– Zeolite
  - mixture of alumina and silica,
  - often exchanged metal ion present
  - shape selective
  - acidic

Again, another catalyst support Zeolite which is widely used in petro chemical and refined industry. So, f c c catalyst generally this Zeolite and there are different varieties of the Zeolites available depending upon the silica to aluminum ratio. So, silicon aluminum to aluminum ratio very important in the case of Zeolite to provide its teffric kind of acidity. So, we will talk of that later. So, basically if you look at these are the alumina and silica mixture; clay type material. These are natural materials are also available silica to alumina have different structures; but they may not be crystalline in nature.

But they can also have the similar composition like Zeolite but they cannot be used as catalyzed directly. So, we need some treatment. So, often exchanges metal ion depending upon the requirements like LPG aromatization, the gallium exchange exclaim ZSM 5 the proton h can be replaced by the gallium metal. And, that can be used for aromatization reaction. So, LPG like or propane, butane so these straight chain compounds can be aromatized by using these catalysts.

Shapes selective they have very definite structure and pore site. So, they also called a molecular shapes right or shape selective activity. So, sometime they do not allow the larger molecule or larger aromatic molecular weight compounds through their pore; because they have a definite channel diameter. So, they are shape selective. So, one kind of molecule can go inside; but not the larger kind of molecule which has a ring type structure. So, they are called shape selective also will talk on that later and they are highly acidic in nature. So, they are also used as a support as well as h catalyst.

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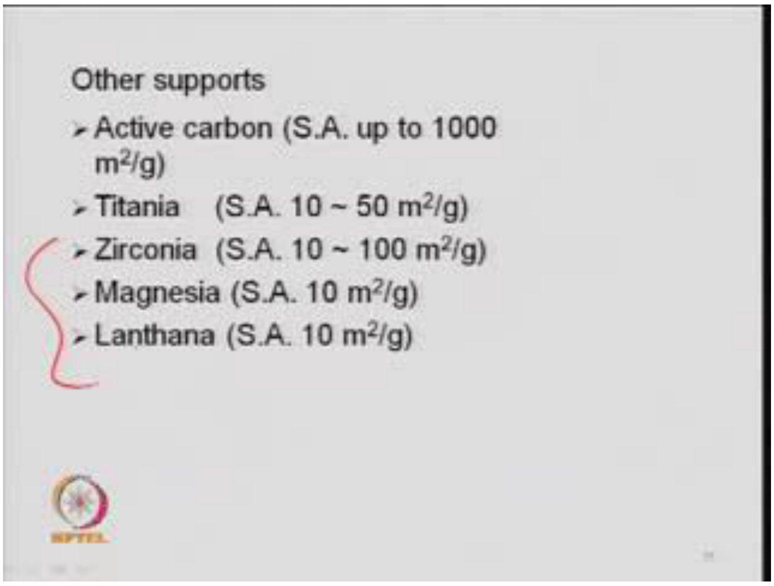

Other supports

- Active carbon (S.A. up to 1000 $m^2/g$)
- Titania (S.A. 10 ~ 50 $m^2/g$)
- Zirconia (S.A. 10 ~ 100 $m^2/g$)
- Magnesia (S.A. 10 $m^2/g$)
- Lanthana (S.A. 10 $m^2/g$)

Beside this the other catalyst supports are also like active carbon, activated carbons has very high surface area. So, this can be used as an adsorbent this is used for separation and purification of the gasses also. Because the high surface area and good adsorption property. But it is also used as a catalyst support also and titania is another one right which has 10 to 50 meter square per gram surface area, Zirconia which is Zro2, Titania is Ti O2, Zirconia Zro2. And, this has again a surface area 10 to 100 meter square per gram. And, similarly magnesia powder can be used as a catalyst; Lanthana can be used as a catalyst.

