Heterogeneous Catalysis and Catalytic Processes
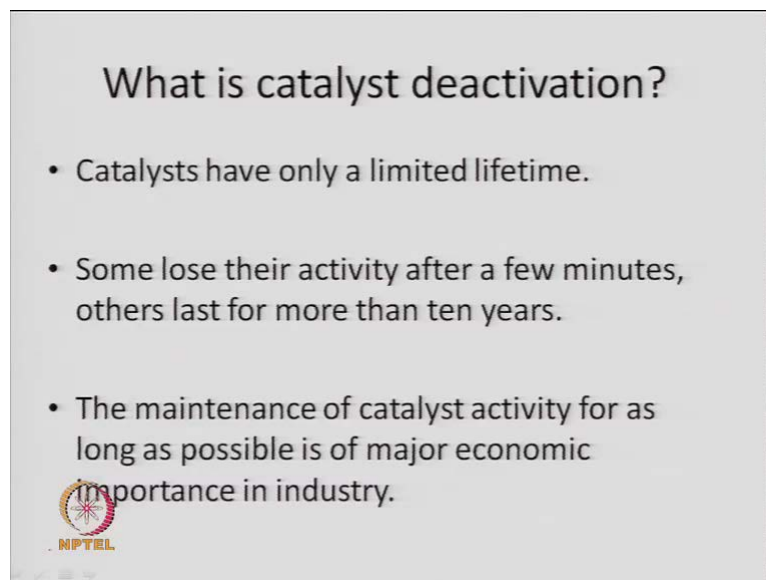**Prof. K K Pant**
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Lecture - 31

Good afternoon. In this lecture I will talk on catalyst deactivation. The first point is what is catalyst deactivation. So, I discussed in my last lecture that the activity of a catalyst is very important, and that is defined as ability of a catalyst to transform the reactant explicit into a product. So, that is one of the important aspect and simultaneously, the selectivity for a desired product.
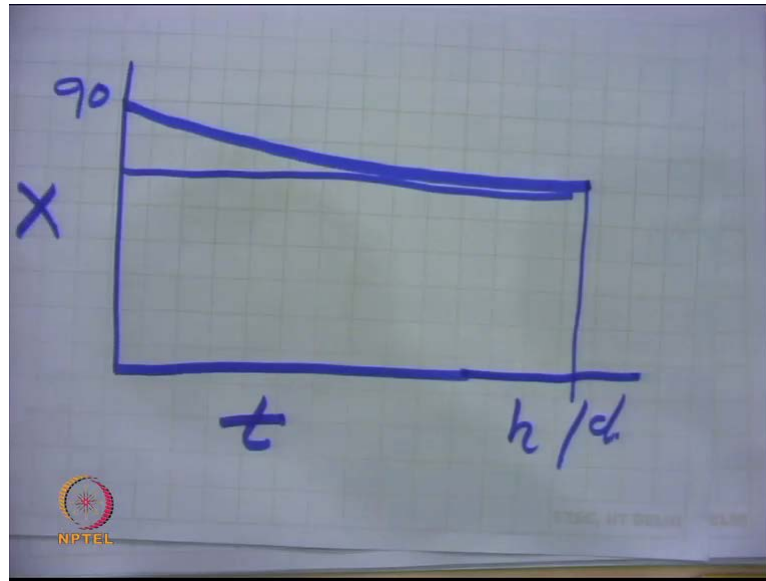
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So, when you look at these two important properties in a catalyst with time on stream, if you look at most of the refinery petrochemical process the activity of the catalyst decrease with time on a stream.

So, it means the conversion, generally if I look at in terms of the graph conversion as a function of time. So, it is operated at a steady state, but the conversion may decrease with time like this, right. So, it means initially the conversion may be ninety percent and after sometime it may be in terms of days or in terms of hours. So, either way the conversion drops with time. So, productivity starts decreasing. So, it means the lifetime of a catalyst is limited. So, we need to change the catalyst, or to replace the catalyst in order to maintain the activity for a given reaction to a certain limit, right.

Some loose the activity after a few minutes. So, few catalysts deactivate very faster; that depends on the type of the reaction, it depends on the type of the poison precursor. And in some cases like in fertilizer industry, the life of catalyst is generally three years and same thing in the refinery catalyst the life of the catalyst is three years. But if you look at FCC process and refinery few catalytic cracking, the activity of catalyst drops very fast. So, it means just within one second or five second the catalyst deactivates. So, a new kind of reactor design is required in these cases.

The maintenance of catalyst activity for as long as possible and this is one of the major economic importances in the industry, because I told you the catalyst is the billion dollar business. And in order to replace the catalyst a large amount of some money is required, right. So, if we can regenerate the catalyst in during the process that is very important; that is one thing that will be helpful, and it will save the revenue. And simultaneously, if

you maintain the activity either by increasing the temperature during the process that will also be of great help. So, efforts are generally made in order to maintain the catalyst activity or in order to look at the new kind of catalyst to make them stable during the process.

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- Catalyst loss of activity with time-, i.e. "deactivation".
- Also known as Ageing
- Catalyst activity is defined as

$$a(t) = \frac{-r'_A(t)}{-r'_A(t=0)}$$

So, activity when we talk it a term activity of a catalyst, I just said it is a conversion. This is the conversion which drops with time and when we talk activity.

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$$\text{Activity} = \frac{(-r_A(t))}{(-r_A)(t=0)}$$

$$\frac{W_{CSTR}}{F_{A0}} = \frac{X_A}{(-r'_A)}$$

So, that is very important when we compare the two catalysts. So, here in terms of deactivation the activity of a catalyst is defined in terms of the rate when the catalyst has been operated for a given time; that is rate at anytime t divide by the rate when the catalyst is free or fresh catalyst free from the poison percussion. So, we call it initial rate. So, rate at anytime t divide by the initial rate. So, that is known as activity of a catalyst. So, rate can be in terms of reactant explicit minus r A. So, that is the decrease in rate of reactant species at anytime t divide by the same thing at when the catalyst is a fresh catalyst. And this rate we measure generally in terms of the conversion data.

So, suppose you have the CSTR type reactor, you know in CSTR the design equation is given by W by F A naught is equal to x A upon minus r A dash. So, this is the mass of catalyst; this is the molar feed rate or mass feed rate of the reactant, x A is that conversion of a reactant species, and minus r A dash is the rate of reaction for the reactant A. So, rate of decrease in the activity of a catalyst. So, this is with time on a stream change. So, when you have a plug flow reactor even in a plug flow reactor we just take a differential reactor, and then the conditions can be similar to that of a CSTR.

