# Chemical Reaction Engineering II
Prof. Ganesh Viswanathan
Department of Chemical Engineering
Indian Institute of Science, Bombay

## Lecture - 6
## Catalyst deactivation and accounting for it in design – I

Friends, let us summarize what we have learnt in the last couple of lectures. So, we have learnt how to deduce the rate law, we from experimental data and we have learnt how to find a mechanism for a given heterogeneous catalytic reaction and then we had looked at how to find the rate parameters concerning the rate law. Then, we had looked at how to design a packed bed reactor and how to find the profile of the conversion as a function of the weight of the catalyst in the last couple of lectures.

So, while doing all this we have assumed that the catalyst activity that is the number of active catalyst sites, which is available for the reactants to adsorb on to the catalyst site for the reaction to occur, is always constant. But unfortunately, mother nature is not so kind and it turns out that the catalyst activity does not remains constant.

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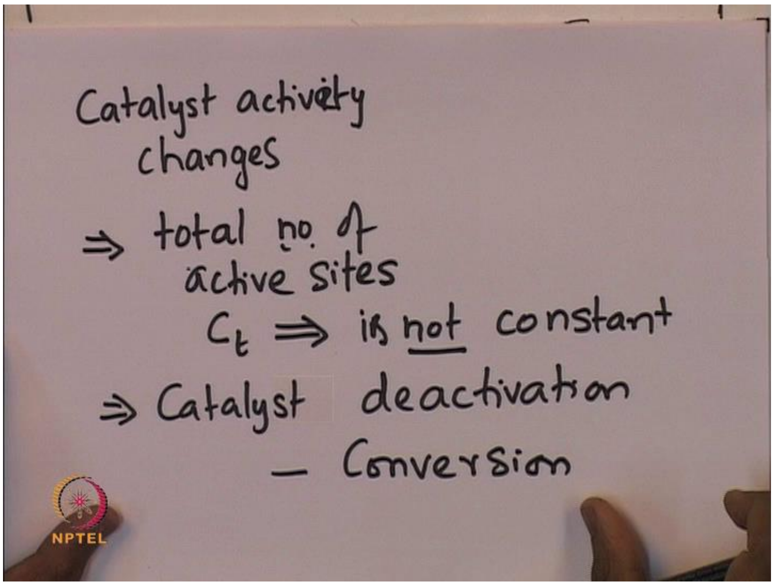

Catalyst activity
changes
⇒ total no. of
active sites
$C_t$ ⇒ is not constant
⇒ Catalyst deactivation
— Conversion

So, we always assume that the catalyst constant, catalyst activity is constant but the catalyst activity catalyst activity changes with time changes with time. Now, what does it mean? It means that the total number of active sites total number of active sites, which may be available for adsorption of the reactant species on to the catalytic site for the catalytic reaction. Now, that nodal number of active sites c t, which is the concentration of the total concentration of the active sites, so that is not a constant. Now, what happens if it is not constant? So, what happens is that the catalyst actually gets deactivated.

So, there is a catalyst deactivation process there is a catalytic deactivation process and in fact, it is a very major problem in that is faced by most of the industries when they conduct a catalytic reaction. It is known to strongly affect the conversion and as a result the performance of the reactor itself. So, catalyst deactivation is a very, very serious problem and it is very important to understand how this deactivation occurs and are there mechanisms are there ways by which one can actually circumvent the catalytic deactivation process in a reactor. Deactivation, is essentially a process by which the active sites, which may be present in the catalyst pore that is somehow not available for the reactants to go and adsorb. So, let us describe a little bit more about deactivation.

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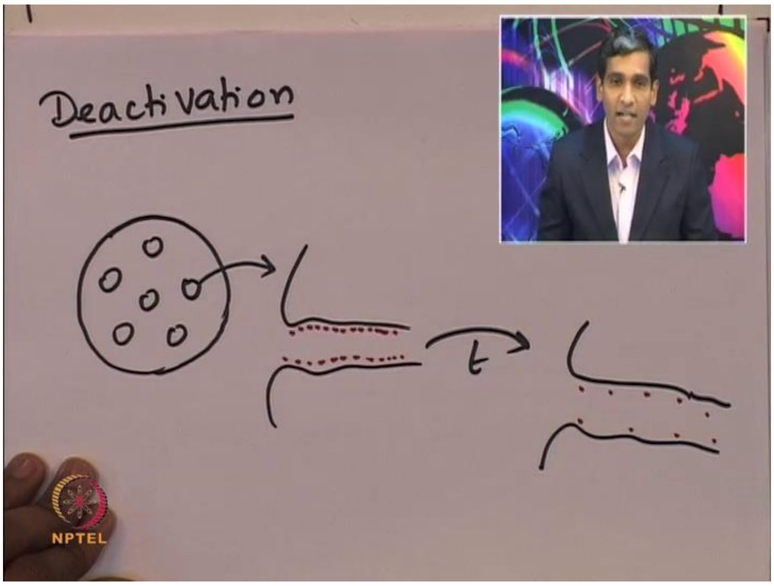

So, deactivation suppose if there is a catalyst if there is a catalyst support, in which a particular catalytic material is actually impregnated. Let us say that these are the pores these are the pores, which is present on the catalyst inside which there are active sites. Suppose, let us say I zoom up one of the pores, which may be present inside the catalyst. So, if this is a pore and the active sites are actually present. So, if these are the active sites, which may be present in the pore onto which the reactance can adsorb in order for a reaction catalytic reaction to take place.

Now after a certain time after the catalyst is actually used for a certain time for various reasons, these active sites reduce in number; number of active sites, which may be present that reduces and you can see that the number of reduce sites, which is available for adsorption of the reactant species for the reaction goes down as a function of time. So, this process of loss of the catalytic sites for the reactants to adsorb and to facilitate the catalytic reaction is what is called as catalyst deactivation.

In this lecture and in the next lecture we are going to see different types of deactivation; what all the mechanisms that govern the deactivation process are and how to incorporate that in the reacted design is what we are going to see in the next couple of lectures. So, as in the case of any process, which is involved in a catalytic reaction the first step is to understand how to get the rate law.

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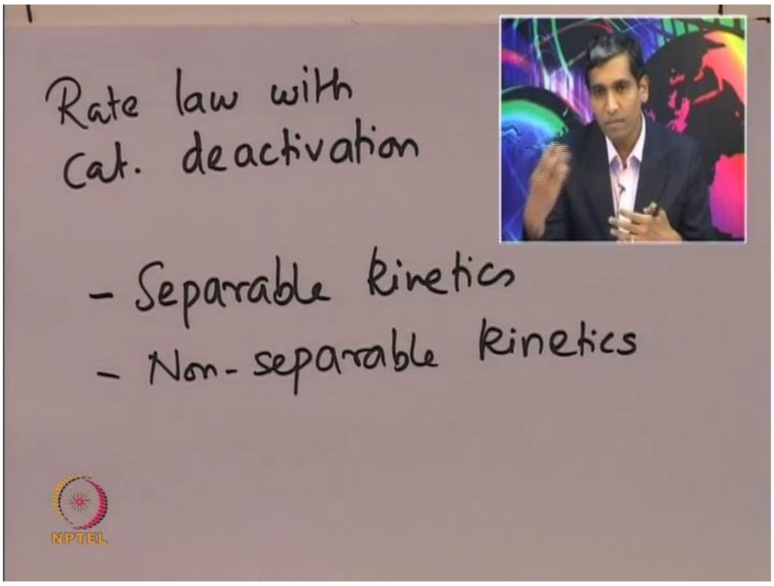

Rate law with
Cat. deactivation

- Separable kinetics
- Non-separable kinetics

So, in this case, how to find the rate law with in the presence of catalyst deactivation? So, this can be broadly classified into two different types; one, where it is called the separable kinetics and other one it is called the non-separable kinetics. So, separable kinetics is one, where the dynamics of the catalyst deactivation process and the actual kinetics of the catalytic reaction; these two can be independently modeled and the mechanisms can be independently understood while the non-separable kinetics is where it cannot be looked at independently.