So, they have low surface area and these are basically the basic catalyst. So, titanium dioxide is generally used for the u v assisted photo catalytic reaction also; because they have a good semiconducting property. So, electron band theory if you look at; so there a good kind of see a gap band gap where you electron can be transferred through that. So, when you have a certain kind of u v light. So, that band becomes active right and it can transfer electrons.

So, it has wide application in the especially in the waves water treatment or advance oxidation process. And, titania is one of the catalyst which is used for photo active or photosystic catalytic reaction. So, not all catalyst can have the those kind of those who are semiconductor property; they can be used as a catalyst for u v under u v light right.

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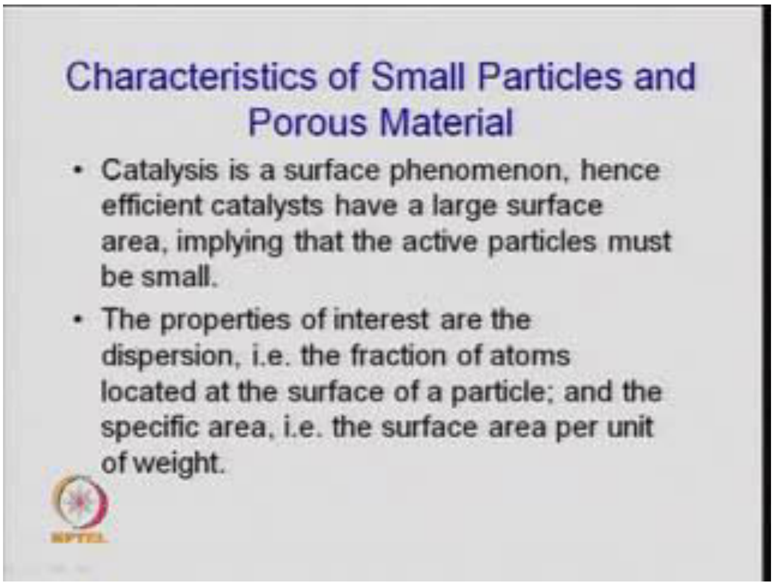

### Characteristics of Small Particles and Porous Material

- Catalysis is a surface phenomenon, hence efficient catalysts have a large surface area, implying that the active particles must be small.
- The properties of interest are the dispersion, i.e. the fraction of atoms located at the surface of a particle; and the specific area, i.e. the surface area per unit of weight.

So, characteristics of small particles and porous material. So, I was talking about the preparation of catalyst; the size of the particle is very important. So, we can have different shape of the catalyst like most of the time we talk cylindrical pellets; the pellets can be spherical in geometry also and they can have a ring shape also. So, the different structures are available also. And, why do we need a definite size of a pellet or shape of a pellet is related to your mass transfer and diffusion limitation. So, we try to avoid the mass transfer limitation or the reaction where the react it is controlled by mass transfer; we try to have large surface area per unit volume. And, that is basically the external surface area. So, because there the reaction takes place between the gas and liquid interface suppose right or a gas and solid interface not the in the inside surface.

So, this is the case what I was talking for the reforming reaction in fertilizer industry; when you look at naphtha forming natural gas is forming. So, the catalyst has almost low surface area 10 meter square per gram. So, where the reaction is taking place it is mainly on the external surface of the catalyst.

So, there the it is a channel geometry is better just like a plate and frame heat exchanger. So, you have different channels and on this you have a large surface area on which the active metal is deposited. So, we are not interested in having diffusion inside that is; that length should be as small as possible and this is the concept when we are talking a monoliths reactor or monolith channel type reactors right.

So, the basic idea is that; the catalyst can have different type of shape different geometry but the selection is done based on the reaction or a different type of reaction will have different kind of catalyst shape, right. So, mass transfer reaction; the catalyst shape maybe a tri-lob, quadra-lob, penta-lob right, because the external; we would like to have large surface area so, just like finny structure where you have a cylindrical geometry but outer side, you have a fins like this right a radiator type device. So, these fins will provide the external surface area, right.