So, this is a tank type reactor and a plug flow reactor when you do the kinetics or when we do this kind of deactivation study, we take a differential amount of the catalyst and then we measure the activity as a function of time on a stream. So, when you say a steady state reactor, then theoretically the conversion should not change with time; if it changes it is changing because of the catalyst deactivation.
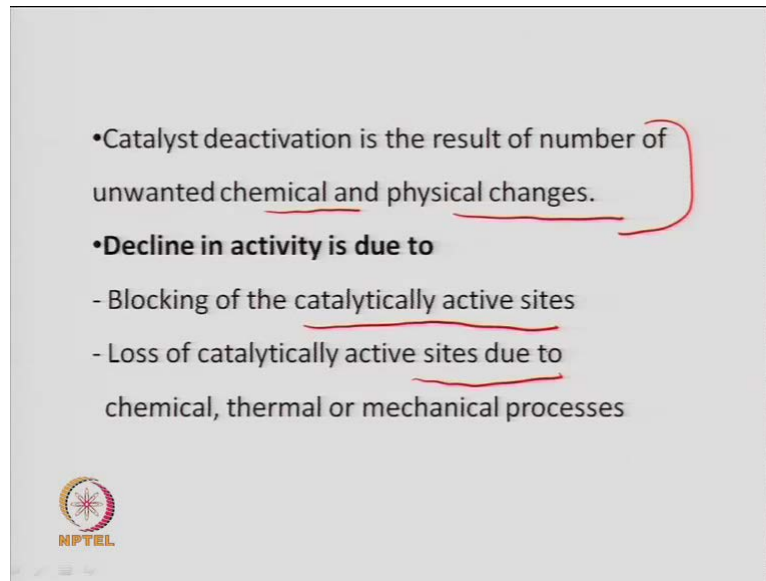
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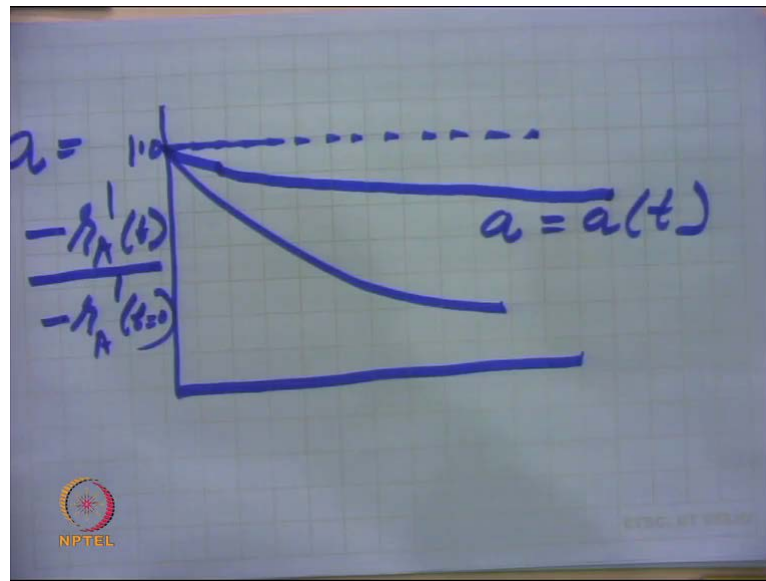
So, we measure this minus r A dash as a function of time and we can plot a graph like this minus r A dash at anytime t divide by minus r A dash when the catalyst is fresh, t is equal to 0; that is initial rate. So, this is rate at anytime t, and this is the rate when the catalyst is fresh. So, obviously, when there is no deactivation in a flow reactor then it should remain constant. So, activity A this is your activity value. So, this value should be one, right, because there is no changes rate, no drop in rate, but in actual reactors the rate or the actual catalytic reaction, the rate may go drop like this or it can even drop like this.

So, this is what the activity which is decreasing with time on stream. So, time on a stream means it can be as I said one hour, it can be six months or it can be year depending upon the activity of a catalyst or stability of a catalyst, and also it depends on the type of feed stock which has been selected. So, the rate of a reaction at anytime t divided by the rate of reaction when the catalyst is fresh and this is known as activity of a catalyst. So, deactivation can be because of the ageing phenomena, because you are continuously using the catalyst for a longer period of time. So, there may some structural changes. It can be because of the feed stock which has some poison precursors, and they deposit on the catalyst. So, we will talk on that.

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So, as I said catalyst deactivation is the result of the number of unwanted chemical and physical changes. So, this can happen some changes on the surface of the catalyst which cannot be regained or which cannot be changed again during the reactivation of the catalyst. And this can be in terms of the structural changes; this can be because of deposition of the carbonaceous species on the surface of the catalyst, right. So, because of the active site concentration decrease, because the rate is related to the number of active sites present on the surface of a catalyst; the rate also depends on the surface area of the catalyst. So, these may change.

It may also depend on the phase which is formed during a sintering during calcinations or during catalyst preparation. So, that may also affect and because of the activity of this the catalyst drops. So, decline in activity can be because of blocking of catalytic active site. So, this can be as I said carbon. The carbon may deposit and it blocks the active site. It may be because of loss on the concentration due to chemical or thermal or mechanical process. So, different kind of deactivation mechanism may be possible in a catalytic reaction.

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Types of Catalyst Deactivation

Catalysts frequently lose an important fraction of their activity while in operation.
Three causes for deactivation:

a. Structural changes in the catalyst itself. These changes may result from a migration of components under the influence of prolonged operation at high temperatures, so that originally finely dispersed crystallites tend to grow in size.

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So, types of catalyst deactivation when we say. So, as I just said that the changes may be structural changes. The surface morphology which we determine by x-ray diffraction technique, by scanning electron micrograph, by transmission electron micrograph, but we discussed during the characterization techniques. So, that may change during the reaction, during the course of reaction or during the contact of the reactant species with catalyst for a longer period of time.

So, because of that the activity of a catalyst may change or drop. So, this is the structural change which may result from a migration of components under the influence of prolonged operation at high temperature. So, that the originally finally dispersed site tends to grow inside.

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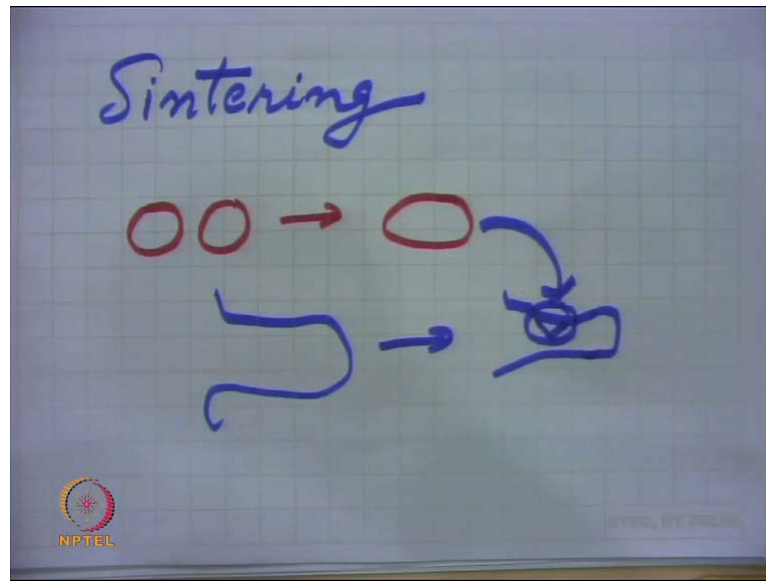
So, this is what I was talking a kind of sintering; because when we look at a good catalyst we try to make a smaller particle, large surface area permanent volume and during the course of reaction because they are highly active. So, these two small particles they may react and make a bigger particle. So, surface area drops, right. This can happen in the surface of a pore also. So, this is a pore structure. So, when the continuously high temperature process happens. So, the pore structure may narrow down like this, something like this. So, there is a kind of construction which has formed here, right, or it can be nothing but in terms of the active sites they grow here and they are now larger in size. So, the size of this active site is increased.

So, it can be because of the change in textural property of the support itself or it can be because of the change or sintering of the active metal part which is the metal precursor on the surface of the catalyst. So, because of high temperature the particles get agglomerated. So, they become a larger two small particle and they just join together and make a particle larger. So, surface area per minute volume decrease in such cases.

Ageing : Temperature fluctuations may cause stresses in the catalyst particle, which may then disintegrate into powder with a possible destruction of its fine structure.

b. Essentially irreversible chemisorption of some impurity in the feed stream, which is termed poisoning.

c. Deposition of carbonaceous residues from a reactant, product or some intermediate, which is termed coking.

