Chemical Reaction Engineering - II

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Module - 3
Lecture - 14
Catalyst Deactivation II

So, let us now try to deduce a rate law for the sintering process.

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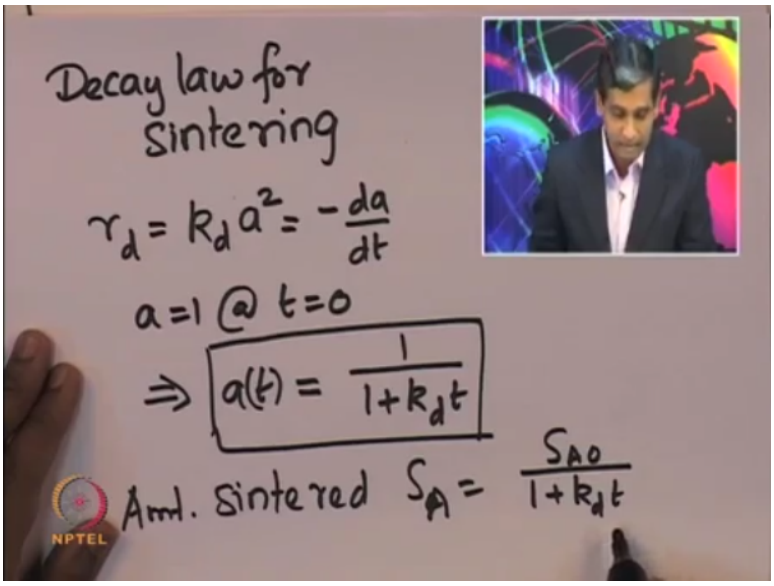

Decay law for sintering

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

$a = 1$ @ $t = 0$

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

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

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 = k d to a square which is = – d a by d t. Note that the order of deactivation for sintering is usually very high, typically about 5 to 8. However, 2 is commonly used and is assumed here. Generally sintering mode of deactivation is very slow compared to other modes.

And suppose we say that the activity is 1, 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 = 1 at time t = 0. And so, integrating this expression, we can find out that the activity is given by 1 divided by 1 + 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 nought is S A is given by S A nought which is the initial quantity multiplied, divided by 1 + 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 nought which is initial quantity divided by 1 + k d into d, t. So, if you look, if you stare at the decay rate law.

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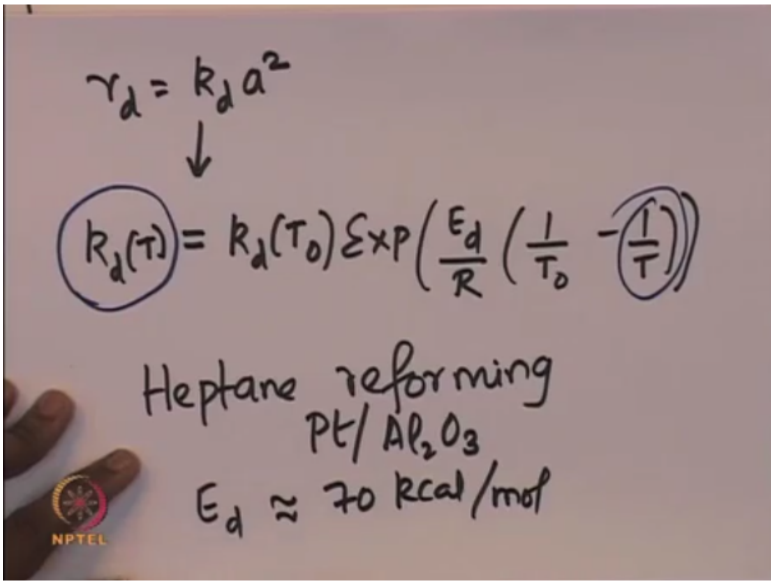