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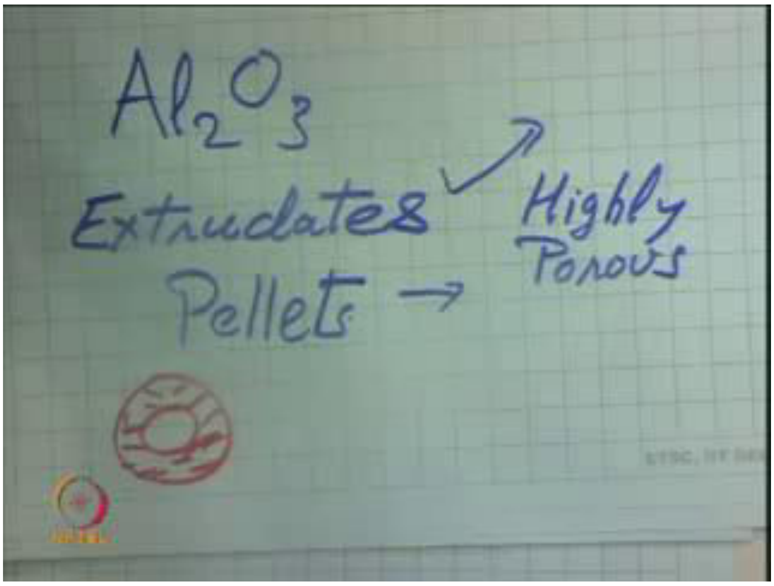

So, same thing can be in the ring shape structure; so rings are when you taking the ring structure when I am saying it is something like a structure like this, right; so this is just like a ring structure. So, again it has large surface area and another advantage is that it has less pressure dope, right. When you have a ring this kind, this kind of ring so, it is a it has less pressure dope compare to a pellet. So, depending upon the reactor system and depending upon the type of reaction; we select a definite shape of a catalyst and we will talk on that later also.

So, as I said the catalyst is surface phenomenon; when we are talking at a heterogeneous catalysis we are more conscious about the size, we are more conscious about the particle size, pore size distribution and then, structure and structure property of the catalyst. So, if you look at in efficient catalyst we want a large surface area that is the first thing; implying that the active particle must be small.

So, smaller particles will have larger surface area; even if, you talk the external. But when, we talked the internal surface area it is because the porous geometry; but that time, inter smaller particle is not because of they have large surface area but rather we are trying to avoid the diffusional limitation inside the pellet, right. So, for a smaller particle the diffusion resistance in the pore will be less or minimum, right.

So, when you look at the kinetic steady you try to have a definite size of a particle and tune in such a way that pressure drop should be minimum, right. But at the same time, the diffusion or internal diffusion resistance should not affect the rate of reaction, right. So, you are ensuring that the; it is the kinetics of reaction which is for the transformation of a reactant special product ((Refer Time: 45:56)).

And, ultimately, when I am talking about a kinetics I am talking about surface reaction; which has the adsorption then surface reaction and then, the desorption is step on transformation into a product species, right. But beside that, the other two steps are the mass transfer; external mass transfer and internal diffusion inter-pore of a catalyst, right. So, all these steps have important role; so, especially when we are looking the reactor design we have to look at the catalyst, type of catalyst its size and the type of reaction. So, bubble column reactor may be one; slithery ((Refer Time: 46:31)) bubble column reactor which is generally used for fissiotropy reaction, right. So, when you need the heat transfer limitation also, mass transfer limitation also; you have to select a definite reactant and then, a definite catalyst right in terms of shape and size of a catalyst.

So, the properties of interest in the catalyst; the first one is the dispersion, right. So, dispersion definition says that, it is the fraction of the atom that is active metal right which is available for chemical reaction, right. So, located at the surface of the particle and a specific area when we report it is the; nothing but the surface area per unit mass of the catalyst, right.

