Chemical Reaction Engineering - II
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Module - 3
Lecture - 13
Catalyst Deactivation I

Friends, let us summarise what we have learnt in the last couple of lectures. So, we have learnt how to deduce the rate law from experimental data and we have learnt how to find a mechanism for a given heterogeneous catalytic reaction and then we have looked at how to find the rate parameters concerning the rate law. And 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 onto 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, it does not remain constant.

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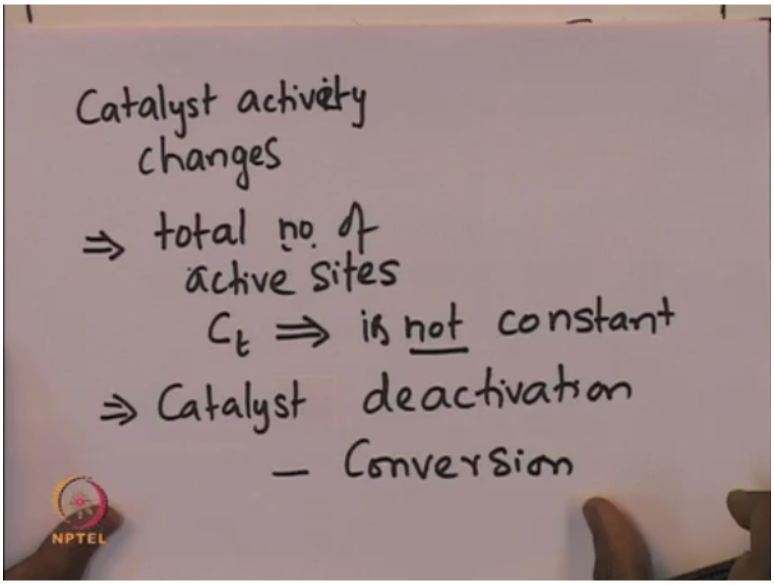

Catalyst activity changes

⇒ total no. of active sites

$C_t \Rightarrow$ is <u>not</u> constant

⇒ Catalyst deactivation

— Conversion

So, we always assume that the catalyst constant, catalyst activity is constant but the catalyst activity changes with time. Now, what does it mean? It means that the total number of active sites, which may be available for adsorption of the reactant species onto the catalytic site for the catalytic reaction. Now that, (()) (02:21) 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. 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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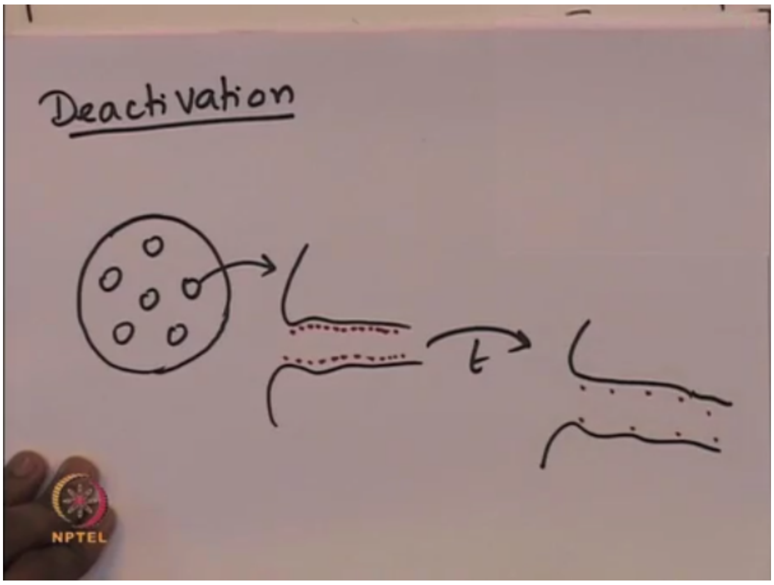

So deactivation, so suppose if there is a catalyst, there is a catalyst support in which a particular catalytic material is actually impregnated. And let us say that these are the pores which is present on the catalyst inside which there are active sites. And suppose let us say I zoom up one of the pores which may be present inside the catalyst. And so, if this is the 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 reactants 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. The number of active sites which may be present, that reduces and you can see that the number of reduced 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 are all the mechanisms that govern the deactivation process and how to incorporate that in the reactor 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. So, in this case how to find the rate law with, in the presence of catalyst deactivation.