$$r_d = k_d a^2$$

$$\downarrow$$

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

Heptane reforming

Pt/Al_2O_3

$E_d \approx 70$ kcal/mol

Which is r d = k d into a square. So, we observe, we set that the sintering can be reduced if the reaction can be conducted at a temperature which is about 40% of the melting temperature of the solid. So, why is it a function of a temperature. So, if we look at the specific decay constant k d, it has 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 which is at the reference temperature multiplied by the exponential of E d divided by R into 1 by T nought – 1 by T. So, this T nought 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 suggests that lowering the temperature can actually prevent the sintering process. As observed before, it may not always be possible to conduct the 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 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 70 kilo calories per mole, will be measured to be about 70 kilo calories per mole. So now, because the catalyst deactive, 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. So, the modified algorithm is the first steps to deduce the rate law.

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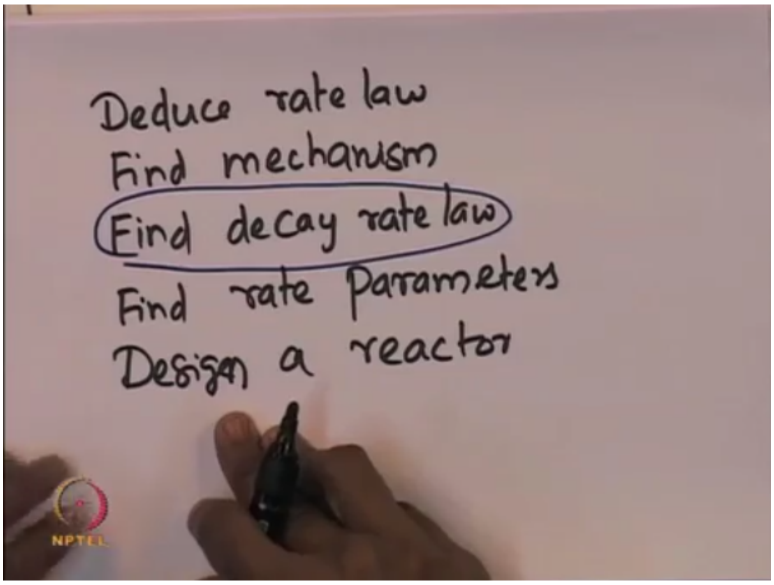

Deduce rate law
Find mechanism
Find decay rate law
Find rate parameters
Design a reactor

This is same as before. And then find 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. Find the decay rate law. This is required because the catalytic reaction actually occurs simultaneously along with the deactivation of the catalyst. So, therefore it is not possible to design the reactor without knowing what is the decay rate law.

So, the next step is to find the rate parameters. And following which the 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 keem 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 conversion as a function of the weight of the catalyst.

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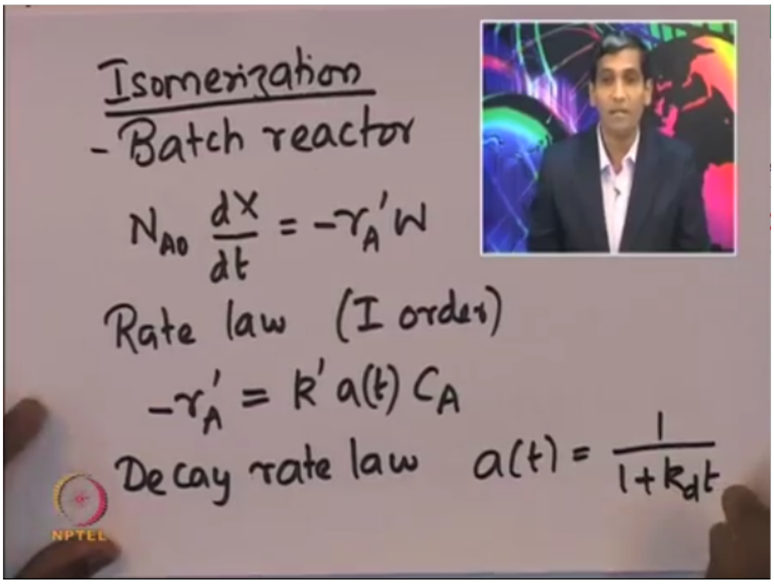

Isomerization

- Batch reactor

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

Rate law (I order)

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

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

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 nought which is the number of moles of the reactant A at, while starting the reactor, multiplied by d X by d t where X is the conversion and t is time. Is given by – r A prime into W. So, now the next step is to find the rate law.