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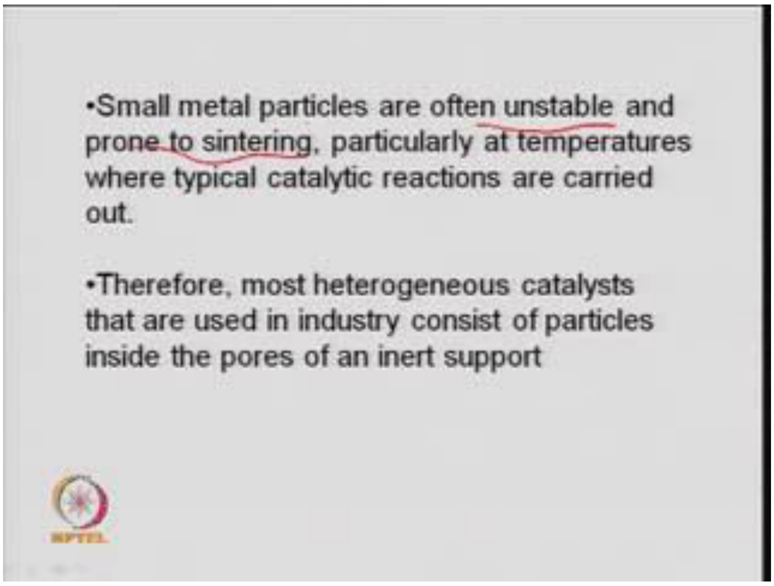

- Small metal particles are often unstable and prone to sintering, particularly at temperatures where typical catalytic reactions are carried out.
- Therefore, most heterogeneous catalysts that are used in industry consist of particles inside the pores of an inert support

So, small metal particles; they are generally unstable and prone to sintering. So, as I said the nano particles everybody looking for nano particles, right; because the reason is that they have high surface area per unit volume, right. So, if surface area is high your rate of reaction will very high; so, especially when you are looking mass transfer of homogeneous catalytic system this fundamental thing is very important that how to generate the nano particles, right.

The only thing that stable nano particles; so, when you have a gel inside the gel, the nano particles are stable. But when you have, rapture that gel right heat it that gel ((Refer Time: 47:48)) then, the nano particles have come out and when you use them in the reaction they agglomerate easily, right. And, so, this is the challenge that how to make stable nano particles, right.

So, the small metal particles they are unstable; because they are prone to sintering right agglomeration. Particularly, at temperatures typical catalytic reactions are carried out; so, this is one problem or one challenge. So, therefore, most of the heterogeneous catalytic that are used in industry; they consist the particles inside the pore of an inert support. So, because there the sintering is avoided; you have the metals on one support which is interacting, right; a kind of interaction between metal and support and that is what we are calling metal support interaction right. So, the one metal is supported another metal is supported and in between you can have promoter; so, chances of sintering is reduced.

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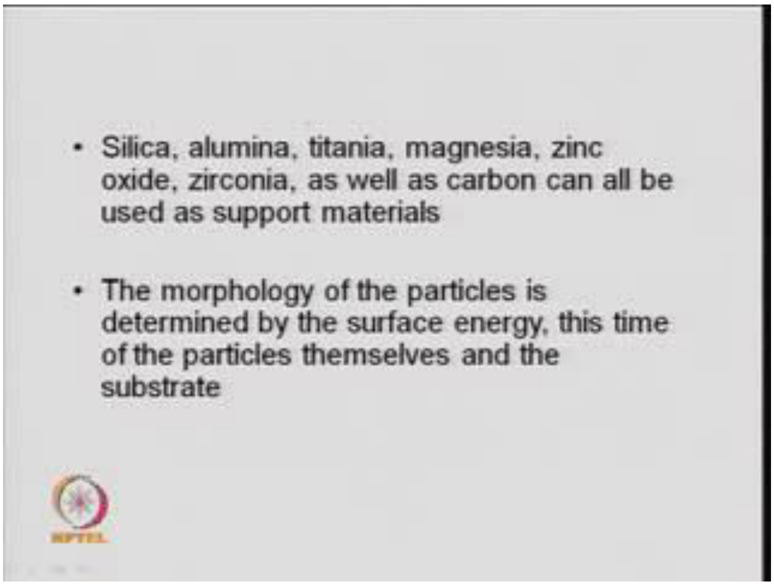