This is known as ageing also, right, because of the temperature and time relations. So, the temperature fluctuations may cause stresses in that catalyst particles which may then disintegrate into powder with a possible destruction of its fine structure. So, sometimes it is a kind of disintegration because of the variation in temperature during the course of reaction. The second one which is a kind of poisoning, right, so it is an irreversible chemisorption of some impurity in the feed stream which is generally known as poisoning. So, what is poisoning.

So, this is kind of irreversible deposition of these poisoned precursors something like suppose if I say a simple pure hydro treatment reaction, so naphtha hydro treatment. So, these feed or hydrocarbon contains a large amount of sulfur precursor. It can be in the form of hydrogen sulfide, it can be in the form of mercaptan; so, something like this or mercaptans. This may be something like C 2 H 5 SH. So, oxygen is replaced by sulfur. So, these are known as mercaptan. So, these sulfur precursors they react directly with the surface or active site of the catalyst.

So, I remove out this like p, a poison precursor. So, your p plus star which is your active site in a catalyst and makes p star. So, this is an active site of a catalyst. So, this active site and this is the poisoning precursor which is like the sulfur compound, nitrogen compound, oxygen compound, which are present in the hydrocarbon feed stock. They deposit with this or they react chemically with this and form a chemical compound which cannot be removed from the surface of the catalyst. So, if you remember when we were talking the mechanism of Kleinberg Hinsberg type, then this adsorbed species appear in the denominator basically, right.

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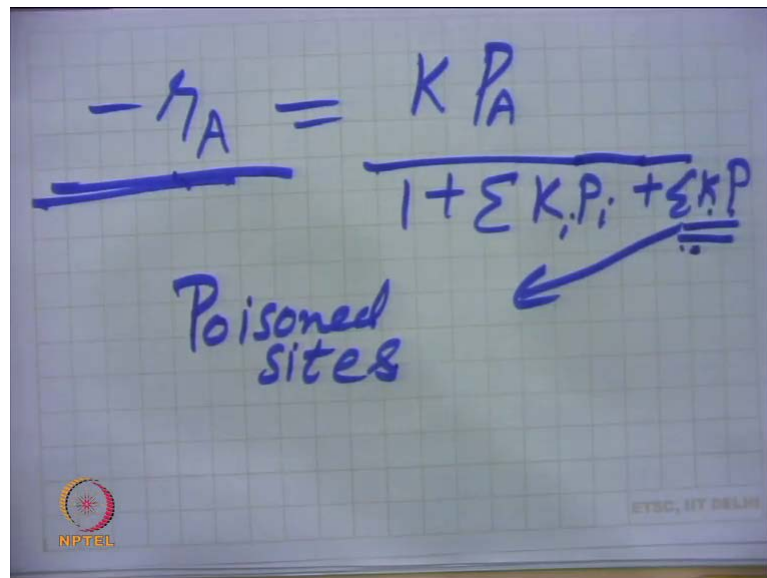
So, if you write the rate of a reaction in general. So, minus r A is equal to k times p A divide by 1 plus sigma of all the species which comes on the surface adsorbed species, right. If this poison precursor is also there, then it will also have some concentration of poisoning precursor times its precursor concentration time the adsorption whatever the

chemisorption rate constant. So, it means overall rate of reaction will now decrease or the sites have been blocked completely. So, these are the poisoned site. So, here rate of reaction will decrease.

So, this is what the irreversible deposition of the poison precursors which are present in the feed stream. So, feed stream whatever especially in the case of hydrocarbon industry, they have lot of sulfur compound, they have lot of nitrogen compound, oxygen compound or metals, and they just deposit on the surface of the catalyst, and this is known as poisoning, right. So, it is a kind of irreversible poisoning which cannot be removed by any treatment. So, catalyst is permanently damaged because of these precursors. The third one which is known coking, so that is basically the deposition of carbonaceous residue from a reactant product or some intermediate and that is known as coking.

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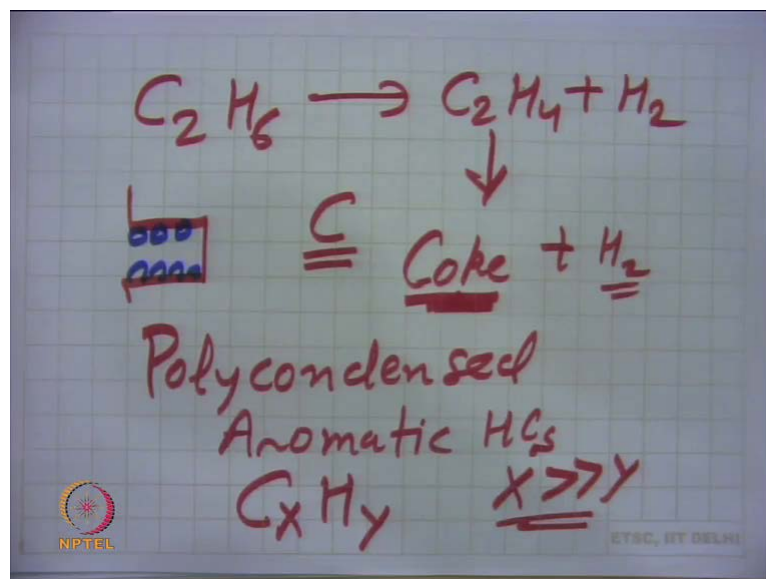
So, what is coking basically? It is something like when you have any hydrocarbon C 2 H 6 suppose ethane and you crack it. So, you get series of the product like say ethylene, right. This may be and simple dehydrogenation if I say, it is a hydrogen something like this, right, but if you crack it further keep on cracking. So, ultimate product is known as coke plus hydrogen like this, right. So, this coke is the carbon material basically c which deposits because of polycondensed aromatic hydrocarbon. So, this is one example, but

when you have the petroleum feed stock, ultimately it is a kind of polycondensed aromatic hydrocarbon.

So, these polycondensed aromatic hydrocarbons generally have a chemical formula C X H Y with x is much more greater than y. So, more than ninety percent by weight if you look at this is the carbon in this and hydrogen content is very very low in this coke, and these coke particles they deposit on the surface of the catalysts. So, whatever the active site of the catalyst or the pore space that is blocked by this carbon materials like this. So, this is what the carbon particle and they cover the surface of the active site of the catalyst. So, again the activity of the catalyst drops down. So, this is known as coking or poly. The only thing here is that once coke is deposited on the catalyst, it can be removed by burning with oxygen.