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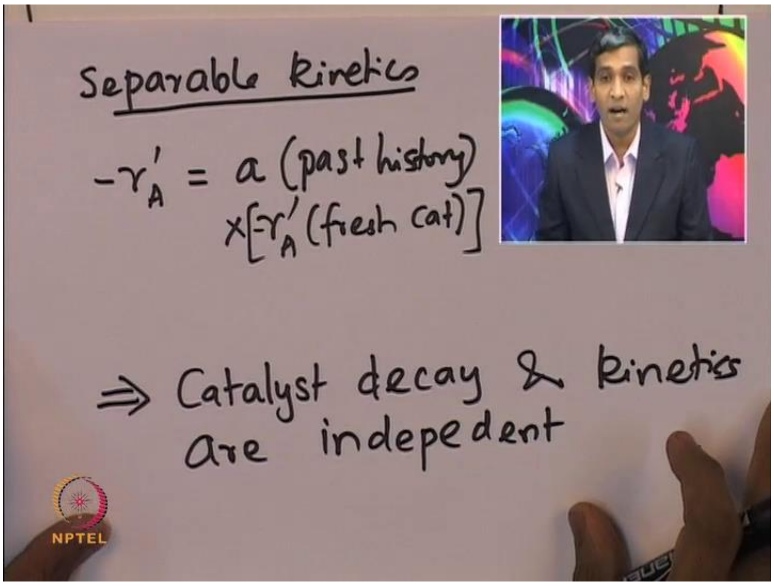

Separable kinetics

$$-r_A' = a\,(\text{past history}) \times [-r_A'(\text{fresh cat})]$$

⇒ Catalyst decay & kinetics are indepedent

So, in the case of separable kinetics in the case of separable kinetics one can actually write the net rate law; suppose if a is the reactant, which is catalytically reacting in order to form products b then one could actually write rate law which looks like this, where a is the activity of the catalyst, which depends only on the past history of the catalyst multiply by the reaction rate as if the catalyst were to be fresh. That means, that the deactivation kinetics and the actual kinetics of the catalytic reaction can be looked at separately and independently.

So, the activity is only a function of the past history and that is scaled with the reaction rate if it were to be a fresh catalyst is what gives what is the reaction rate; what is the reaction rate at a particular level at which the deactivation has occurred. So, this suggests that the catalyst decay and kinetics are independent. So, in this modal of separable kinetics the catalyst decay and the kinetics of the catalytic reaction are independent.

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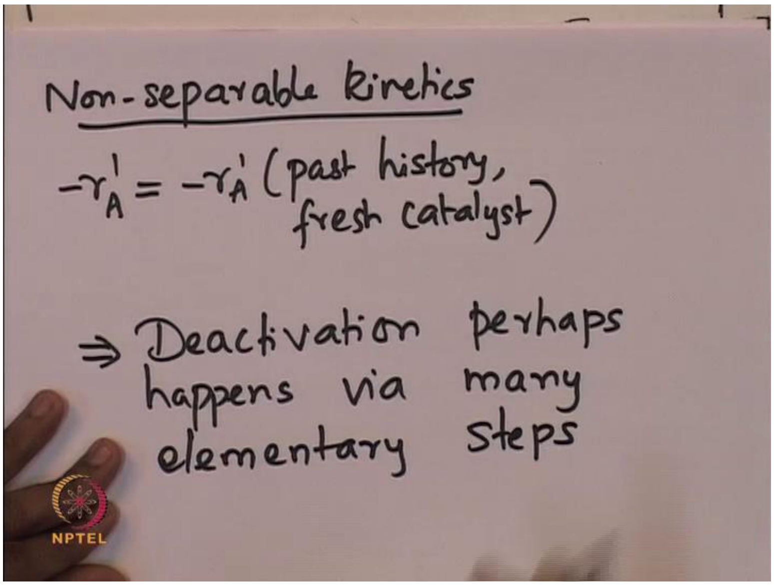

Non-separable kinetics

$-r_A' = -r_A'$ (past history, fresh catalyst)

$\Rightarrow$ Deactivation perhaps happens via many elementary steps

Now, what happens in the non-separable kinetics? In the non-separable kinetics case, the net reaction rate the rate at which the species a is being consumed is now dependent both on the past history and the rate if as if the catalyst was not deactivated that is what is the rate if the catalyst were to be a fresh catalyst. So, it depends on both on the properties or the nature of deactivation simultaneously along with the actual reaction rate of the catalytic reaction. So, which suggest that the deactivation perhaps happens on perhaps happens via many elementary steps. So, in the next couple of lectures we will not deal with the non-separable kinetics, which will be dealt with separately later.

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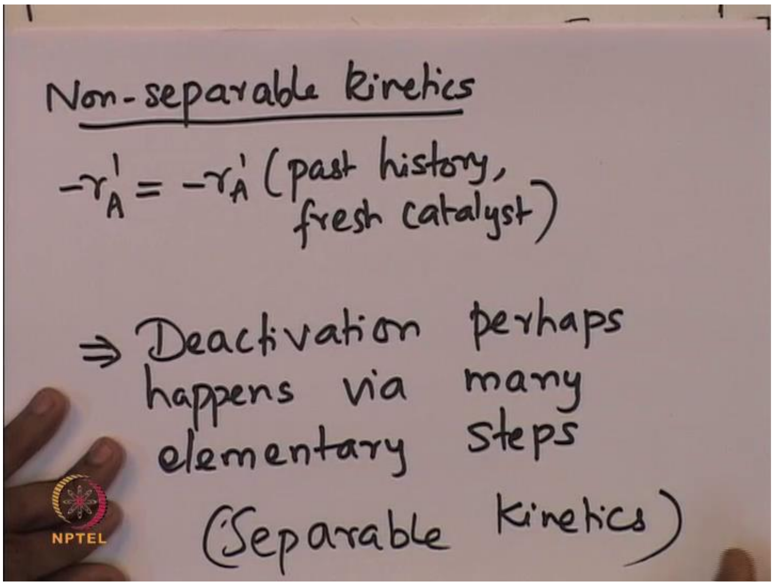

Non-separable kinetics

$-r_A' = -r_A'$ (past history, fresh catalyst)

$\Rightarrow$ Deactivation perhaps happens via many elementary steps

(Separable kinetics)

So, in this couple of lectures we will only be looking at the separable kinetics. Now, when we talk about separable kinetics the most important quantity that needs to be described is the activity of the catalyst.

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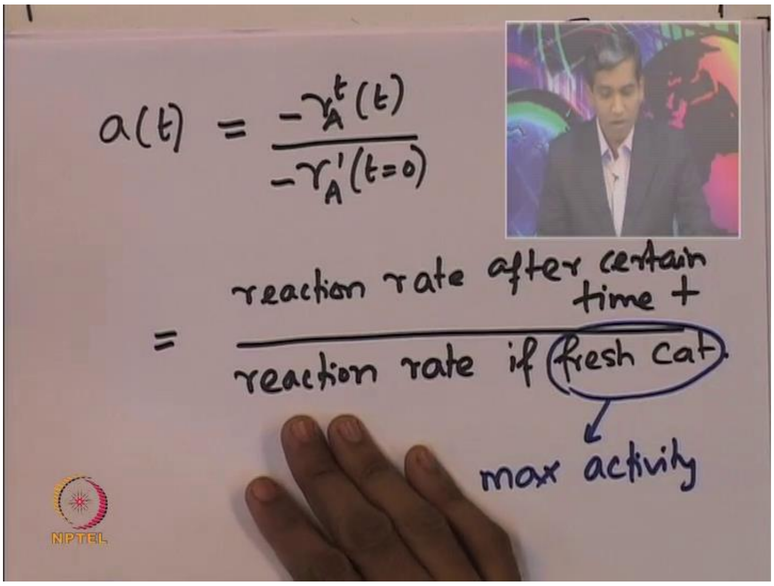

$$a(t) = \frac{-r_A^{t}(t)}{-r'_A(t=0)}$$

$$= \frac{\text{reaction rate after certain time } t}{\text{reaction rate if fresh cat.}}$$

fresh cat → max activity

So, a of t, which is the activity of the catalyst is defined as the rate, the reaction rate on the catalyst for a given activity or at a given time divided by the rate the reaction rate in the same catalyst if it were to be a fresh catalyst. So, it is the reaction rate after the catalyst has been used after certain time t, after certain time t divided by the reaction rate if it is a fresh catalyst.

Now, it is important to realize that the maximum activity is possible only in a fresh catalyst. So, it is important to realize that the maximal activity that is the maximum possible sites may be available for the catalytic reaction when the catalyst is fresh. So, therefore, it is important to so the exercise is going to be as to how to characterize and how to obtain the deactivation process as a function of time in the presence of catalytic reaction. So, naturally the activity of the catalyst is going to change with time.