So, let us assume that it is a first order reaction. So, the rate law is given by, rate that is the moles of A which is reacted per gram of catalyst per unit time. So, that is given by k prime which is the specific constant, a 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 catalysts. 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. And next we need to know what is the decay rate law due to sintering. So, if we 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 + 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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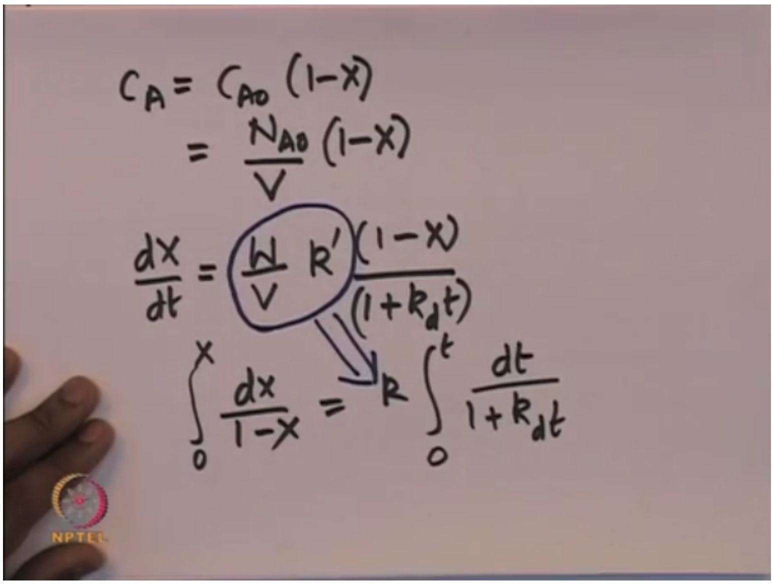

$$C_A = C_{A0}(1-X)$$
$$= \frac{N_{A0}}{V}(1-X)$$
$$\frac{dX}{dt} = \frac{W}{V}k' \frac{(1-X)}{(1+k_d t)}$$
$$\int_0^X \frac{dX}{1-X} = k\int_0^t \frac{dt}{1+k_d t}$$

So, C A is = C A nought into 1 – X where X is the conversion. And that is = the number of moles of A which is initially present divided by the volume of the batch reactor into 1 – X where X is the conversion. So now, plugging in all these quantities that is the rate law for the reaction rate d k 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 d X by d t. That is = W by V where W is the weight of the catalyst which is present inside the batch reactor multiplied by the k prime which is the corresponding specific reaction rate into 1 – X divided by 1 + k d into t. So, we can now integrate this expression. So, we can, it is a little bit of algebra. We can rewrite this as 0 to X, integrate between 0 to any conversion; d X by 1 – X. It is = k into 0 to t, d t by 1 + k d into t. Here I have assumed that this term W into k prime by V is = this constant k. So, after integrating this expression we will find that the conversion;

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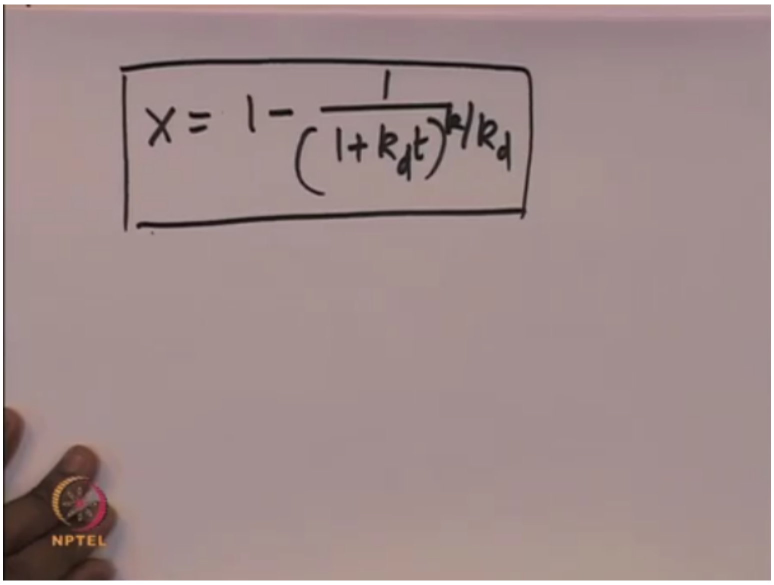