- Silica, alumina, titania, magnesia, zinc oxide, zirconia, as well as carbon can all be used as support materials
- The morphology of the particles is determined by the surface energy, this time of the particles themselves and the substrate

So, thing we have already talked silica, alumina, titania, magnesia, zinc oxide, zirconia, carbon; they can be used as a support, right. So, a definite but which support is good that will depend on the porous structure of the support; that will depend on its reducibility also. Because depending upon the type of the metal; how does the metal interacts on the support is also equally important. Because we do not want strong metal support interaction, right; S M S I is also related to the catalytic property because if it is, strongly binded activity will be poor, right. So, morphology of the particles is determined based on the surface energy; this time the particle themselves and the substrate.

So, this thing I will discuss later; but basically, the energy is very important surface energy of a particle, right; what you call galima ((Refer Time: 49:36)). Generally, we report the energy of a particle and depending upon the distance free, that is; what the wolf construction chart which we are talks which talks on the how a surface creates, right.

So, whether it is pentagon, hexagon or square geometry or spherical in shape it will depend on the wolf energy; because the surface tries to have a minimum energy. So, whatever, the space or the crystal geometry that depends on so many factors; that is preparation condition and they are the metal support and the valency of these; that is the are electronic configuration of metal and support; so, that we will discuss later.

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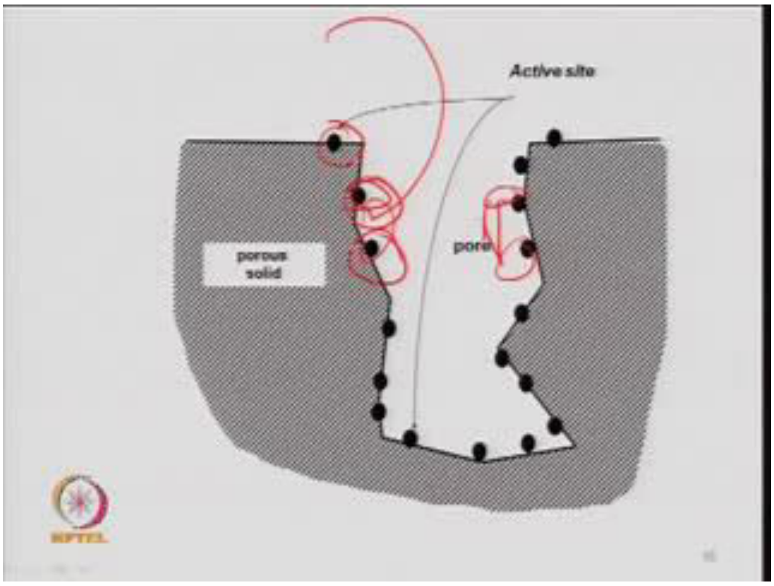

This thing what I was talking a support, right. So, this is a porous solid if you look at here so one solid and now, this is cavity inside that; a kind of crack which you can say but it is not actually the crack. It can be the pores in the particle itself, right; or it can be the pore between 2 particles right. So, this but the structure which you are looking is the; nothing but the, wide space in a support right and there will be millions of this kind of channels, right.

So, this is kind of cylindrical geometry of a definite diameter, right; it can be a micro, it can be macro or meshopore, right different pore structure. But generally, ((Refer Time: 51:01)) these are the cylindrical in shape, but the; it can have a kind of ink bottle if a shape also. That is, they are narrower towards neck then, widens at the end. So, but the formation of these kind of pore is during the catalyst preparation.