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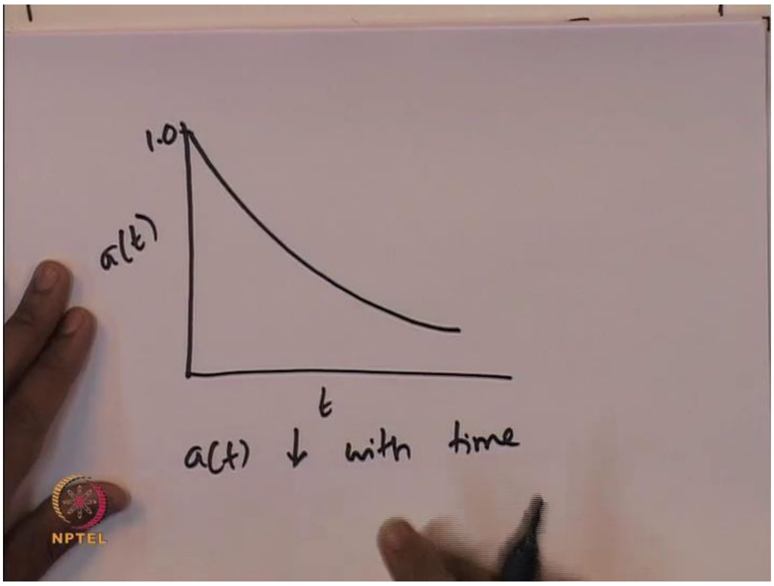

The typical profile, it starts with one because it is a fraction and it is a fraction of catalyst that activity which is left and so it goes from it exponentially decreases with time. So, clearly a of t decreases with time; so suppose if there is a reaction, how do we write the reaction rate law when there is catalytic deactivation process occurring simultaneously.

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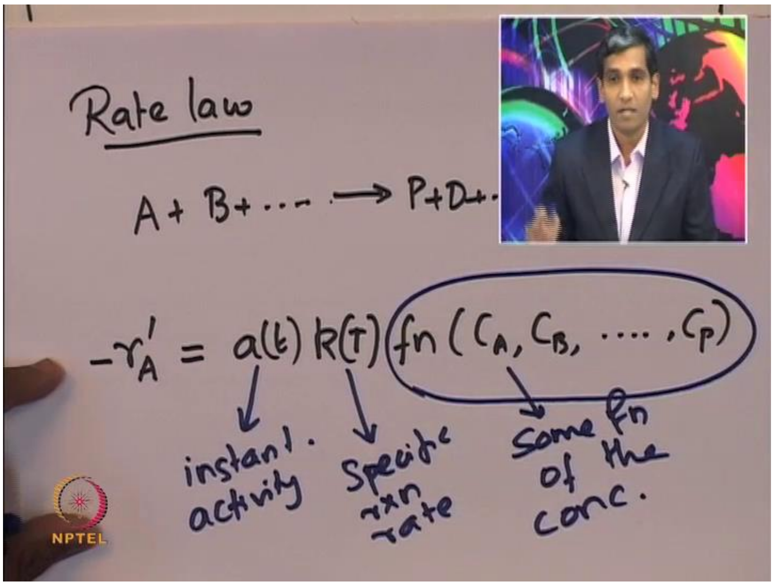
Rate law

$A + B + \cdots \longrightarrow P + D + \cdots$

$-r'_A = a(t)\,k(T)\,\boxed{fn\,(C_A, C_B, \ldots, C_P)}$

So, suppose if the catalytic reaction is A plus B plus gives P plus D plus. So, now, we can write the rate of consumption of species A because of catalytic reaction as the product of activity of the catalyst multiplied by the corresponding specific reaction rate, which is dependent on the temperature at which the reaction is being conducted multiplied by some function, which is a function of the concentration of all the species that may be participating.

So, let us stare at this equation. So, a t is the activity instantaneous activity of the catalyst; k T is the specific reaction rate and it is a function of temperature. So, as you increase the temperature the specific reaction rate increases and this is the some function of the concentration of species. How it affects the reaction rate law and that is what is captured by in this function f n, so now the decay rate. So, as the catalytic deactivation occurs simultaneously along with the catalytic reaction. So, there has to be a certain decay rate. So, the decay rate can be captured in terms of the properties or the quantities of the species that is the concentration of various species which is present, so that can be written in the in the following form.

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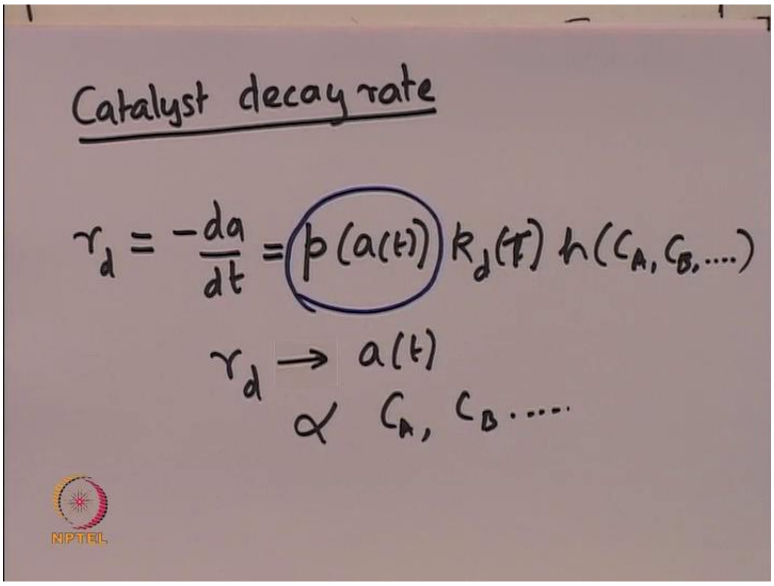

Catalyst decay rate

$$r_d = -\frac{da}{dt} = \boxed{p(a(t))}\, k_d(T)\, h(C_A, C_B, \ldots)$$

$$r_d \rightarrow a(t)$$

$$\propto C_A, C_B \ldots$$

So, the decay rate typically takes the same form as that of the rate law. So, therefore, the decay rate r d is given by is minus da by dt that reflects the rate of change of activity, which respect to time. This should be equal to some function p, which depends on the activity itself multiplied by the corresponding specific decay constant, which depends which is a function of temperature multiplied by some function of concentration of all the species.

So, clearly from here you can see that r d depends on the activity its proportional to the concentration of species. So, therefore, it is important to know the concentration and it is important to find out what is the functional form of this p in order to estimate what is the catalyst decay rate.

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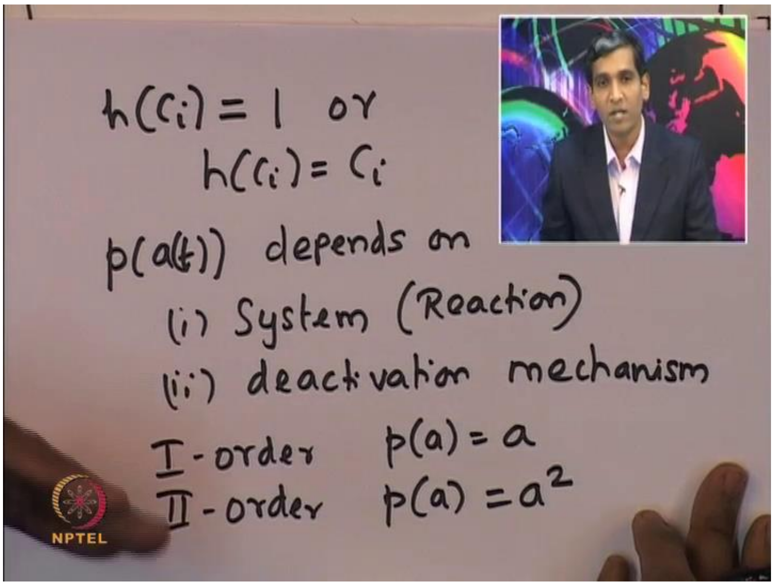

$h(c_i) = 1$ or

$h(c_i) = c_i$

$p(a(t))$ depends on

(i) System (Reaction)

(ii) deactivation mechanism

I-order $p(a) = a$

II-order $p(a) = a^2$

So, for the purpose of this course we will assume that h of c i, which is basically the dependence of the concentration in the decay rate law as one or utmost as h of c i to be equal to c i. That is, it is either does not depend upon the concentration of the species or we will assume that it depends utmost linearly on the concentration of the species. So, and also we will assume that this function p, which takes the functional form of the activity of the catalyst depends on, what is the catalytic system that is what is the catalytic reaction; what is the catalytic reaction that is being conducted.

We will assume that this dependence of the activity the functional form that captures the dependence of the activity on the decay rate will depend upon the reaction, which is being conducted and also on the deactivation mechanism, which we will describe shortly. So, suppose if it were to be a first order decay if the decay processes first order with respect to the activity. Then, if it is a first order process then p of a will be equal to a; and if it is a second order process then p of a will be equal to a square. So, depending upon what is the order of the dependence of the activity on the decay rate; we can accordingly assume certain dependence of p on the activity itself.