$$X = 1 - \frac{1}{(1+k_d t)^{k/k_d}}$$

Conversion X is = 1 – 1 by 1 + k d into time to the power of k by divided by k d. So, that is the relationship between conversion as a function of time. So, this expression provides a 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.

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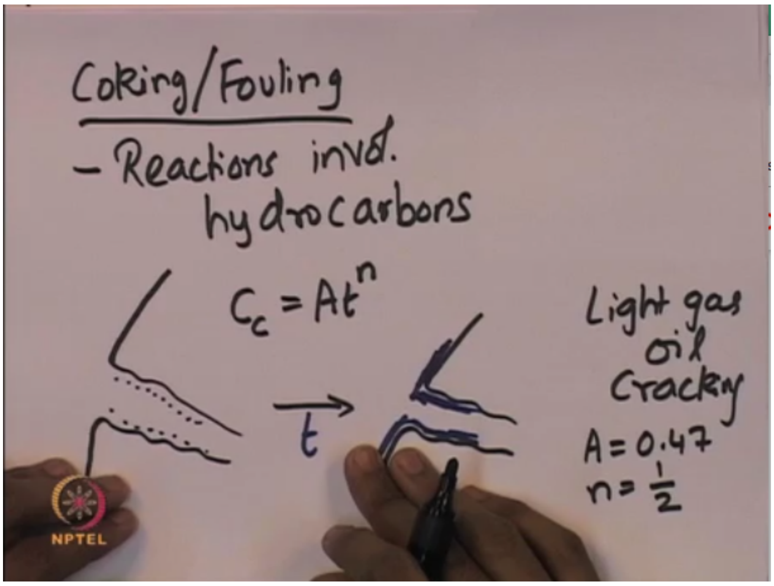

Coking/Fouling

- Reactions invol. hydrocarbons

$C_c = At^n$

Light gas oil Cracking

$A = 0.47$

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

Which is the 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 primary 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.

And that therefore blocks the sites of the catalyst. And that results 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 a, 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. 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 a coking constant or the fouling constants. And t is time. So, as time increases the coke gets deposited on the surface of the catalyst active sites. And for a 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 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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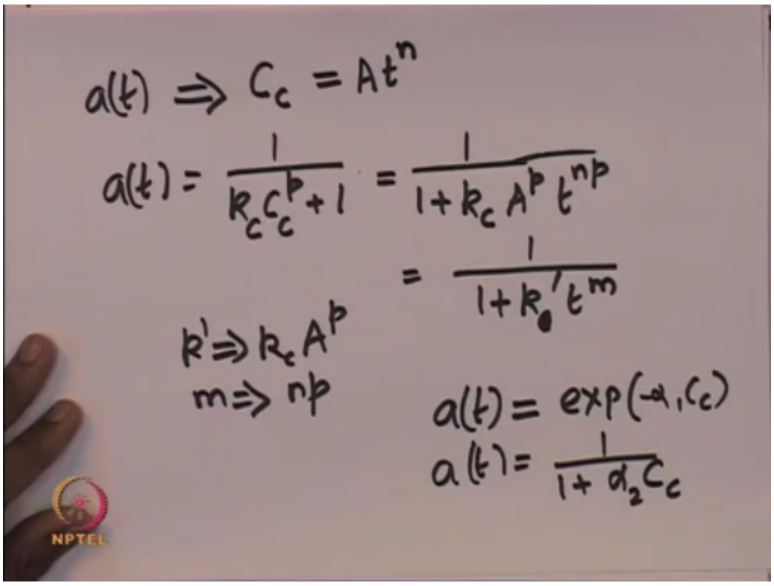