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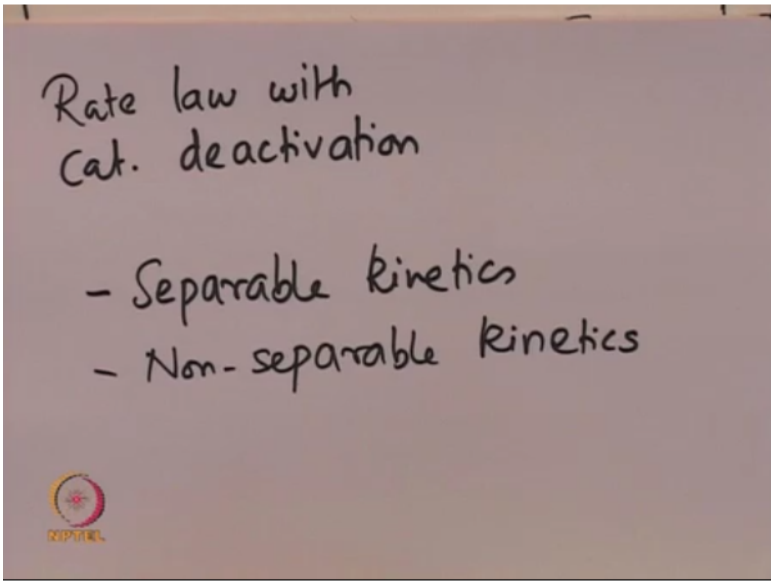

Rate law with
Cat. deactivation

- Separable kinetics
- Non-separable kinetics

So, this can be broadly classified into 2 different types. One where it is called the separable kinetics and another one, it is called the non-separable kinetics. So, separable kinetics is one where the dynamics of the adsorption catalyst deactivation process and the actual kinetics of the catalytic reaction, these 2 can be independently modelled and the mechanisms can be independently understood. While the non-separable kinetics is where it cannot be looked at independently.

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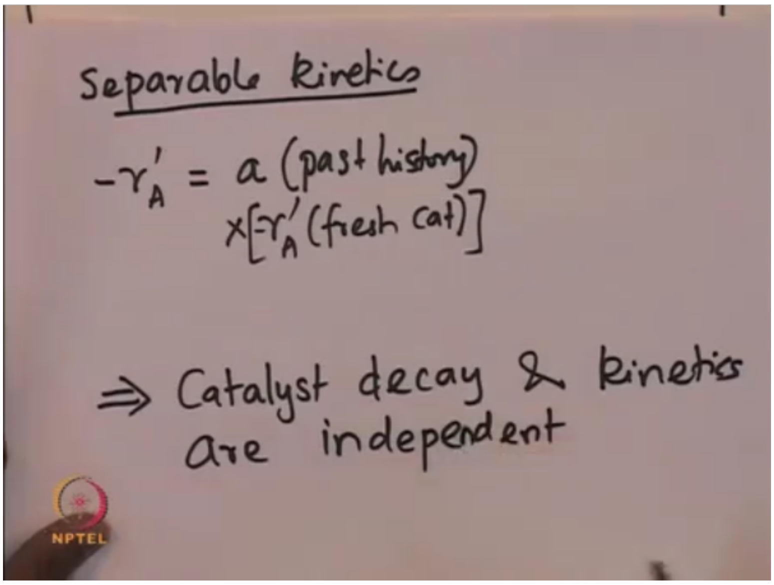

Separable kinetics

$$-r'_A = a\,(\text{past history}) \times \left[-r'_A\,(\text{fresh cat})\right]$$

$\Rightarrow$ Catalyst decay & kinetics are independent

So, 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 a 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. And so, the activity is only a function of the past history. And that scaled with the reaction rate if it were to be a fresh catalyst is what gives what is the reaction rate, and 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 model of separable kinetics the catalyst decay and the kinetics of the catalytic reaction are independent. Now, what happens in the non-separable kinetics?