Now, the decay of the catalytic sites that is the loss of catalytic sites in a catalyst will depend upon many different aspects. So, based on the nature of the loss or the type of loss of the catalytic activity; they are three broad classification have been identified.

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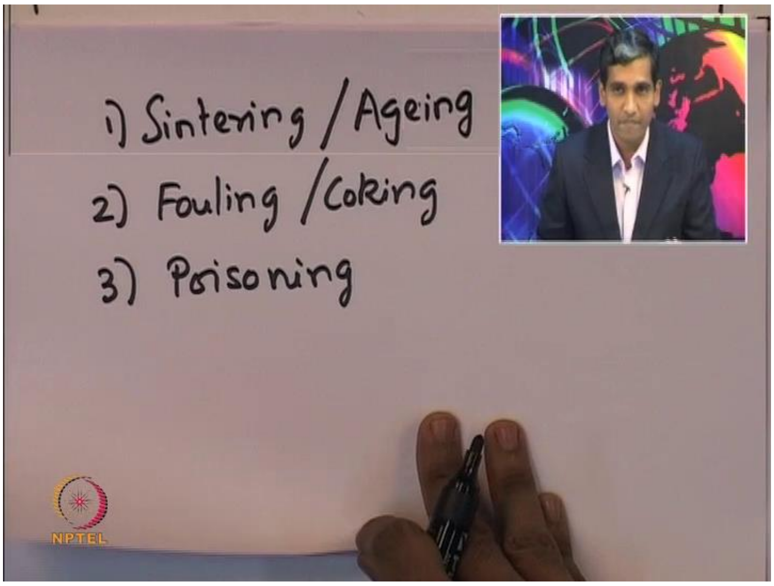

1) Sintering / Ageing
2) Fouling / Coking
3) Poisoning

These are sintering slash ageing process. So, this is essentially captures the loss of the catalyst because of long exposure of the catalytic sites to the reaction and then the fouling or coking process. So, this is essentially the deposition of various carbonaceous or coke material on the catalyst site; the deposition of the coke on the catalyst site it leads to strong deactivation of the catalytic sites and it is possible to regenerate the catalyst which we will describe later. Then, the third type of deactivation of catalyst is called the poisoning process. So, there may be poison present in the feed stream, which may enter the catalyst pores and they make get deposited on the catalyst site.

It may destroy the activity of the catalyst or the reactants or the products itself may actually go and irreversibly bind or get adsorption on to the catalyst surface and as a result may poison the activity of the catalyst site, and therefore deactivating the catalyst itself. So, we will see in detail what these three different types are and how to characterize; what are the mechanisms that are associated with each of these deactivation process is a how to find the rate law for each of them.

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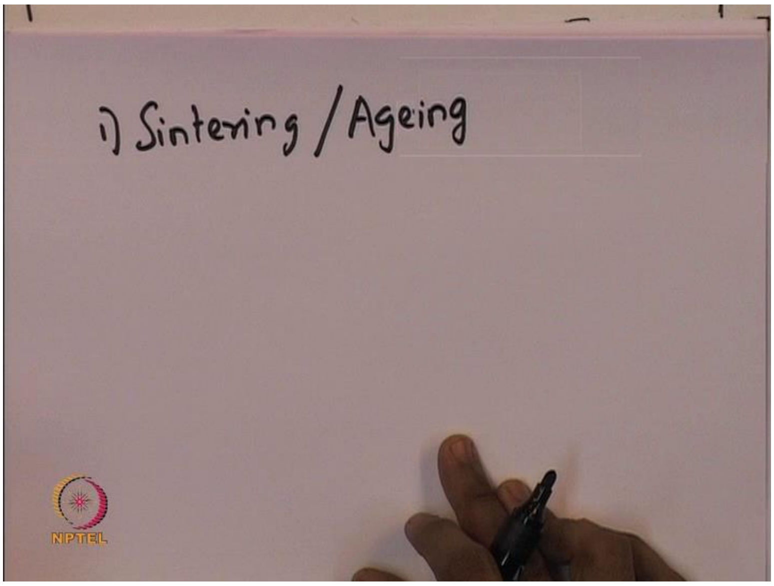

So, let us take the first one which is the sintering process sintering method of a deactivation. Let us take the sintering method of deactivation. So, sintering is basically the deactivation of the catalyst, because of the prolong exposure of the catalytic sites to the reactants on the gas stream, which is present as a result, because the reactants are conducted at a high temperature the metal particles, which act as a catalyst and which are impregnated on the catalyst site. So, that actually leaves the catalytic sites and then those starts they start agglomerating together.

As a result, the net surface area which is available for the reactants to go and adsorb on to the catalytic site that significantly reduces and as a result the catalyst activity is completely lost. So, this can be captured.

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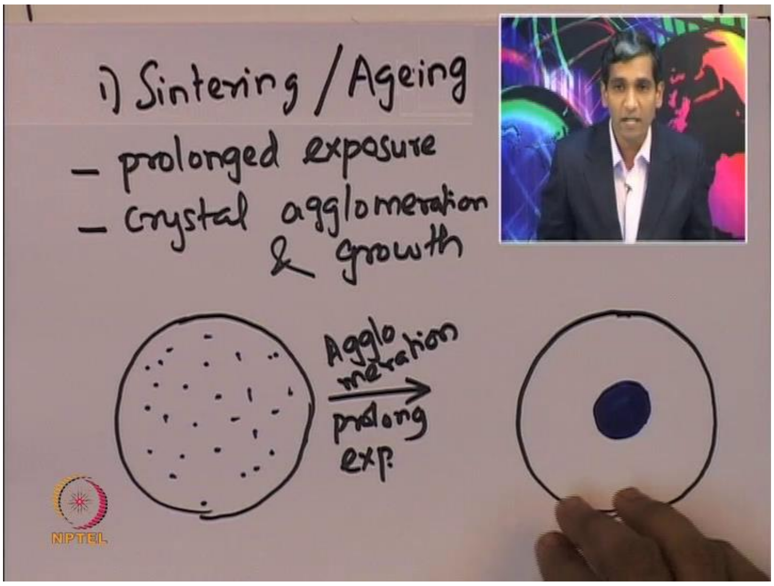

So, there are two causes for sintering. One is the prolonged exposure and the second is the crystal agglomeration and growth. So, this can actually be captured in this figure here. So, suppose if this is a catalyst suppose if this is a catalyst and there are several catalyst sites, which are actually spread across in various locations on the catalyst. Let us say that this is the cross section of the catalyst. So, we cut open the catalyst particle and this is the cross section. So, now if the catalyst is expose to the reactance to the gas stream for a very long time. So, it is prolonged exposure; then what happens is that the particles they start agglomerating they start agglomerating together.

So, they get deposited and the metals which may be present the noble metals, which may be present at a specific location they start agglomerating and they start growing together in a specific location So, this can be depicted like this. So, all the catalyst particles they start migrating to and agglomerating in one location and as a result the activity of the catalyst is completely destroyed. So, this process is what is called as a sintering or ageing process.

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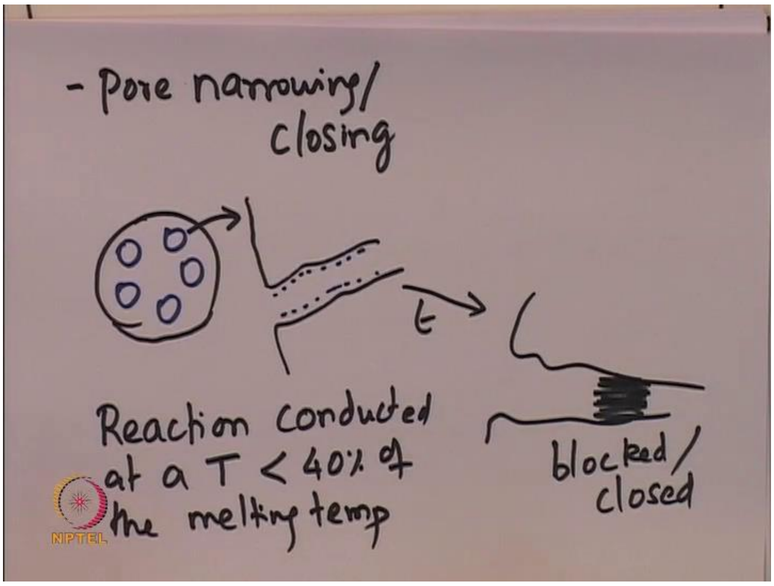

- Pore narrowing/ closing

Reaction conducted at a $T < 40\%$ of the melting temp

Now, the other method by which this sintering can happen is basically called as the pore narrowing or closing. So, the pores which are actually present in the catalyst;, so which contains the catalytic sites. So, because of these prolonged exposure to these to the reacting gas and at a very high temperature the various particles can actually go and clog the pores and thereby block the pores and therefore, the catalytic activity is destroyed. So, that can be captured in this way. So, suppose here is the catalyst and there are these catalytic sites there are this pores, which are present here and at the start of the reaction that is at time t equal to zero.