$$a(t) \Rightarrow C_c = At^n$$

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

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

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

$$m \Rightarrow np$$

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

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

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 the relationship between the activity and the carbon that gets deposited. And they are like this. So, a of t is = 1 by some constant k c multiplied by C c to the power of p + 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, into expression relating the activity and the amount of coke that is deposited, given as 1 divided by 1 + 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 + k c, 1 + 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 1 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 deactivation of the catalyst. The other forms which have been used are given in, are as follows. a is, it is exponentially dependent on the amount of coke that is deposited on the catalyst site or 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 minimise the amount of coking that is actually happening. That is the amount of carbon material that gets deposited onto the catalyst site. And so, the way it can be done is, it can be minimised by performing the, conducting the reaction at elevated temperatures.

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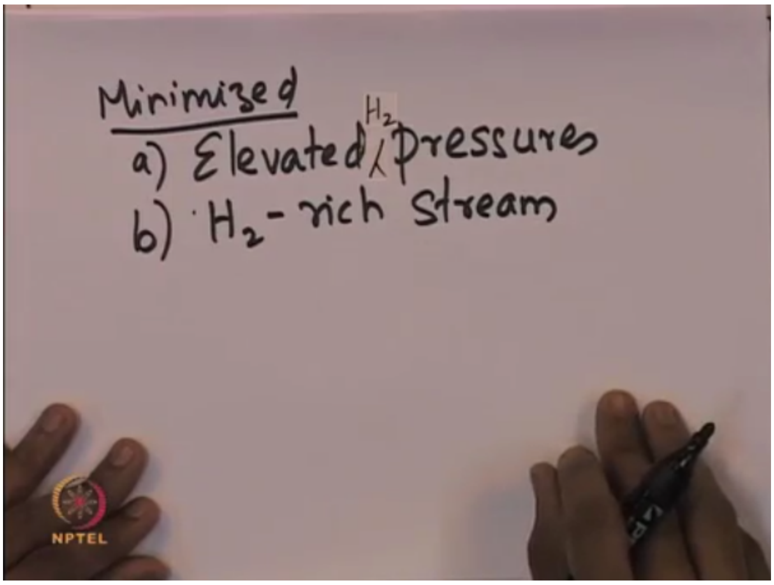

Minimized

a) Elevated H_2 pressures

b) H_2- rich stream

So, it can be minimised by conducting the reaction 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 2 methods have been used to minimise 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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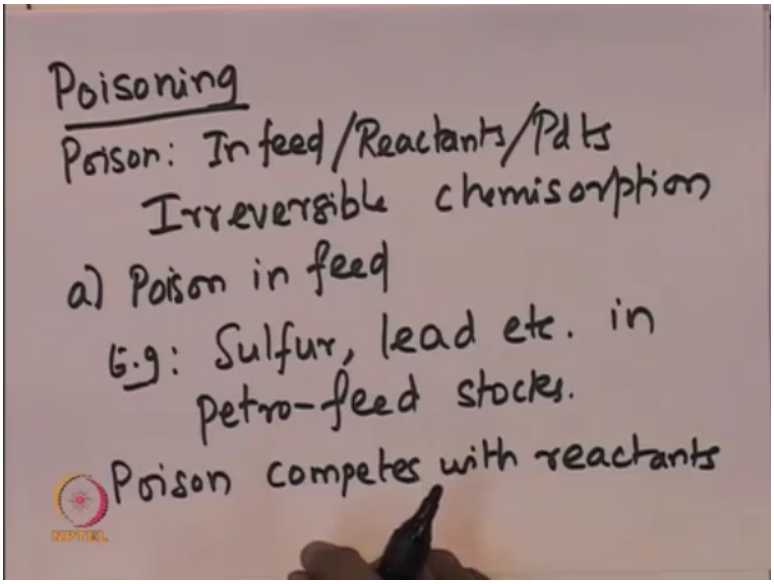

Poisoning

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, the poison could actually be present in the feed or it could be present, the reactants or the products itself could be poison. For example, that is, in a catalytic site, when the gas stream is carrying a certain reactants, it might be containing traces of some poisons. And these compounds can actually get deposited onto the catalyst site. And thereby deactivating the catalyst itself and or the reactants 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. 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.