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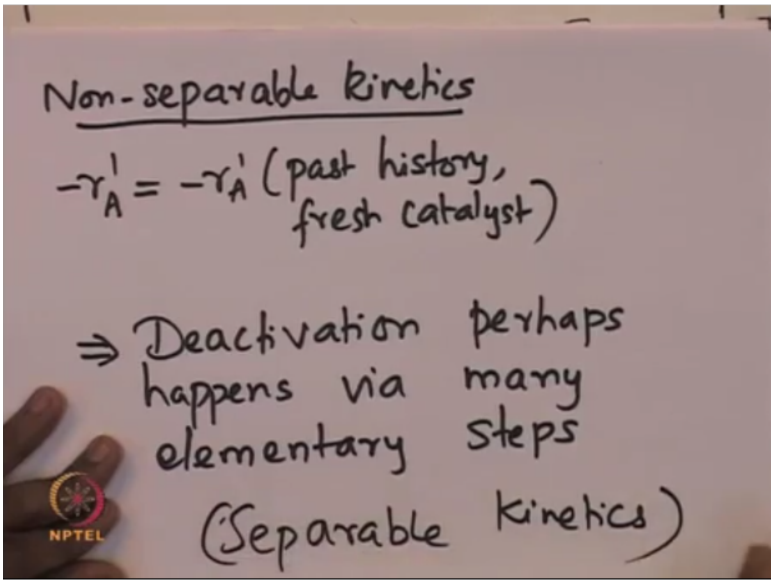

Non-separable kinetics

$-r'_A = -r'_A$ (past history, fresh catalyst)

$\Rightarrow$ Deactivation perhaps happens via many elementary steps

(Separable kinetics)

In non-separable case, in the non-separable kinetics case, the net reaction rate, 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 both on the properties or the nature of deactivation simultaneously along with the actual reaction rate of the catalytic reaction.

So, which I suggest that the deactivation perhaps happens on, perhaps happens via many elementary steps. So, in the next couple of lecturers we will not deal with the non-separable kinetics which will be dealt with separate, separately later. 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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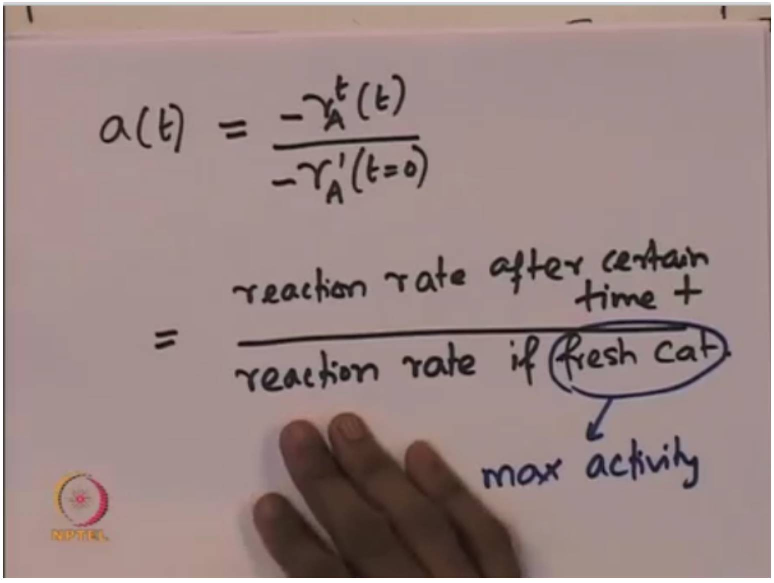

$$a(t) = \frac{-r_A^{t}(t)}{-r'_A(t=0)}$$

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

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, divided by the reaction rate if it is a fresh catalyst. Now, it is important to realise that the maximum activity is possible only in a fresh catalyst.

So, it is important to realise 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 characterise and how to obtain the deactivation process as a function of time in the presence of catalytic reaction. So the, so naturally the activity of the catalyst is going to change with time.