So, when you do the calcinations, when you do the aging or drying of your catalyst right; so, there you; then are developing the pore and you are adding pore form the more pores will be form. So, what is important in the case of catalyst preparation; especially, when you are looking a monodispanse pellets, right. Then, the; a single size pore or a definite pore size distribution or narrower pore size distribution is very important but very difficult to conclude, generate this kind of pores, right. So, in the reproduce in the catalyst preparation is again a crucial issue right.

So, you have to prepare the catalyst then, again check cut it try it do the hexaldy measure; the crystal size dispersion and then, prepare the same catalyst again and then recheck, right. And, especially, when you are making a bulk of the catalyst in large amount; then, these things become more and more crucial and challenging, right. So, this is a typical that; these points are nothing but the active site what I am talking any metal which is deposited; so, it will go inside the pore and it will deposit here.

So, this is the channel or zone where the gas species will come and adsorb, right; so, any gases will come adsorb here and then, it will react either with this or another adsorb is species and transform into the product. There is a kind of surface diffusion or what you call spillover; term which is known is nothing but the molecule; which adsorbs and it migrates into the; towards the support, see kind of surface diffusion, right. And, because of that so sometime it happen that it migrates and reacts with the support itself and the remainder, right. Another thing, that it migrates and reacts with another adsorb specie and transform. So, that is a kind of a spill over phenomenon or surface diffusion; so, the molecule is coming here on this, like this and here another B and this and these two are interacted right. How these are interacted? Because of the spillover phenomenon or surface diffusion, right.

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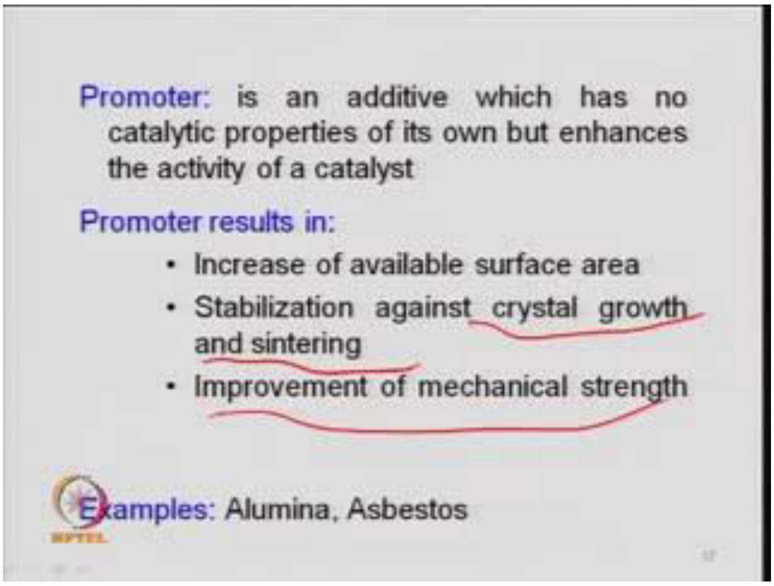

**Promoter:** is an additive which has no catalytic properties of its own but enhances the activity of a catalyst

**Promoter results in:**

- Increase of available surface area
- Stabilization against crystal growth and sintering
- Improvement of mechanical strength

**Examples:** Alumina, Asbestos

So, support part what we are talking; the principally serves as a framework on which the catalyst is deposited. So, that is what we have seen, but the catalytic activity is rare sometimes it has; so I will say no catalytic properties of its own but when you are alumina type your silica types sometime they acts as a catalyst also. So, carrier results in highly porous structures; so, when you are selecting a support a definite support is required so, preparation of the support can be done or support can be taken directly here the metal can be impingated on it or loader on to it. So, it has highly porous structure so increase of available surface area right; that is important, it improves the stability of the catalyst and it improves the heat transfer.