So, if I zoom up this pore here. So, you will see that, so these catalyst which are present in various locations. So, they are present inside the pore here. Now, after certain after certain time when the reaction occurs for a long time after a certain long period of time then the catalyst pores will get blocked will get filled with this material. So, clearly the pores will get blocked and therefore, they get closed and as a result the activity of the catalyst is lost. So, this sintering process can actually be prevented remember that the temperature is a major factor in the deactivation of the catalyst by the sintering or ageing mechanism.

So, therefore, the sintering can be prevented; if the reaction is conducted at temperatures, which is less than forty percent of the melting temperature of the solid. If the reaction can be conducted at a temperature, which is less than the forty percent of the melting temperature; then this sintering process can be significantly reduced. So, this is a remedial measure for sintering; however, there are several reactions which main may not be able to conduct these reactions at such a low temperature because the conversion that is desired is a strong function of the temperature.

So, the temperature at which the reaction has to be conducted is very important because the higher is the temperature then there is a chance that for exothermic reactions the reaction rate is going to be higher. So, as a result it is not always possible to conduct a reaction at a significantly lower temperature. So, one has to look at different aspects of the catalytic reaction while deciding, what is the correct method to conduct a reaction in order to avoid sintering or ageing method of deactivation.

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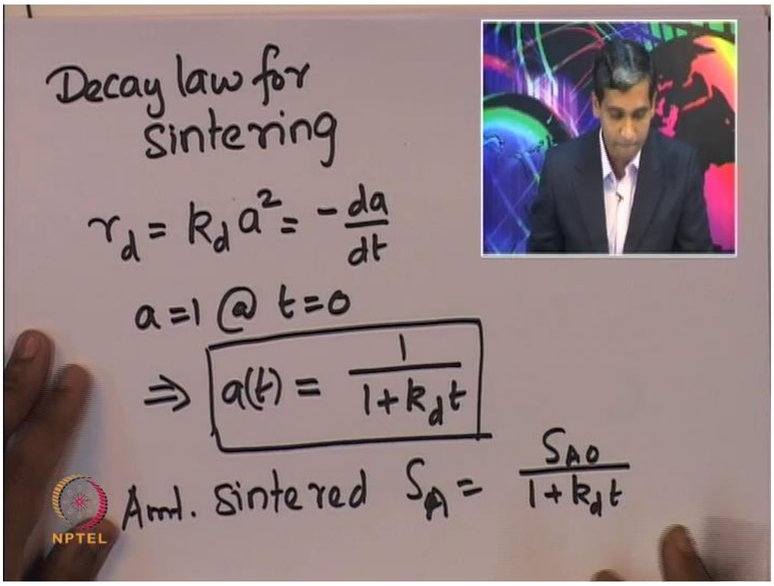

Decay law for sintering

$r_d = k_d a^2 = -\frac{da}{dt}$

$a = 1$ @ $t = 0$

$\Rightarrow \boxed{a(t) = \frac{1}{1+k_d t}}$

Amt. sintered $S_A = \frac{S_{A0}}{1+k_d t}$

So, let us now try to deduce a rate law for the sintering process, try to estimate a rate law for the sintering process. So, suppose if we assume that it is a second order process; then the decay rate is equal to k d into a square which is equal to minus da by dt. Note that the order of deactivation for sintering is usually very high typically about five to eight; however, two is commonly used and is assumed here. Generally, sintering mode of deactivation is very slow compared to other modes. Suppose, we say that the activity is one which is not unreasonable, because if the catalyst is fresh then all the sites are actually available for the catalytic reaction and by definition the activity has to be equal to one at time t equal to zero.

So, integrating this expression we can find out that the activity is given by 1 divided by 1 plus k d into t. So, that is the expression for the activity of the catalyst as a function of time. So, now, if we know the activity of the catalyst as a function of time, then we will be able to estimate how much of the catalytic site is actually sintered what extent of the catalyst has been sintered. So, the amount sintered is given by amount sintered S naught is S A is given by S A naught which is the initial quantity multiplied divided by 1 plus k d into t. So, what the activity tells you what fraction of the catalyst site actually is available. So, the amount that is sintered is given by S A naught which is the initial quantity divided by 1 plus k d into d t.

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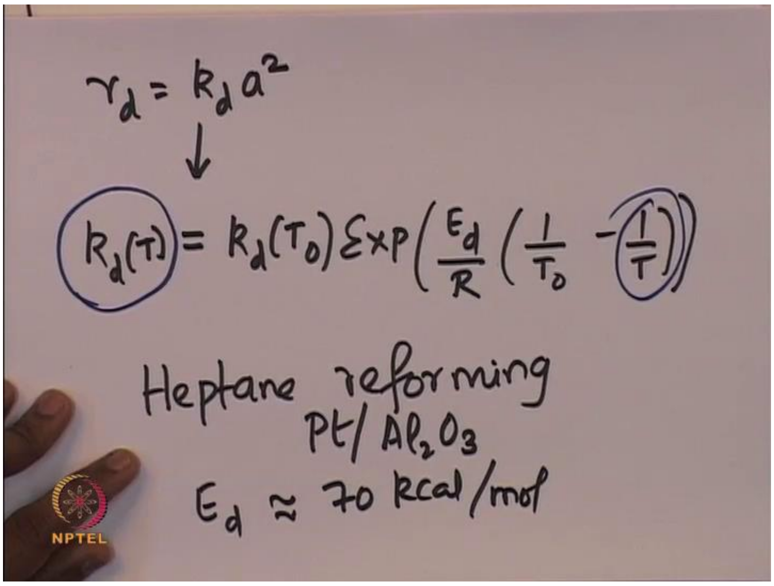

$$r_d = k_d a^2$$

$$\downarrow$$

$$\boxed{k_d(T)} = k_d(T_0)\, Exp\left(\frac{E_d}{R}\left(\frac{1}{T_0} - \boxed{\frac{1}{T}}\right)\right)$$

Heptane reforming

$Pt/Al_2O_3$

$E_d \approx 70$ kcal/mol

So, if you look if you stare at the decay rate law, which is r d equal to k d into a square. So, we observe we said that the sintering can be reduced if the reaction can be conducted at a temperature, which is about forty percent of the melting temperature of the solid. So, why is it a function of a temperature? So, if we look at this specific decay constant k d; it is been observed that this decay constant actually follows an Arrhenius type expression Arrhenius type dependence on the temperature. So, we can write k d as a function of temperature as k d, which is at the reference temperature multiplied by the exponential of E d divided by R into 1 by T naught minus 1 by T.

So, this T naught is some reference temperature it could be the temperature at which the reaction was started. So, the decay constant it strongly depends on the temperature at which the catalytic reaction is being conducted. So, this suggest that a lowering the temperature can actually prevent the sintering process as observed before it may not always be possible to conduct a reaction at a lower temperature; because of the demands of the conversion which is required or the desired conversion. An example of a real process in which sintering or ageing actually is has been commonly observed is the Heptane reforming process.

Heptane reforming on a platinum alumina catalyst and it is been observed that E d, which is the activation energy for the deactivation of the catalyst it is about seventy kilocalories per mole. So, it is been measured to be about seventy kilocalories per mole. So, now because the catalyst gets deactivated the original algorithm that we followed for to design a reactor starting from an experimental data needs to be modified; because we need to now incorporate the deactivation process into the algorithm for designing the reactor.