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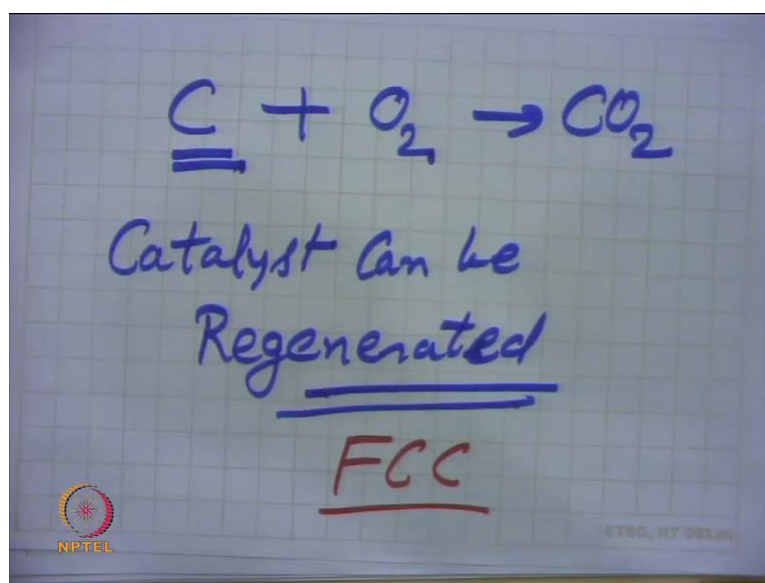
So, if carbon is deposited if you burn it with oxygen under controlled condition, then it gives you carbon dioxide. So, it means the under certain conditions of temperature this coke deposited on the catalyst can be removed, and you get a regenerated catalyst. So, when the coke formation is on the catalyst then the catalyst can be regenerated. So, regeneration is possible in this case of coking. So, this is what in the fluid catalytic cracking. So, the catalyst is continuously regenerated and known as FCC cracking, fluid catalytic cracking. So, we will talk on that later.
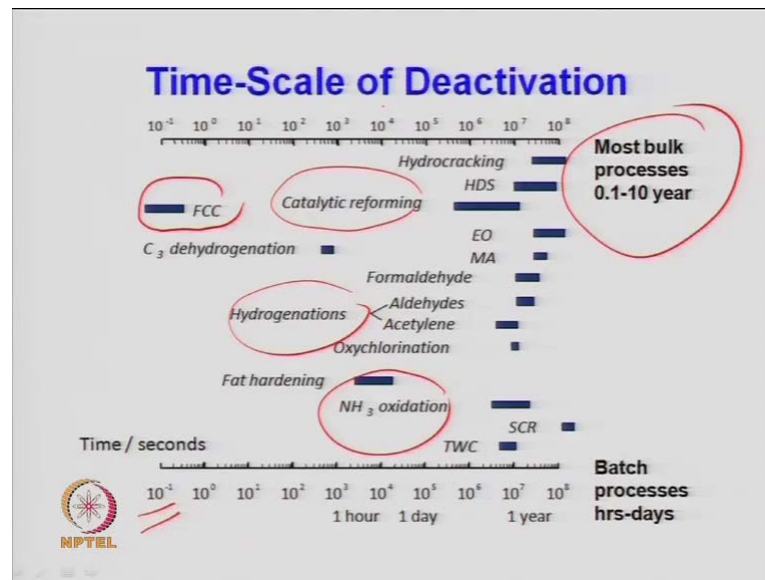
In general now if you look in a process industry the catalytic process industry, the time scale of deactivation vary from fraction of the seconds to years, right. So, most of the bulk process they have the life from 0.1 to 10 years. So, you need not worry about in those cases because it takes six months, it takes one year or three year or five year, and after that the catalyst can be replaced, right. So, that is most of the fertilizer industry as I said or some of the refinery operation, the catalyst life is approximately three year. Actually it depends on the type of operation, it depends on the type of feed stock, it depends on the reactor design also a good kind of reactor design. And under optimal process conditions, the deactivation can be minimized or the catalyst life can be improved.

But if you look at in certain process as I said like in FCC fluid catalytic cracking, the time scale is of the order of one second, right. So, here you can see that dehydrogenation reactions, the time scale is somewhere between 10 bar 2 to 10 bar 3, right. And if you look at here in the FCC the time scale is of the order of 10 of minus 1 in seconds, right, and these are intermediates the catalytic reforming, the hydrogenation, fat hardening, ammonia oxidation. So, these processes have some kind of the time where the time of operation is one hour or it can go up to one day. So, depending upon the process one needs to identify a definite type of catalyst to make it stable.

So, stability is one of the important aspect that how to select a good catalyst which can have a longer life and which deactivates less in order to improve the activity and productivity without replacing the catalyst, because catalyst replacement and maintenance of that reactor, once you replace the catalyst again put the fresh catalyst. So, maintenance all these consumes time as well as money. So, one needs to identify the optimum catalyst and the process and the selection of a definite kind of reactor design depending upon the time scale of deactivation.
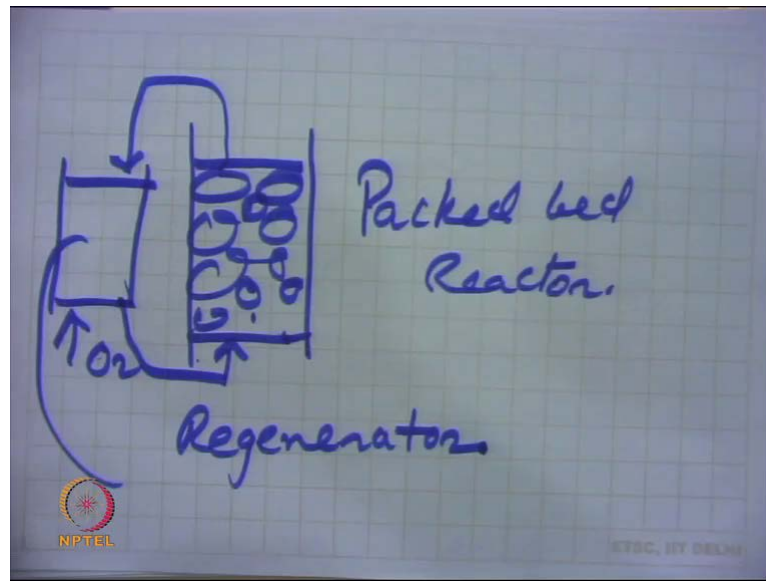
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So, as I just said the reactor design becomes very important in this case when the deactivation is very fast or deactivation is slow. So, accordingly the different kinds of reactors are selected.

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So, fixed bed reactor generally these are just you have a catalyst inside the belt like this, right. So, you put the catalyst inside the reactor and continuously operate it; do it just like a packed bed reactor. In this kind of reactor the frequent replacement of catalyst is not desired. So, it means after six months or after three years the catalyst has to be replaced. So, the operation can be done in a fixed bed or packed bed reactor. So, no resolution is required when the time scale of deactivation is in the terms of years like one year, two year, three year. So, resolution is not important and even after one year the resolution is to be done. So, we can have two reactors in parallel.

So, one is under operation and the second one the catalyst can be regenerated there, and then reuse in the process. So, that can be. So, six months, one year, in the semi batched semi regenerative process if you look at for the reforming or plate forming where the platinum on alumina catalyst is used. So, generally there were in the past the process like a fixed bed reactor and the process were known as semi regenerative process, right. So, that is the one aspect. When the run time or the time of catalyst deactivation is large a fixed type of catalytic reactor can be used. Second are the months. So, again here when the catalyst life is three months or six months as I said, there again one can use a fixed bed reactor, right.

So, there can be fixed bed versus a continuous or semi regenerative type process or a continuous regenerative type process, so that depends on the type of catalyst which has

been used, and the type of operation that is the production capacity. So, if you look in terms of that, so regeneration can be done off and on. So, one you can have two reactors or three reactors, and one is in regenerations mode and another one is in operation mode and so on; after six months the cycle can be replaced, right, or the reactor can be replaced by the second reactor. So, extend by reactor you can call.

And when it is in weeks the deactivation of the catalyst is faster compared to the first two, then the deactivation time may be in weeks. Here you need a swing type mode moving bed catalyst. So, again in the fluid catalytic cracking a moving bed type of reactors were used earlier in past. So, there continuously the catalyst moves up. So, you have a bed like this, and this bed is moving up. So, you take it again and send into a regenerator unit. So, you have a regenerator here where you burn it with the oxygen and this is known as regenerator unit. So, this will be done only when the carbon is deposited or a process where the catalyst can be regenerated easily; otherwise, if there is a chemisorption or poison precursor, then this regeneration is not possible.

So, only this is burning of carbonaceous material in the presence of oxygen at around 550 degree centigrade. So, carbon burns and gives you carbon dioxide carbon monoxide. So, a suitable regenerator design is again important. So, you have a regenerated catalyst and that is sent back into the system. So, that is again a kind of moving bed type of reactor or the fixed bed reactor running in the swing mode, right. So, that can be used when the catalyst deactivates or deactivation time is in weeks. When it is in minutes and days, then fluidized bed reactor is preferred. So, as I said that most of the time in FCC cracking, the fluidized bed reactors are used, right.