So, depending upon these, you have to select a definite support for a given reaction. Same thing, for promoter; so, promoter is an additive which has no catalytic property of its own but enhances the activity of a catalyst, right. Like potassium can be added as a promoter, iron can be added as a promoter. So, main catalyst is different; but a small concentration of the promoter is desired; because if you have higher concentration it may cover the surface of the active metal and no chemical reaction may happen right or activity will reduce. So, that is again important; so, promoter generally results sometimes the increase of available surface area, right; if the surface area is low, you add a small concentration and then, you can enhance the surface area. Stabilization against the crystal growth and sintering; so, most of the time we look these factors.

A definite which can made them could dispersion, right; say copper if you have a small concentration of copper or zinc it may enhance the dispersion in the catalytic reaction especially, when your fissio type reaction, right. So, it enhances the dispersion of that iron or cobalt catalyst. And, sometime, it is added to improve the mechanical strength and sometime it can be added to reduce the coke on the catalyst also, right. So, alumina, asbestos these all are can be used as a promoter as well as support.

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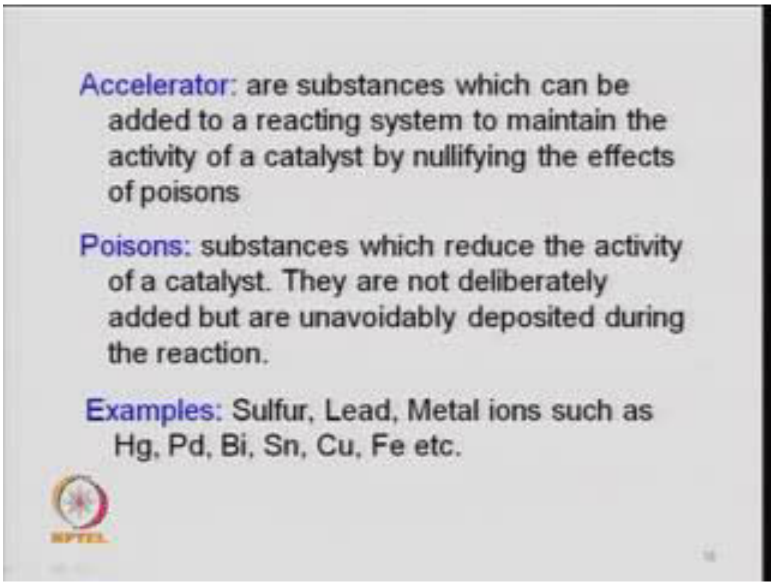

**Accelerator:** are substances which can be added to a reacting system to maintain the activity of a catalyst by nullifying the effects of poisons

**Poisons:** substances which reduce the activity of a catalyst. They are not deliberately added but are unavoidably deposited during the reaction.

**Examples:** Sulfur, Lead, Metal ions such as Hg, Pd, Bi, Sn, Cu, Fe etc.

Then, accelerator again I have already discussed; so, these are substances which can be added to a reacting system to maintain the activity of the catalyst by nullifying the effect of poisons. So, basically, they are the substance which can reduce the poisoning of a reaction. So, passivator or inhibitor when you say but they are accelerating the reaction of main reaction by suppressing activity of the coke forming reaction right; so they are known as accelerator. So, poisons these are substance which reduce the activity of catalyst; so, these maybe present in the feed stop itself sometimes these maybe in the catalyst also, right. So, they are not deliberately added but are unavoidably deposited during the reaction. So, the poison precursor which may come from the feed stop, which may come from the product and deposits on the catalyst; so, they will reduce the activity of the catalyst. So, sulfur, lead, metal ions, mercury, lead, bismuth, tin, copper, iron these can be a catalyst for some other reaction; but if, you are some other reaction then iron copper they can be a poison, right. So, it means depend because the catalyst is very trusting activity right very selective.

So, does not mean that, metal A is effective for one; so, for all reaction it is effective, it may be a poison for other reaction, right. So, vanadium in sulfuric acid manufacture V 2 O 5 is used right. But in other case, the vanadium is a poison right in hydrocarbon reaction vanadium confers the feed stop hydrocarbon; so, it acts as a poison. So, I stop here and I will continue it next time.