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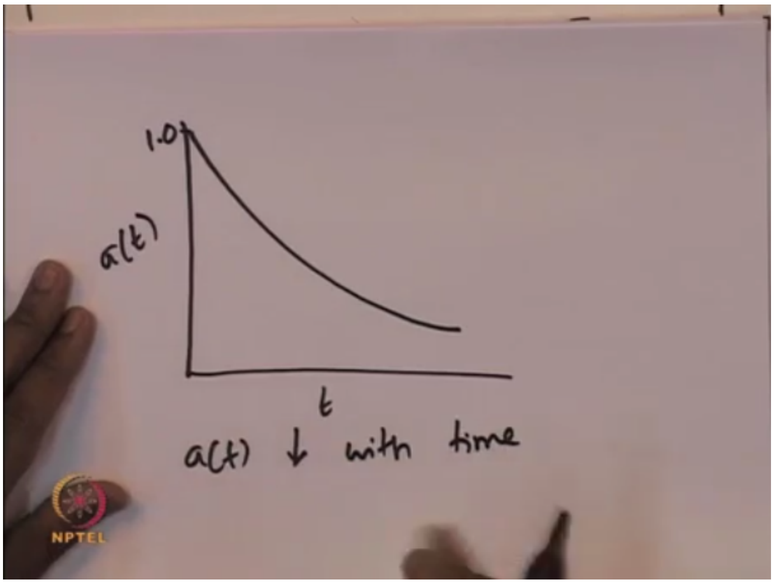

And, the typical profile, it starts with 1, cause it is a fraction and it is a fraction of catalyst that, activity which is left. And so, it goes from, it exponentially decreases with time. So, this, so clearly the a of t decreases with time. So, suppose if there is a reaction, so how do we write the reaction rate law when there is catalytic deactivation process occurring simultaneously.

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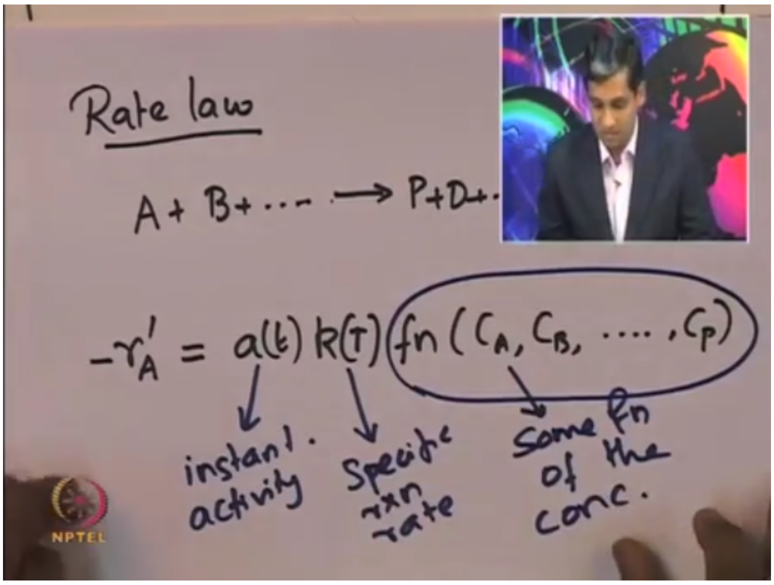

Rate law

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

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

instant. activity

Specific rxn rate

Some fn of the conc.

So, suppose if the catalytic reaction is A + B + gives P + D +. 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 a bit. So, a t is the activity, is the 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 this function f n.

So now, the decay rate, 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. And so, that can be written in the following form.

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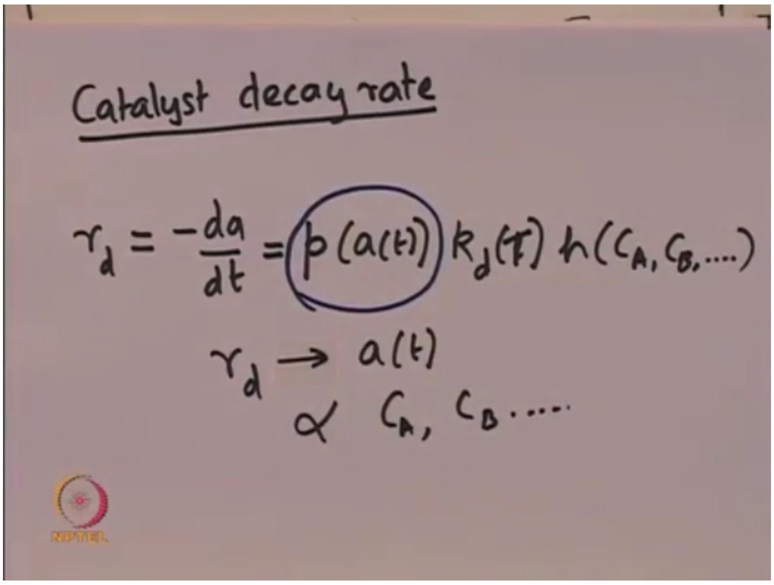