There can be a slurry reactor also or a continuous regeneration just like in case of a plate forming process, the continuous regeneration of the catalyst is done. And when the deactivation is very fast and their time of deactivation is in seconds, the catalyst needs to be replaced continuously. So, again either the FCC type reactor fluidized bed reactors or entrained flow reactor with continuous regeneration of the catalyst is desired, right, in order to maintain the activity of the catalyst. So, one needs to identify the catalyst, then process, then deactivation time or time required for reactivation, and then accordingly you can select a combination of reactor and regenerator for the process.

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Cause of Catalyst Deactivation

- Four causes of Catalyst Deactivation
  - Poisoning of the catalyst
  - Deposits on the Catalyst Surface
    (Fouling, coking)
  - Thermal Processes and sintering
  - Catalyst loss via Gas Phase

So, once you look at the selection that is selection of a catalyst design of a reactor system that will depend on the type of deactivation. So, for a given reaction how the catalyst deactivates that should be known mechanism of catalyst deactivation becomes very important, and that will depend on the type of feed stock, type of reaction, and the type of catalyst that has been chosen for a given reaction system. So, what I have discussed so far and what type of deactivations we have discussed so far basically as I told that that deactivation can be because of the poisoning of the catalyst which is the irreversible chemisorption. So, it means the poison precursors are to be removed if you want to prolong the activity of a catalyst.

So, especially as I said when the sulfur is present in the feed stock catalyst deactivates faster. So, it means the concentration of sulfur should be kept at its minimal level. So, hydride desulfurizers are generally used in refinery then petrochemical. So, in order to treat the feed stock which contains large amount of sulfur same thing natural gas desulfurizers are used. There is crude oil has to be desulfurized or your naphtha has to be desulfurized, diesel has to be desulfurized which you must have seen in the automotive exhaust also, the sulfur concentration should be kept as low as possible; otherwise, the catalyst will damage faster. So, this is poisoning.

So, once the poison deposits on the catalyst the catalyst cannot regain its activity. So, the life will be just a fraction of the second, right. So, these are costly catalyst. So, one needs

to remove them. The concentration of the poison precursor has to be removed from the feed stock itself. The second one which we discussed is deposition on the catalyst. So, again you will talk on that later, right, which is nothing but the fouling that is deposition of the dirt or carbonaceous material on the surface of the catalyst. And that reduces the concentration of the active site, and because of that activity of the catalyst drops.

The thermal process that is the catalyst is in contact with the reactor system, and that is high temperature operating at high temperature and for a longer period of time. So, because of that temperature and time there is a kind of solid-solid reaction that may happen. So, freezes may change, right, and simultaneously as I said that the crystal may grow inside. So, that is known as sintering, right. So, that is again a kind of deactivation in the case of catalyst, and one needs to look at the process how to minimize these kind of that is the stable particles, right. So, you need to look at the catalyst materials which are stable to high temperature, then the reaction is to be carried out at high temperature.

And sometimes the mechanical strength of the active catalyst is not very good because attrition it may lose its activity though; that is again a deactivation type of deactivation or it can be that the active metal is not strongly binded to the surface; just mainly the problem when you have a monolith type of catalyst and you have a high flow rate of gas, then this may wash away along with the gas space, right. When you have a liquid product say water steam that is flowing through the catalyst and it may happen that the surface of the metal or metals is not strongly binded with the support, then there may be some kind of wash away of the catalyst. So, that is again a problem.

So, active metal is lost because of high flow rate of the gas. So, that is nothing but the catalyst material, the catalytic active site has to be strongly binded with the support and a proper binding is desired in that case.
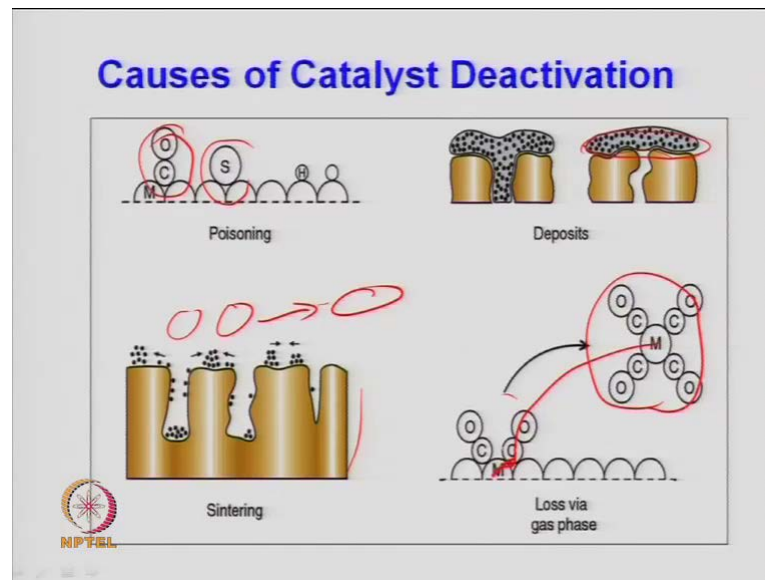
So, what I have discussed is picturized here. This is a poisoning kind of poisoning. So, as I said the sulfur, oxygen, carbon, carbon monoxide, right. All these are a kind of poison precursor. So, they adsorb on the surface of the catalyst, and this is what is chemisorptions; a strong bonding between the sulfur precursor and the catalyst, and now this cannot be removed. It is not a reversible process; it is an irreversible process; so, the catalyst damage. So, active sites have been dropped here or decreased in these cases. Here if you look at it is a deposition of the dirt material, right, or carbonaceous material. So, either in this case, there is a kind of pore blockage.

So, catalyst pore has been blocked, or it can be just covering this two cavity here, and this completes covers this carbonaceous material deposited on the mouth of a pore. So, these kinds of deposits are known as coking. This is again a sintering as I said the increase in the crystal site because of the agglomeration of the particle or just the pore surface where the blockage agglomerates and this surface area of the catalyst decrease or it is a nothing but the recrystalization of the structure of the support itself because of the phase transformation. So, either possibility may happen here right.

So, one thing is that the particles get agglomerated like this as I said, right; they become larger. So, crystal size is that is growth of crystal. You want a nano particle, but the particles have grown inside because of that temperature high temperature, right, or the pore blockage because the pores are just narrowing down and they block. So, pore size

reduces in one way, right. So, that is again a decrease because of the high temperature and time both; this is what I said loss via the gas phase material. So, active material and the gas are flowing over that. So, it has taken along with the active metal m, right. This is the catalyst particle and the gas has taken that because it is not strongly binded.

So, as I said that to have a good catalytic activity some kind of tuning is desired. The active material has to be deposited on the support, but with certain kind of binding. It should not be too strong, and it should not be too weak also. So, that is again important aspect, because if the binding is weak the catalyst will lose its activity because the part of the metal has been lost and taken away by the gases species. So, these kinds of deactivation which may happen and these are the root cause of decrease in activity of a catalyst.

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So, let us just look at the definitions that are the poisoning of a catalyst that loss of activity due to strong chemisorption on active site of impurities present in the feed stream. So, impurities mean this may be sulfur, this may be nitrogen, this may be oxygen, this may be any metal precursor like vanadium, nickel, right. So, these are the poisons for some kind of reaction. So, metal precursors, right, and these all may present in the hydrocarbon feed stock or crude oil as I said which have been treated and then taken to a distillation column distilled out.