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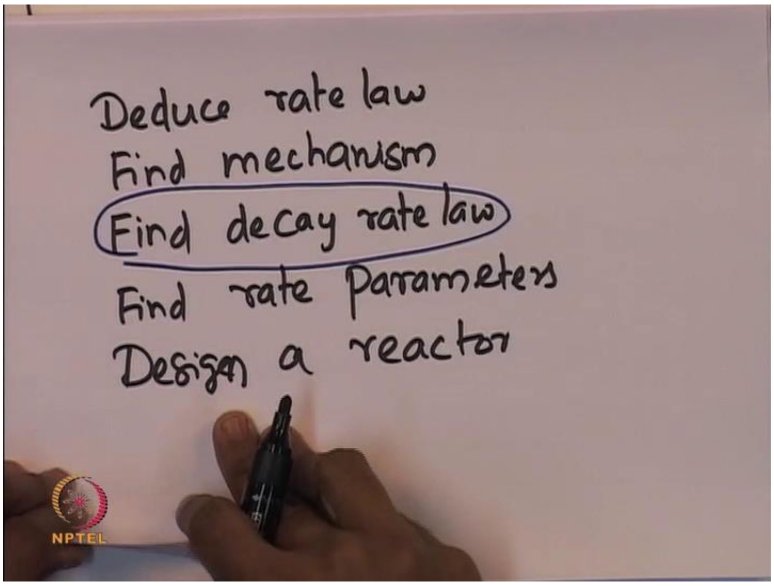

Deduce rate law
Find mechanism
Find decay rate law
Find rate parameters
Design a reactor

So, the modified algorithm is the first steps to deduce the rate law. This is same as before and then finds the mechanism of the catalytic reaction? Find the mechanism that is governing the catalytic reaction and the next step this is the new step that is added finds the decay rate law; this is required because the catalytic reaction actually occur simultaneously along with the deactivation of the catalyst. So, therefore, it is not possible to design reactor without knowing what the decay rate law is.

So, the next step is to find the rate parameters and following which the design of the reactor can be performed design of the reactor can be performed. So, this is the new step that has been added the finding the decay rate law that is the new step that has been added to the theme of designing a reactor. So, let us look at an example of example reaction where sintering process may occur and see how to design a reactor and get the get the conversion as a function of the weight of the catalyst.

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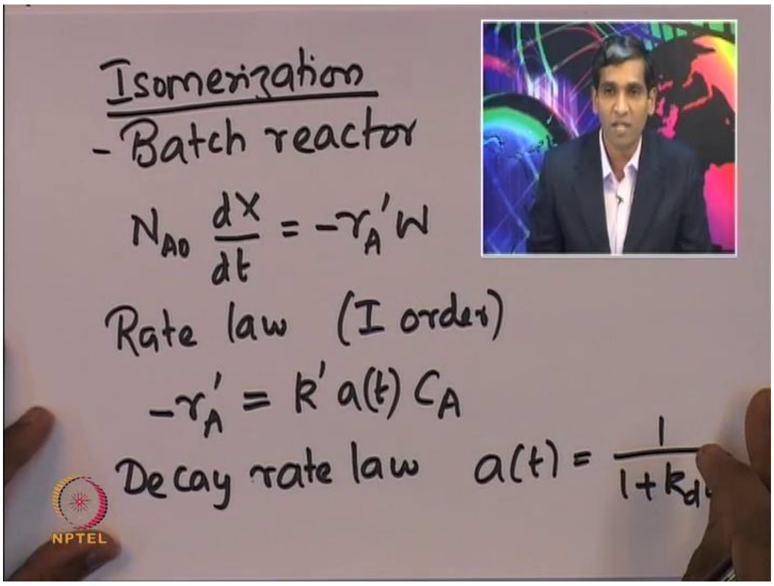

Isomerization

- Batch reactor

$$N_{A0} \frac{dX}{dt} = -r_A' W$$

Rate law (I order)

$$-r_A' = k' a(t) C_A$$

Decay rate law $a(t) = \frac{1}{1+k_d}$

So, let us look at the isomerization process and let us consider a batch reactor. So, the mole balance in the batch reactor for conducting reaction is given by N A naught, which is the number of moles of the of the reactant A at while starting the reactor multiplied by dx by dt, where x is the conversion and t is time is given by minus r A prime W. So, now, the next step is to find the rate law. So, let us assume that it is a first order reaction let us assume that it is a first order reaction. So, the rate law is given by rate that is the moles of which is reactor per gram of catalyst per unit time. So, that is given by k prime, which is the specific constant specific reaction rate multiplied by the catalyst activity.

So, remember that the catalyst is also getting simultaneously deactivated. So, a of t is the activity of the catalyst;, so k times a of t into c A. So, that depicts the rate at which the species a is being consumed because of the catalytic reaction. Next we need to know, what the decay rate law due to sintering is. So, if you assume that the dependence of the activity on time that we derived a short while ago is valid then a of t is given by 1 by 1 plus k d into t. So, that is the dependence of the activity with respect to time. So, now we can express the concentration of the species a in terms of conversion.

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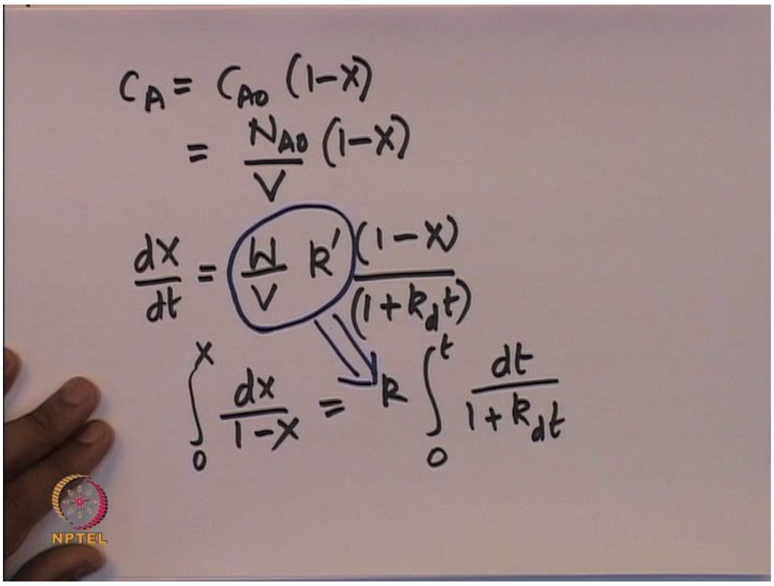

$$C_A = C_{A0}(1-X)$$

$$= \frac{N_{A0}}{V}(1-X)$$

$$\frac{dX}{dt} = \frac{W}{V} k' \frac{(1-X)}{(1+k_d t)}$$

$$\int_0^X \frac{dX}{1-X} = k \int_0^t \frac{dt}{1+k_d t}$$

So, c A is equal to c A naught into 1 minus X, where X is the conversion and that is equal to the number of moles of a, which is initially present divided by the volume of the batch reactor into 1 minus X, where X is the conversion. So, now plugging in all these quantities that is the rate law for the reaction and rate decay dependence of the activity as a function of time and the relationship between the concentration of species a and the conversion into the original mole balance. We can rewrite the mole balance as dx by dt that is equal to W by V, where W is the weight of the catalyst, which is present inside the batch reactor multiplied k prime, which is the corresponding specific reaction rate into 1 minus X divided by 1 plus k d into t.

So, we can now integrate this expression. So, we can with a little bit of algebra; we can rewrite this as zero to x integrate between zero to any conversion dx by 1 minus X its equal to k into zero to t dt by 1 plus k d into t. Here, I have assumed that this this term W into k prime by V is equal to this constant k.

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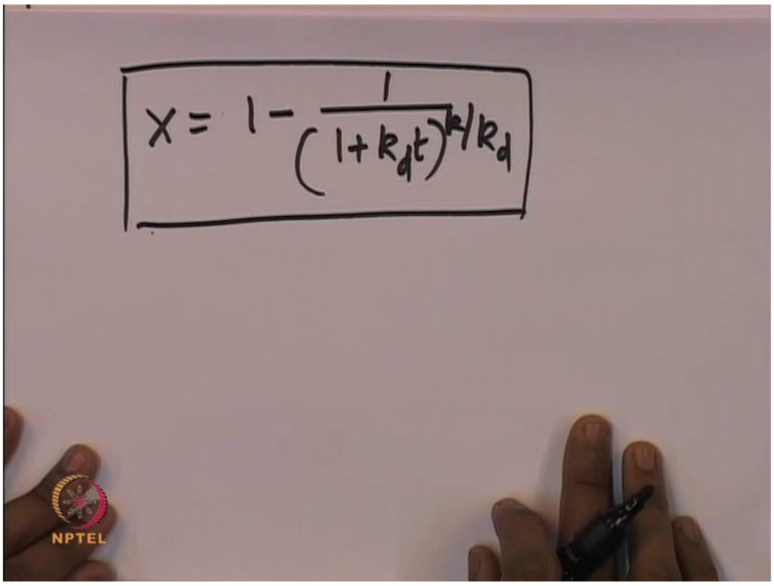

$$\boxed{X = 1 - \frac{1}{(1+k_d t)^{k/k_d}}}$$

So, I after integrating this expression we will find that the conversion X is equal to 1 minus 1 by 1 plus k d into time to the power of k by divided by k d. So, that is the relationship between conversions as a function of time. So, this expression provides way to find out what is the conversion as a function of time and other parameters in a batch reactor, where the catalyst is simultaneously getting deactivated. So, next we look at the next mechanism by which the catalyst deactivation can occur which is the coking or the fouling process.