And what happens is that it irreversibly, there 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 catalysing the catalytic reactions; they are very expensive. 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 marketing that particular product.

So, therefore it is very important to understand the poisoning because of these irreversible chemisorption and attempts to minimise them is extremely important. So, let us look at the first case where we look at the poison in the feed. So, a nice example of that is the presence of sulphur, lead, etcetera in the petroleum feed stocks. In the natural petrol and diesel that is used in automobiles, it is very important not to have sulphur and lead.

And one of the reasons is that the exhaust muffler which contains catalyst, they may get deactivated in the presence of sulphur and lead. So, therefore these 2 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 minimum sulphur or no sulphur or and no lead in the petroleum feed products, particularly in the gasoline.

So, that 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 they; so, these poisonous materials, they actually compete with reactants. So, what happens is that the reaction at, the catalytic reaction actually happens by the reactants which go adsorb onto the catalyst site.

Now, the poison also has exactly the same behaviour. So, they also are looking towards getting adsorbed onto the surface of the catalyst sites. 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. So, here is the cartoon which depicts the poisoning process.

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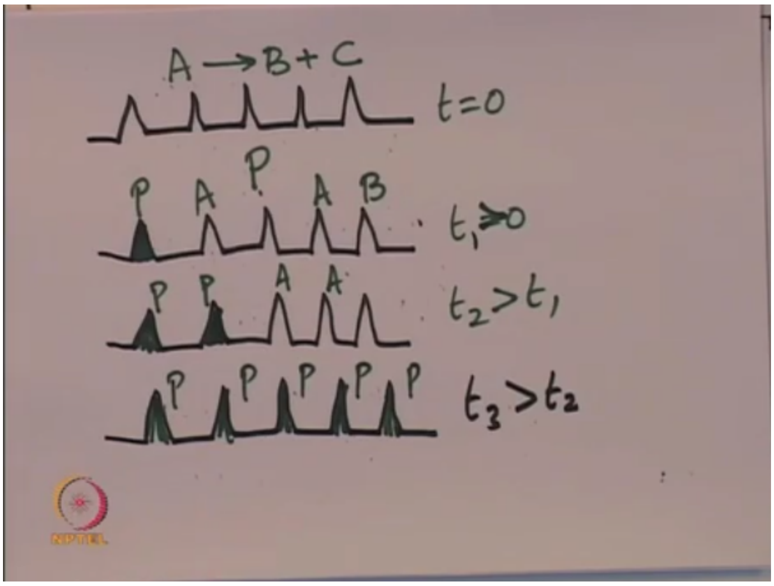

Suppose if this is the catalyst particle, if this is the catalyst site, then if the reaction that is being conducted is A giving B + C. And suppose if the, at time t = 0, all the catalyst sites are vacant and are available for the adsorption of the reactants and also the poison. So, let us say that P is the poison which is present in the feed stream. It could be sulphur, lead or any other compound. And after a certain time t 1, the; so some of these sites, the poison will get adsorbed into some of these sites.

And some other sites the reactant A may be adsorbed and a product may be formed in some sites. And B may be adsorbed onto the, some other site where the product is already formed. So, at a further later time t, this should be the t 1. This is >, t 1 > 0. So, at a further later time t 2 which is > 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 t 3 which is also > t 2, all the sides 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 summarise 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 the various types of deactivation process.

And 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.

And 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 the end product of the reaction which is being conducted in a catalytic reactor. So, therefore characterising deactivation is very important. And what we will see in the next lecturer is how to characterise the poisoning process and look at some examples. Thank you.