But again it has the different streams like naphtha, right, at processed gas oil, vacuum gas oil, and when these contain the sulfur and nitrogen and oxygen compounds, right. These are ring compounds basically, and these are difficult to remove once they poison the catalyst, or they cannot be removed from the surface of the catalyst. In the heterogeneous catalysis if you look at the poison molecules are adsorbed more strongly to the catalyst surface than the reactant molecule. And the catalyst becomes inactive, and this is what the point which I was discussing the poisoning phenomena that this p adsorbs strongly compared to the reactant species which is A and adsorb on the surface, right.

So, suppose you have the diesel compound or you have a naphtha compound which contains the paraphrase naphthenes, cyclic, olefins and aromatics and along with it contains the sulfur nitrogen. So, the binding of sulfur on this metal part which is the cobalt or nickel size suppose if you look at your hydro treatment unit. So, cobalt and nickel have stronger binding with sulfur like cobalt sulfide, nickel sulfide compared to the reactant species. So, these poison precursors even at low concentration the concentration is in PPM level or they are at PPM level, but their small concentration is enough to deactivate or to poison the catalyst completely. And this cannot be removed because it is strong binding between the poison precursor and the catalyst surface. So, one has to remove them from the source itself or from the feed stock itself. So, this is known as poisoning.

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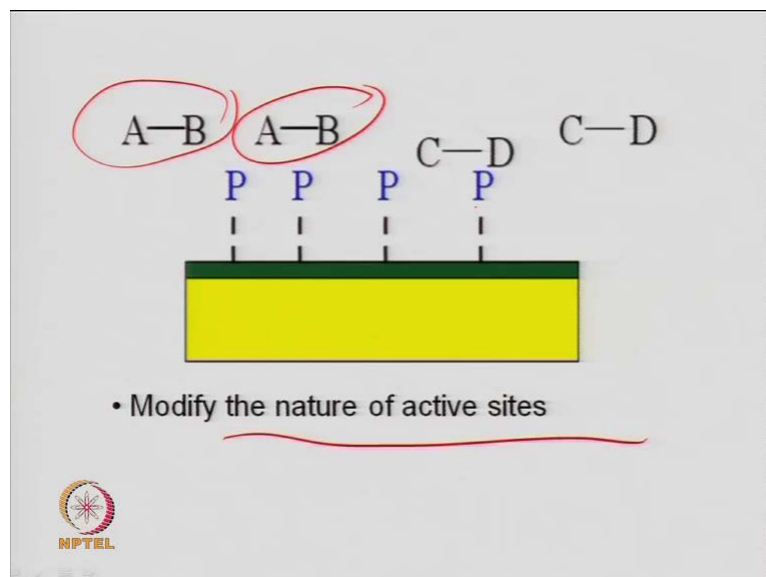
So, this is what the example here shown that these are the poison precursor; these are the reactant species. So, poison precursors can strongly bind with the support, right, and they modify the nature of the active site. So, whatever the activity of the catalyst that declines faster than the poison precursors are present in the feed stock, because they are permanently binded here on the surface of the catalyst.

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Poisons of Industrial Catalysts

| Process	Catalyst	Poison
Ammonia Synthesis	Fe	CO, CO_2, H_2O, C_2H_2, S,P
Steam reforming	Ni/Al_2O_3	H_2S,As,HCl
Methanol Synthesis	Cu	H_2S, AsH_3, HCl
Catalytic Cracking	SiO_2-Al_2O_3, Zeolite	NH_3, Na, heavy Metals
CO hydrogenation	Ni, Co, Fe	H_2S, COS, As, HCl
Oxidation	V_2O_5	As
Ethylene to Ethylene Oxide	Ag	C_2H_2

If you look at some of the example of the catalysts which have been used in industry and the poison precursors like ammonia synthesis, iron is used as a catalyst and carbon monoxide, carbon dioxide, water, acetylene, sulfur, phosphorus, they act as a poison precursor for this catalyst, right. So, it changes the oxidation state; it changes the morphology of the catalyst completely. So, these are the poison precursor. In steam reforming generally nickel alumina catalyst is used and again hydrogen sulfide, arsenic, hydrochloric acid; these are the poison precursor. So, when these precursors are present the catalyst activity drops at a faster rate, and these are chemically binded to this nickel metal.

Same thing for methanol synthesis; copper is used as a catalyst or hydrogen sulfide, arsine, hydrochloric acid; these are the poison precursor. For catalytic cracking silica alumina type catalyst or zeolites are used, right, and ammonia, sodium metal, heavy; metal these are the poison precursor for this catalytic cracking catalyst. Similarly, CO hydrogenation, nickel, cobalt, iron are used as a catalyst, and for these metal precursor

hydrogen sulfide, carbonyl sulfide, arsenic, hydrochloric acid; these are the poison precursor.

For oxidation reaction generally vanadium pentaoxide is used as a catalyst, and arsenic is the poison which is present in the feed stock in the reactant field. Same thing for ethylene to ethylene oxide, right, for making at oxide regions, the silver is used as a catalyst and acetylene is the poison precursor for this catalyst. So, one needs to remove them or minimize their concentration in order to enhance the life of the catalyst.

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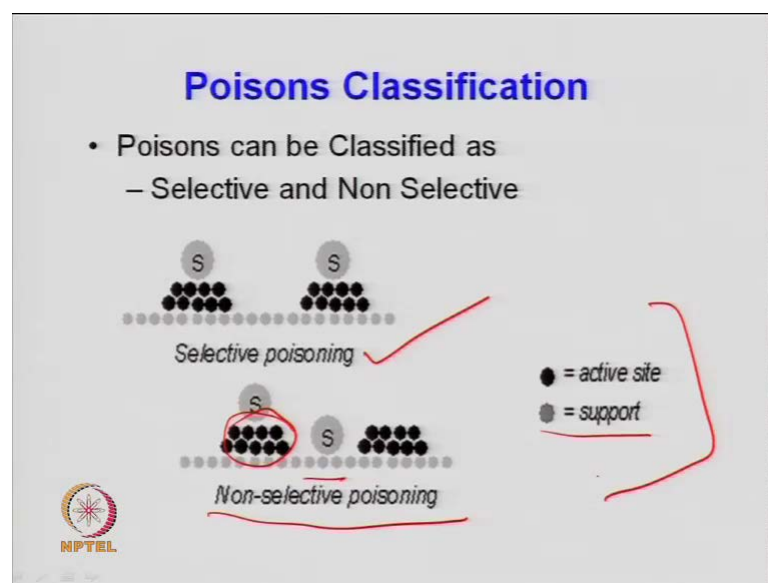
So, classification of the poison is selective and nonselective. So, selective means the poison precursor adsorbs on selective sites, right, and that is known as selective poisoning. So, here you can see that the sulfur precursor, and they adsorb on the particular type of localized site on the active site of the catalyst, and that is the selective type of poisoning. Here if you look at the nonselective, the same sulfur molecule adsorbs on this that is the metal sites or which is the active site of a catalyst, but simultaneously it also adsorb on the support side also. So, this becomes a nonselective type of poisoning.

So, both type of poisoning may happen; that is sometimes suppose nickel on alumina is the catalyst. So, the sulfur adsorbs on nickel site; it is strongly binded with the nickel site, but simultaneously it adsorbs on the alumina surface also. So, whether it is nickel alumina, cobalt alumina, so the sulfur adsorption may be a kind of nonselective type of poisoning, right. So, in some cases suppose the carbon monoxide is the gas it may

happen that the carbon monoxide gas adsorbs on the nickel site only not on the alumina or silica site.