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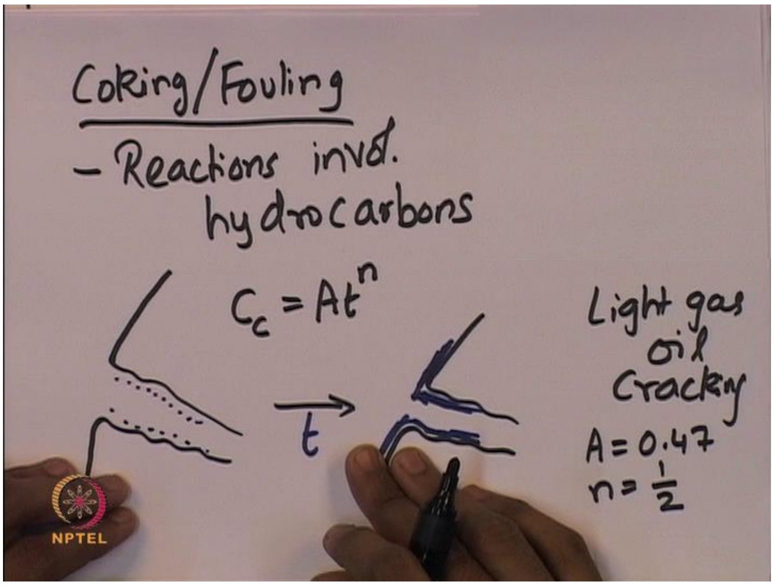

Coking/Fouling

- Reactions invol. hydrocarbons

$C_c = At^n$

Light gas oil Cracking

$A = 0.47$

$n = \frac{1}{2}$

Coking or the fouling process, now this typically occurs in those reactions which involve hydrocarbons, so reactions involving hydrocarbons. So, this primarily occurs in those reactions this type of deactivation of the catalyst primarily occurs in those reactions, where hydrocarbons are involved and whenever hydrocarbons are involved the carbon material, which is present that gets deposited onto the catalyst site. Therefore, blocks the sites of the catalyst and that result in the deactivation of the catalyst. Now, it is important to note that there are methods to regenerate the catalyst that is to remove the coke from the catalyst and that aspect will be dealt with separately in a different section of this course.

So, in we will simply look at how to understand the mechanisms behind the carbon deposition on the catalyst site and how it affects the activity of the catalyst. So, suppose if the catalyst pore is like this, where the catalyst sites are present along the wall. Now, after the reaction happens for a certain time that is the sufficient time for the carbonaceous material to go and deposit onto the active catalyst site. So, the carbonaceous material gets deposited onto the surface of the catalyst and thereby they block the active sites, which may be available for further reaction to occur.

So, this typically happens after the reaction occurs for a certain amount of time. Now, this is actually very commonly observed phenomenon and many reactions that involve hydrocarbons particularly that of the light gas oil cracking of light gas oil, cracking of light gas oil and the amount of coke that is deposited on the catalyst site that plays an important role. So, the amount of catalyst that is deposited c c is typically given by some constant A multiplied by time to the power of n, A and n are typically called as the coking constants or the fouling constants and t is time. So, as time increases the coke gets deposited on the surface of the catalyst active sites.

For light gas oil cracking of light gas oil, A has been found to be about 0.47 and n is about 1 by 2. So, that is the typical numbers that have been found for the light gas oil cracking process and the amount of carbonaceous material that a gets deposited on the catalyst site. So, let us now look at how to find the mechanism behind this and how to model how to find the relationship between the decay rate as a function of the concentration and how to write the design equations.

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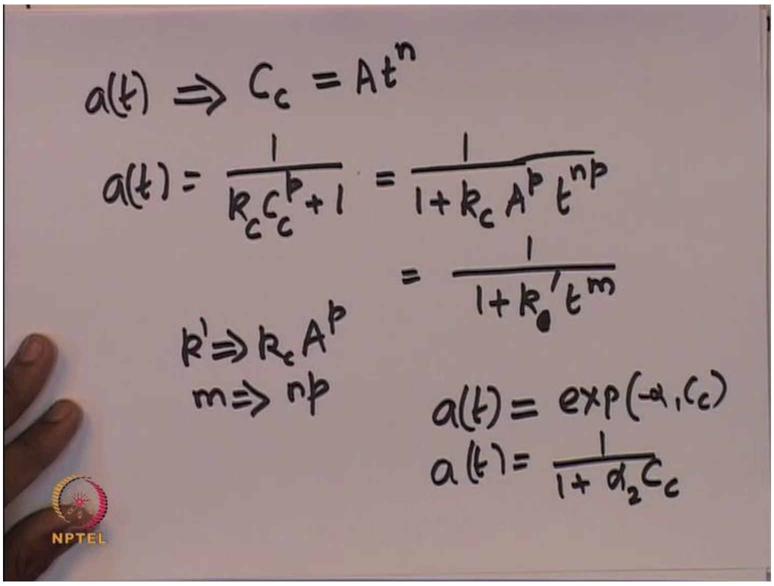

$$a(t) \Rightarrow C_c = A t^n$$

$$a(t) = \frac{1}{k_c C_c^p + 1} = \frac{1}{1 + k_c A^p t^{np}}$$

$$= \frac{1}{1 + k' t^m}$$

$$k' \Rightarrow k_c A^p$$

$$m \Rightarrow np$$

$$a(t) = \exp(-\alpha_1 C_c)$$

$$a(t) = \frac{1}{1 + \alpha_2 C_c}$$

So, a t which is the activity of the catalyst in the case of coking or fouling process certainly depends upon the amount of carbon, which gets deposited on the surface. So, there have been some common forms of relationship between the activity and the carbon that gets deposited and they are like this. So, a of t is equal to 1 by some constant k c multiplied by c c to the power of p plus 1. So, recall that c c is can be written as some constant A multiplied by t to the power of n. So, plugging this expression into the expression relating the activity and the amount of coke that is deposited given as 1 divided by 1 plus k c into A to the power of p in t to the power of n into p.

So, now, this can be rewritten as 1 by 1 plus k c one plus k prime into t to the power of m, where k prime is nothing, but k c into A to the power of p and m is nothing, but n into p. So, this is one form of the activity as a function of time by incorporating the amount of coke that is actually being deposited on the site, because of the coking or fouling process, which is fouling process of a deactivation of the catalyst. The other forms, which have been used are given and are as follows a is a exponentially dependent on the amount of coke that is deposited on the catalyst site or it may be it may be a function, which looks like this alpha into the amount of coke that is deposited on the surface.

Now, how do we minimize the amount of coking that is actually happening that is the amount of carbon material that gets deposited onto the catalyst site? So, the way it can be done is it can be minimized by performing the conducting the reaction at elevated temperatures.

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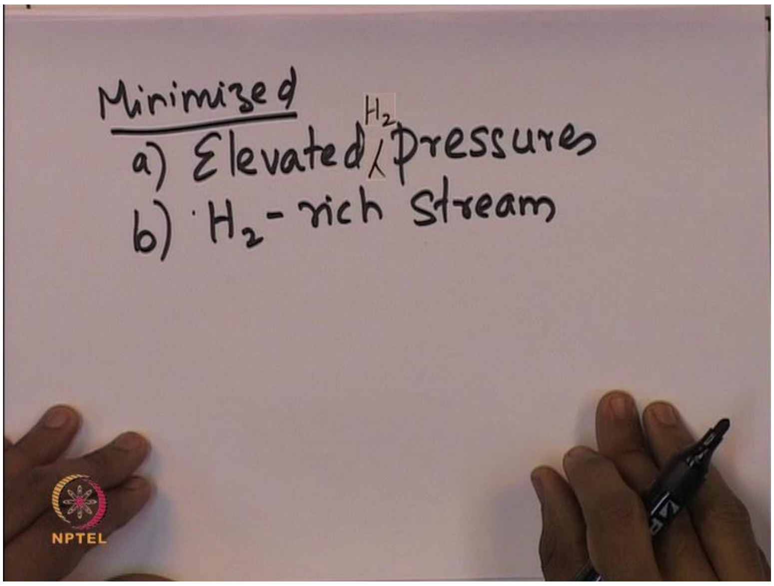

Minimized

a) Elevated $H_2$ pressures

b) $H_2$- rich stream

So, it can be minimized by conducting the reactant at elevated hydrogen pressure and the other strategy that has been observed to work is by conducting the reaction at a hydrogen rich stream. So, these two methods have been used to minimize the coking or the fouling process on a catalytic site. So, let us look at the third method of deactivation of the catalyst, which is the poisoning process.