Catalyst decay rate

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

$$r_d \to a(t)$$

$$\propto C_A, C_B \ldots .$$

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 – d a by d t that reflects the rate of change of activity with respect to time. And that should be = 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. It is 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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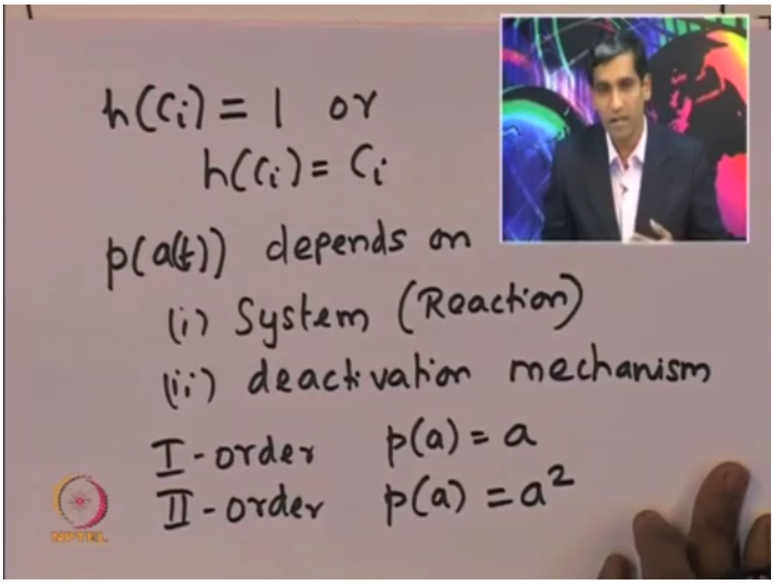

$h(C_i) = 1$ or

$h(C_i) = C_i$

$p(a(t))$ 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 on the decay rate law as 1 or utmost as h of C i to be = C i. That is, it is either does not depend upon the concentration of the species or will assume that it depends utmost linearly on the concentration of the species. So, and also we will assume that this function p which is, 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 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 it were to be a first order decay, if the decay process is first order with respect to the activity, then if it is a first order process, then p of a will be = a.

And if it is a second order process, then p of a will be = a square. So, depending upon what is the order of the dependence of the activity on the decay rate, we can accordingly assume a 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, the, there are 3 broad classification have been identified.

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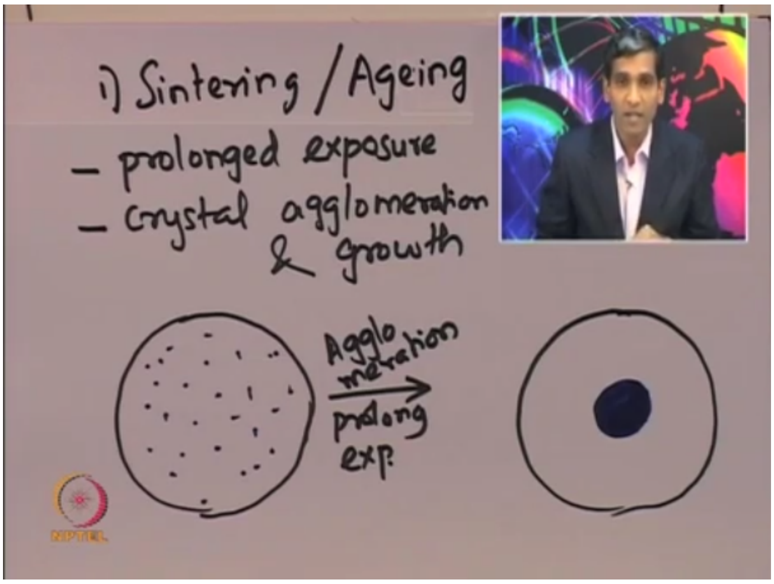

i) Sintering / Ageing

- prolonged exposure
- crystal agglomeration & growth

And these are sintering / ageing process. So, this 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.