So, it means this selective and nonselective both kind of poisoning may happen, and one needs to look at the mechanism when we design a reactor or when select a process for the given catalytic reaction. Because understanding of these kind of mechanism, how the poisoning or what kind of deactivation is happening in a catalyst, and how does it drops, how does it decrease the activity of catalyst; that should be clearly understood in order to look at the rate or regeneration of the catalyst if possible.

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So, it can be reversible; it can be irreversible as I said. Reversible poisoning which may be due to the oxygen compound like oxygen, water, CO, CO 2. So, they are reversibly poisoning. So, that this can be regenerated also although bit difficult, but it can be done. But if it is irreversible poisoning that is connected with nonmetals like sulfur, chloride, arsenic, phosphorus. Then these are very difficult to remove, right, phosphine; all these are chemically bind with the surface.
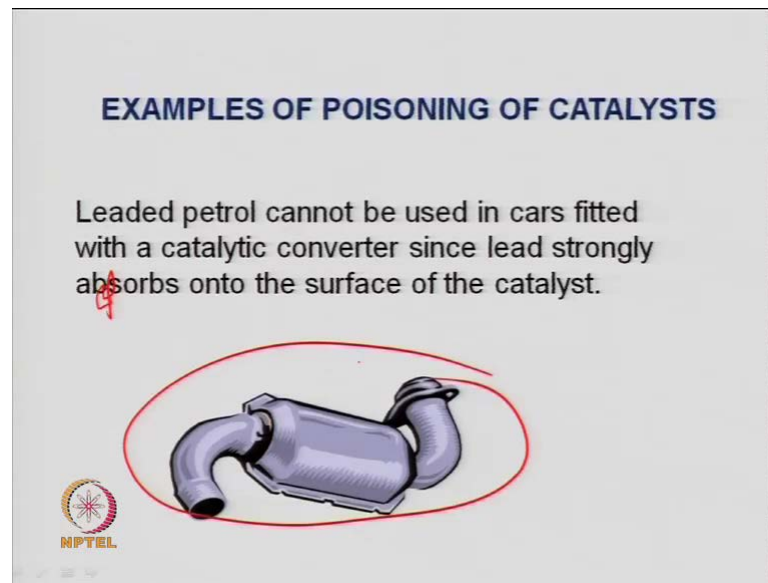
So, this is just an example that what happens when you look at your automotive exhaust catalyst, right. And earlier lead was used right, but because lead is itself is a catalyst, and it poisons the catalyst. So, leaded petrol cannot be used in cars fitted with catalytic converter, right, because lead strongly absorbs on the surface; this is rather adsorbs on the surface of the catalyst, and poisons it faster. So, for the case of automotive adsorbed catalysts as I said that sulfur should also be very very low. So, that is why if you look at new norms for the petrol diesel, the sulfur concentration in petrol has been reduced to a zero PPM level or, say, in underdeveloped country is still it is 10 PPM or 50 PPM in some of the country.

But if you look at in the same for the diesel also, the sulfur concentration should be less than 250 PPM, but in most of the country they are following not less than 10 PPM, right. So, the reason is that because all this catalytic converters, right, which are three way catalyst nowadays, selective catalytic reduction SCR type of process which is used for removal of carbon monoxide, sulfur oxides, nitrogen oxides, right. So, the catalyst is very selective in its action here in this selective catalytic reduction. So, large concentration of sulfur may poison the catalyst. So, it will damage the total catalytic converter.

So, the sulfur concentration has to be reduced to a certain level, and this is a kind of the catalytic converter which is generally put at the exhaust of the automotive vehicles, right,

the petrol engine, diesel engine. So, these are the kind of systems or catalytic converters which have been used in the automotive process.

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So, generally the catalysts are noble metal type, say, rhodium is used for this purpose in this selective reduction catalytic reduction, right. And nickel and copper can also be used, but with them the deactivation is faster. So, use of copper and nickel in a catalytic converter is avoided, right. The platinum or rhodium which are known as PGM group metal; although they are costly, PGM group metals I told they are very costly noble metals, right. But they are huge because this sulfur dioxide which is present in the exhaust fumes even in trace amount, it poisons the catalyst.

So, the concentration of these copper and nickel you need a larger amount, and even the small concentration of sulfur oxides they will damage the catalyst, but this PGM group metals like platinum or rhodium, they are stable in terms of the deactivation. So, that is why they are used. So, once the catalytic converter has become inactive it cannot be regenerated. So, you have to just throw this one and replace it by a new catalytic converter.

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So, preventing poisoning as I said that especially in the hydro desulphurization reaction you have to remove the poison precursor, because the life of the catalyst has to be enhanced or increased. So, try to make the concentration of these poison precursors as low as possible. So, decrease poison content in feed and for example, just if you look at hydrodesulphurization which is the hydro treatment, in fact, a trickle-bed reactor is generally used followed by hydrogen sulfide adsorption to remove the sulfur compound. So, that is one; the hydrodesulphurization is done to remove the sulfur compound.

So, overall the process is known as hydro treatment and widely used in the refinery, because the sulfur concentration has to be reduced. So, to remove the sulfate the process is known as hydro desulfurization. So, generally cobalt molybdenum based catalysts are used for this purpose known as CO MO x, cobalt molybdenum or Ni MO x nickel molybdenum. So, these types of catalysts are generally used for hydro desulfurization.

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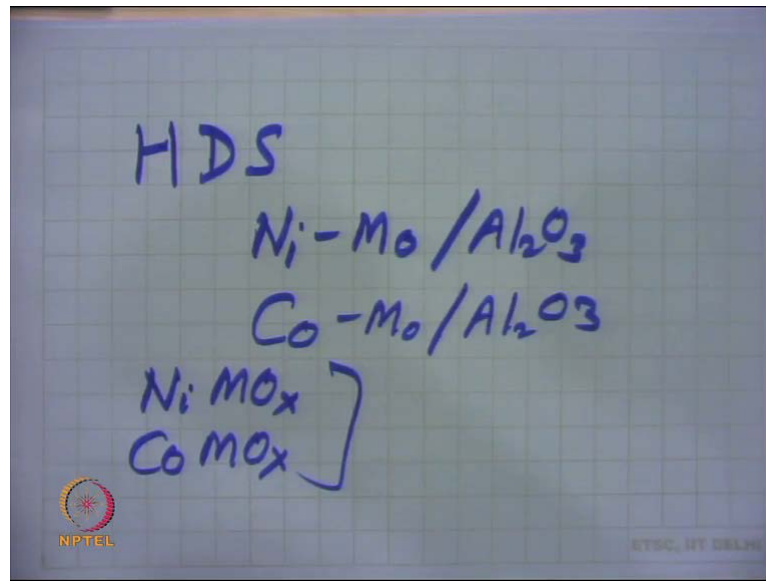
So, the process known as HDS, right, and catalysts used are nickel, molybdenum known as Ni MO x on alumina or cobalt molybdenum on alumina. So, they are known as Ni MO x oxides of this or CO MO x used for hydro desulfurization, but as I said that these sulfur is a poison to them also, right. So, you have to reduce the concentration to a certain level in order to enhance the life of this catalyst. So, sometime a guard reactor is used first which contains the similar catalyst, but most of the sulfur compounds or sulfur is removed in the first reactor, and then it is taken into a second hydro treater unit where the treatment is done in presence of hydrogen.

And all the sulfur compound reacts in the presence of hydrogen, and hydrogen sulfide will come out as a product gas. And that can be absorbed in some adsorbent or in some liquid or adsorbent or absorbed by using some different kind of liquid absorbent, or it can be adsorbed also. So, sulfur can be removed, and it can be reused also in the process. So, RND is being done in this kind of treatment process. So, second thing is that catalyst formulation; that is again important aspect nowadays. So, catalyst formulation and design; just for example, the copper based methanol synthesis are strongly poisoned by sulfur.