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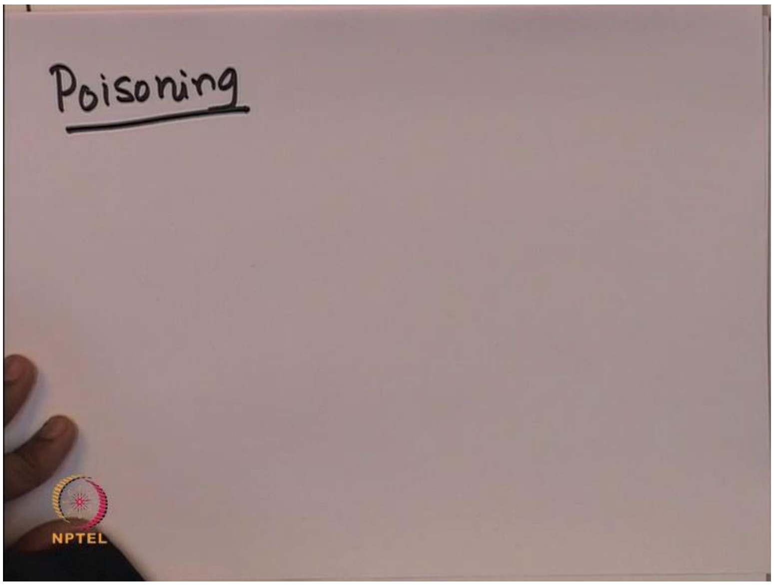

Poisoning

So, the poison could actually be present in the feed or it could be reactance or the product itself could be poison. For example, there is in a catalytic site when the when the gas stream is carrying a certain reactance it might be containing traces of some poisons and these compounds can actually get deposited onto the catalyst site. Thereby, deactivating the catalyst itself and or the reactant or the products of a specific reaction can actually act as a poison. They may actually go and get adsorbed onto the catalyst site and therefore, destroy the activity of the catalyst completely or partially.

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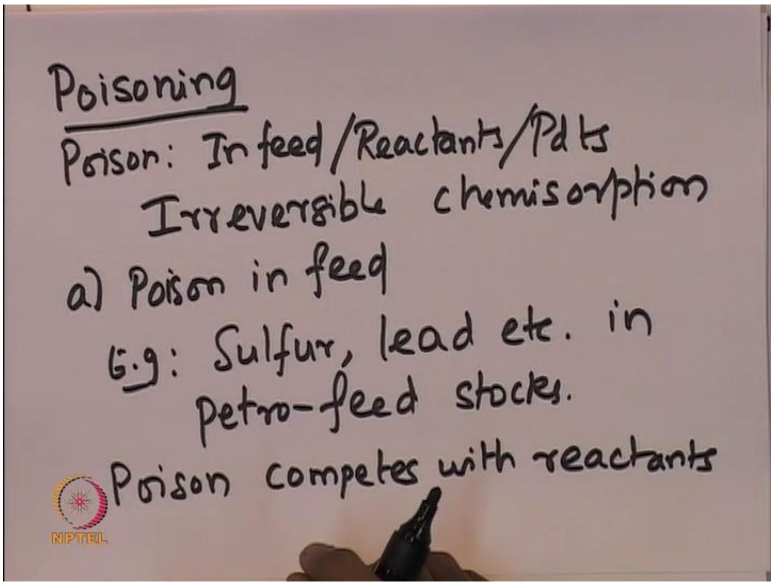

Poisoning

Poison: In feed/Reactants/Pdts
Irreversible chemisorption
a) Poison in feed
E.g: Sulfur, lead etc. in petro-feed stocks.
Poison competes with reactants

So, poisoning is basically you have poison and these poisons could be present in the feed; it could be present in the reactants; it could be reactants itself that may act as a poison or the products that are formed because of the catalytic reaction that may act as a poison by itself. What happens is that it irreversibly that is an irreversible chemisorption process; that is an irreversible chemisorption process, which results in the deactivation of the catalyst? So, remember that these catalyst particles which are impregnated with noble metals for catalyzing the catalytic reaction; they are very expensive they run they run into several millions of dollars.

So, therefore, loss of activity of the catalyst is strongly affects the performance of a company, which is actually a marketing that particular product. So, therefore, it is very important to understand the poisoning because of these irreversible chemisorption and attempts to minimize them is extremely important. So, let us look at the first case, where we look at the poison in the feed we look at poison in feed. So, a nice example of that is the presence of sulfur, lead, etcetera in the petroleum feed stocks. In the natural petrol and diesel that is used in automobiles is very important not to have sulfur and lead and one of the reasons is that the exhaust muffler, which contains catalyst they may get deactivated in the presence of sulfur and lead.

So, therefore, these two can act as a poison for the muffler and that significantly affects the performance of the muffler and thereby polluting the environment with toxic gases. So, therefore, it is very important to have minimal sulfur or no sulfur or and no lead in the petroleum feed products particular in the gasoline. So, that can it can improve the efficiency of the muffler and thereby protecting the environment from passing of this passing of environmentally, unfriendly gases into the atmosphere. So, the poisons typically, so these poisonous materials they actually compete with the reactants.

So, what happens is that the reaction at the catalytic reaction actually happens by the reactants, which go and adsorb onto the catalyst site. Now, the poison also has exactly the same behavior. So, they also are looking towards getting adsorbed onto the surface of the catalyst site. So, therefore, the poisonous materials they are strongly competing with the reactants in order for the vacant sites and therefore, it can it simultaneously happens along with the chemical reaction.

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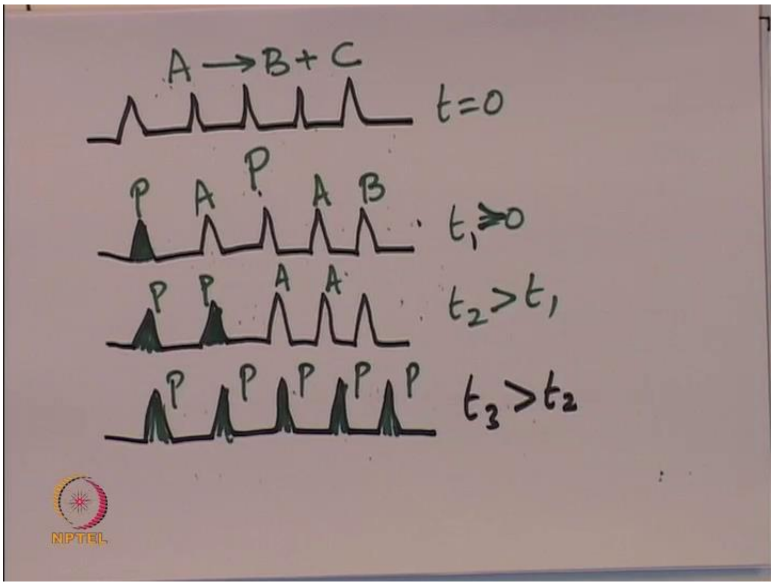

So, here is the cartoon which depicts the poisoning process suppose if this is the catalyst particle if the if this is the catalyst site, then if the reaction that is being conducted is A giving B plus C. Suppose, if the at time t equal to zero at time t equal to zero all the catalyst sites are vacant and are available for the adsorption of the reactants and also the poison. So, let us say that p is the poison which is present in the feed stream; it could be sulfur, lead or any other compound and after a certain time t 1 after a certain time t 1. So, some of the sites the poison will get adsorbed into some of these sites and some other sites the reactant a may be adsorbed and product may be formed in some sites and b may be adsorbed onto the some other site where the product is already found.

So, at a further later time at a further later time t this should be t 1 this is greater than t 1 greater than zero. So, at a further later time t 2, which is greater than t 1 then more sites are filled with the poison. So, the number of sites which are available for adsorption of a constantly continues to decrease with time and at a much later time at a much later time, t 3 which is also greater than t 2 all the sites are actually filled with the poison. So, at this point the catalyst appears completely deactivated and it is of no use to conduct the catalytic reaction.

So, let us summarize what we have learnt so far in this lecture. So, we have looked at we have defined what is catalytic deactivation; we had looked at various types of deactivation process. Then, particularly we looked at sintering and ageing; we looked at coking and coking or fouling process and we initiated discussion on the poisoning of poisoning method of deactivation of the catalyst. So, catalyst deactivation is a very, very serious problem because it strongly affects the conversion of the reaction.

It may be that the extent of conversion of a particular reactant is if it is affected strongly then it can strongly affect the economy of the industry, which is actually marketing that particular product, which is of end product of the reaction which is being conducted in a catalytic reactor. So, therefore, characterizing deactivation is very important and what we will see in the next lecture is how to characterize the poisoning process and look at some examples.

Thank you.