And then the third type of deactivation of the catalyst is called the poisoning process. So, there may be poison present in the feed, feed stream which may enter the catalyst pores and they may get deposited on the catalyst site and that may destroy the activity of the catalyst. Or the reactants or the product itself may actually go and irreversibly bind or get adsorbed onto 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 3 different types are and how to characterise, what are the mechanisms that are associated with each of these deactivation processes and how to find the rate law for each of them. 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 prolonged exposure of the catalytic sites to the reactants on the gas stream which is present.

And as a result, because the reactions 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 they start agglomerating together. And as a result, the net surface area which is available for the reactants to go and adsorb onto the catalytic site, that significantly reduces.

And as a result, the catalyst activity is completely lost. So, this can be captured. So, there are 2 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 and there are several catalyst sites which are actually spread across in various locations on the catalyst.

And you, 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 exposed to the reactants to the gas stream for a very long time; so, it is a prolonged exposure. Then, what happens is that the particles they start agglomerating together and 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.

And 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. And so, this process is what is called as a sintering or ageing process. Now, the other method by which sintering can happen is the, is basically called as the pore narrowing or closing.

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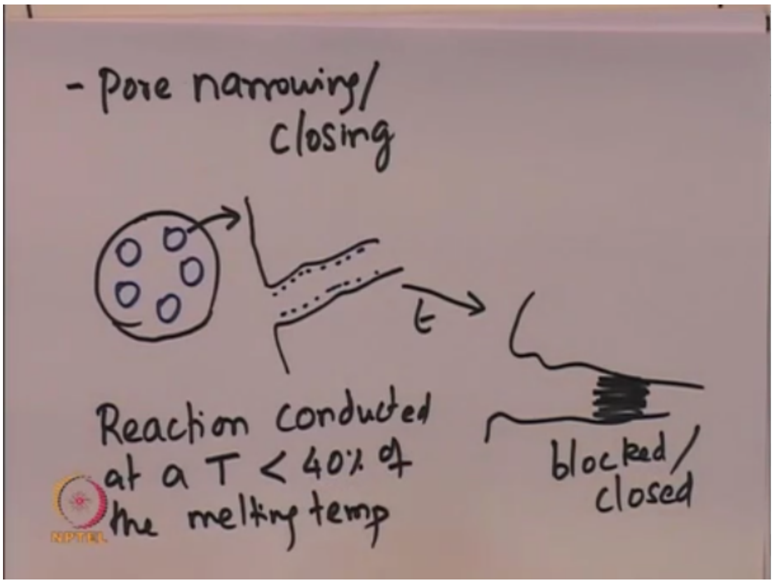

- Pore narrowing/ closing

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

So, the pores which are actually present in the catalyst, so which contains the catalytic sites, because of this prolonged exposure to these various, 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 a catalyst and there are these catalytic sites.

There are these pores which are present here. And at the start of the reaction, that is at time t = 0. So, if I zoom up this pore here, so you will see that, so these catalysts which are present in various locations, so they are present inside the pore here. Now, after certain time when the reaction occurs for a long time, after certain long period of time. Then the catalyst pores will get blocked, will get filled with this material.

And so, clearly the pores will get blocked. And therefore, they get closed. And as a result, the activity of the catalyst is lost. So, the 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 a temperature which is less than 40% of the melting temperature of the solid.

If the reaction can be conducted at a temperature which is less than the 40% of the melting temperature, then the sintering process can be significantly reduced. So, this is a remedial measure for sintering. However, there are several reactions which may, one 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 the, for exothermic reactions, the reaction rate is going to be higher. So, as a result, it is not always possible to conduct the 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.