So, this is the present method for the methanol synthesis carbon monoxide and hydrogen reacts in the presence of copper based catalyst, and methanol is produced, but the poison sulfur a small concentration of sulfur it poisons the catalyst. So, new method, new

treatment methods are to be developed; same thing here also the hydrodesulphurization. At presently nickel molybdenum catalyst are used, but these catalyst have roughly three years of life, right, and that to depend on the concentration of sulfur in the feed stock. So, if the sulfur concentration is high the catalyst life will drop.

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So, we have to look at the kinetics of poisoning reaction, kinetics of deactivation reaction; in order to introduce the terms for the main reaction rate, because now if you look at as I said that activity of a catalyst drops.

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So, activity now is a function of time, right, and this is defined as r A at anytime t divide by r A at t is equal to zero initial rate. So, it means if you want to write the rate of main reaction at any time t. So, r A dash at any time t is written activity at that time multiplied by r A 0. So, at t is equal to 0 I will write it like this initial rate first rate. So, the rate at any time can be defined, right, and that has to be incorporated in terms of the size in a reactor or in order to look at the productivity, because rate is related to the productivity conversion. So, for that you need to find out this activity, right, and activity will depend on that type of that is precursor poison precursor it is concentration and by what mechanism it deposits.

So, it can be first just like the kinetics of the main reaction is studied, the kinetics of deactivation reaction should also be studied. So, it can be a first order, it can be second order, right, and like that; it can be some kind of a complex mechanism also. So, that is the order of deactivation is to be known, and again this may be a function of time. So, the rate constant for deactivation should also be noted, but in general if you look at here the adjustment for the decay of the catalysts, we need to find out that, right. And the reactions may be a separable type of kinetics whereas the rate is it is activity which is a function of past history, right, and times the rate which is a fresh catalyst.

So, same term which I have used here are a zero fresh catalyst times activity. So, activity will depend on how the catalyst has behaved before that, right. I told you activity is a function of time, right, the history of the catalyst. So, that is to be found out first.

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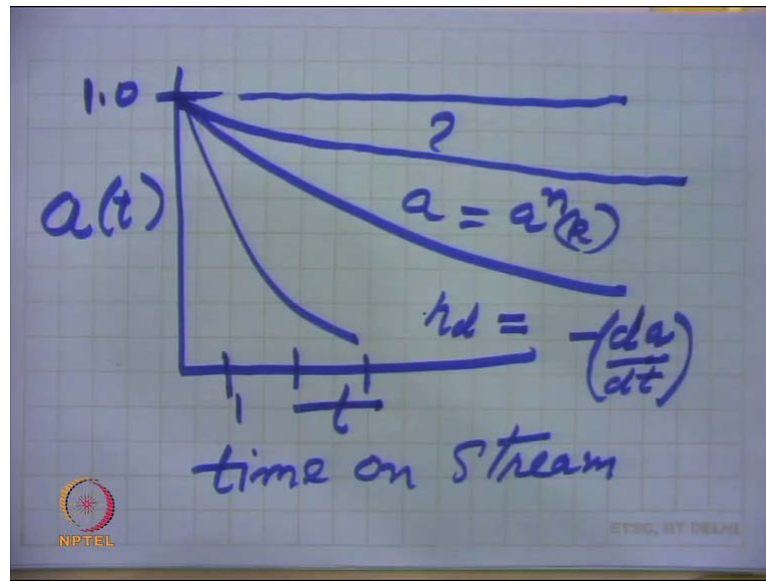
And for that you have to look at this graph. Activity A as a function of time on stream; remember this is time on stream, right. That is it is just something like I said that it can be a number of days. So, one day, two day, three day, like that; it can be in terms of the years, right; it can be in terms of the seconds also. It depends on the type of deactivation. So, if the catalyst is all that time very stable, then it should be like this a constant, right. There should not be any drop, and that is what we want to have a stable catalyst, but this is not true; most of the time the activity may go like this, right; it can go like this; it can go like this also.

So, it means we have to find out what is this function A as a function of A which is some folder I will write n, right, and times some constant which may be a function of temperature. Just like rate you write a temperature dependent term and the concentration dependent term, here also how this changes with time. So, one thing is clear that you have written it activity decreases with time. So, just like conversion decrease with time. So, it means that decrease in activity with respect to time I will write it minus d a by d t. This simply says that how the activity of a catalyst change with time, right, but since activity can never increase it decrease with time. So, that is why a minus sign has been kept here.

So, this graph talks; if you take the tangent or you should take the slope at different time, you will get the rate of deactivation; that is minus I will write it r d at this point, right;

that is deactivation rate. It is not the main reaction rate; rather it is how the activity of the catalyst decreases with respect to time, and that will depend on several things. Several thing means whether it is centering, whether it is poisoning or whether it is coking and fouling.

So, we have to understand first the mechanism of deactivation and then we need to write the expression A as a function of whether it is a carbon precursor, it can be sulfur or a poison precursor or it can be something where the crystal surface area is decreasing because of centering phenomena. So, we need to collate the properties in terms of the activity of the catalyst, and then we can substitute it in the main reaction rate which is written here, right. So, this is the rate of a main reaction which is related to activity times the rate when the catalyst was fresh; there was no effect of the centering; there was no effect of the poison precursor, and there was no change in terms of the concentration. So, we need to correlate these rates.

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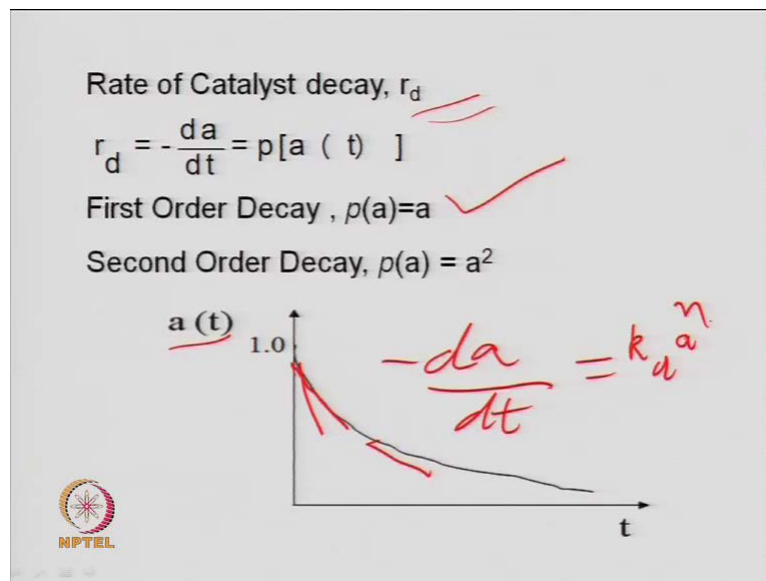
So, this is what the discussion which I was talking that rate of a catalyst decay r d is given by minus d a by d t, and that will depend on the activity. It will depend on some concentration; it may be the concentration sometime we write the reactant feed concentration which is related. So, basically it is the concentration of the poison precursor, but the concentration of poison precursor may be a function of the

concentration of the main feed. So, sometimes we write it in terms of the main feed concentration also. So, we will talk on that later.

So, depending upon that this order this deactivation function it can be written first order deactivation which one can find out by doing this experiment. So, for that one needs to do the experiment like this activity as a function of time and then calculate the tangent; that is tangent at each point here like this and find out minus d a by d t. And once minus d a by d t is known, it is related to some constant k d times A to the power n. And we can find out either by differential method of analysis or integral method of analysis as we have discussed in our reaction engineering, right, that we have done that during reaction engineering. So, same approach can be used here. So, I will continue it next time.

Thank you.