Chemical Reaction Engineering

Prof. Jayant Modak
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture No. # 13
Catalytic reactions – Introduction

Friends, let us continue our discussion on complex reactions and in the last class, we saw two examples of complex reactions namely chain reactions and polymerization reactions. Today, we will take a look at another important class of complex reactions namely catalytic reactions.

Now, if we talk we talked about kinetics of the reactions and the kinetics that is the rate is determined by temperature, determined by the concentrations of the species and so on. Now, if we are looking for ways to increase the rate of a reaction. There are two possibilities, one is the temperature and other one is the concentration, but concentration would involve taking lot more reactants lot more at higher pressures and So on. That is not really an option that is; if you start with higher concentration you get a rate higher rate. If we look at temperatures although temperature is a possibility, temperature increasing temperatures is not always desirable. For one it would involve investing more in energy, because if you want to increase the temperature of a reaction you have to increase the, you have to supply the energy and thereby increasing the energy investments.

Increasing temperatures also have another drawback, namely, at high temperatures some of the reactants may be unstable. And if that is the case, then we may lose we may end up losing our valuable reactant. What is an alternative? Alternative came accidentally, when it was observed that rates of many reactions actually increase in presence of a third substance. A substance which at that point of time and I am talking about couple of centuries back was thought of not participating in the reaction, but just it is presence increase the rate of a reaction.

For example, it was observed that if you want to hydrolyze starch you add little bit of acid the rates suddenly go up or in case of synthesis of ammonia, if you have a platinum and that to a spongy platinum and we will worry about why spongy platinum and so on. As we move this discussion. But the point is that in presence of such substances, the rates of reactions for where found to increase suddenly.

We now know that all these substances are nothing but the catalyst, and then we call them as catalyst. Now these word catalysts also have been used or what is a catalyst has been explained by various people in various different manners. For example, one definition goes that it alters the rate of reaction without appearing in the reactant or products. Another definition says the same thing by saying that it alters the rate of reaction by appearing both on the reactant side and the product side. So, that the net result is as if it does not appear in the reaction.

Yet another definition says that a substances who whose concentration appears in the rate of reaction more than or higher power than the strychometry suggest. These are all various concepts of a catalyst, but we should remember that there are two things that we know now, that catalyst does or does not do. For example, a substance which someway affects the equilibrium of the reaction is definitely not a catalyst or in other words, catalyst is a substance which will not influence the equilibrium of the reaction. So, equilibrium or thermodynamic considerations are not influenced by the catalyst.

We also know that it is not as if catalyst does not participate in the reaction. In fact, it does undergo several changes. It does participate in the reaction, but it is regenerated somewhere along the line, when the reaction is taking place. So, it does interact with the reactants, but when products are formed this catalyst is regenerated. And therefore, we call such substances now as catalyst or this is what is our understanding of catalyst. Now, let us try to see what exactly does a catalyst do?

Now, if we say that the catalyst does not affect the equilibrium, what are it is implication?

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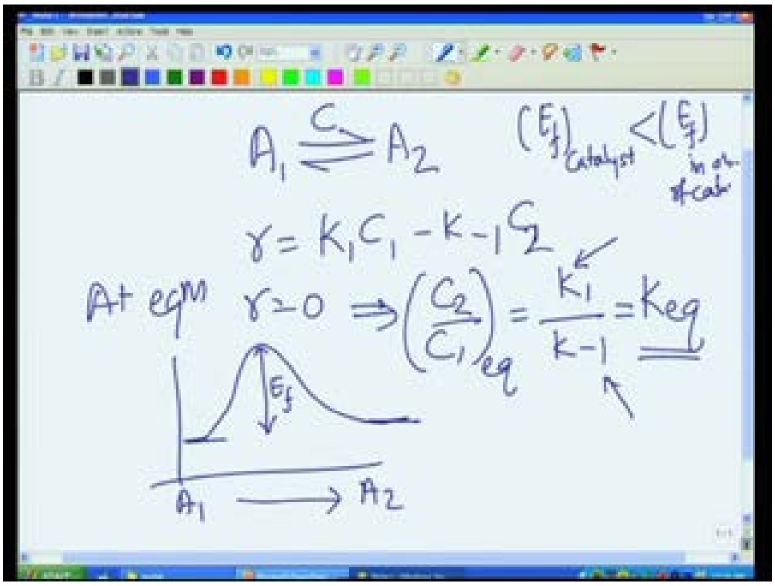

$A_1 \underset{}{\overset{C}{\rightleftharpoons}} A_2$ $\quad (E_f)_{\text{Catalyst}} < (E_f)_{\text{in ab. of cat.}}$

$r = K_1 C_1 - k_{-1} C_2$

At eqm $\quad r = 0 \Rightarrow \left(\frac{C_2}{C_1}\right)_{eq} = \frac{K_1}{k_{-1}} = \underline{\underline{K_{eq}}}$

So, let us say that we have a reaction A 1 going to A 2, a reversible reaction and there is a catalyst which enhances the rates of these reactions. Let that catalyst be C. In presence of this catalyst, the rates of these reactions are enhanced. Now, we call the forward rate constant K 1 and reverse rate constant k minus 1 and we can write the rate of these reactions as K 1 C 1 into K minus 1 C 2. So, that is our rate of reaction.

Now, what is the rate at equilibrium? We know that rate at equilibrium is 0. So, at equilibrium rate is 0 implies that C 2 by C 1 at equilibrium, which is K 1 by K minus 1 must be same as K equilibrium. K equilibrium is something that thermodynamics tells us. So, we are our catalyst C is not going to change the value of this thermodynamic equilibrium. If we say that catalyst C increases the rate of reaction that is it increases K 1, then it must also increase K minus 1 by the same amount, so that the equilibrium constant is unaffected. Now, how does catalyst in general work? There are of course, different mechanisms for different catalyst, but if you recall our progress of reaction from A 1 to A 2. We draw an energy diagram saying that this is the energy level at the reactant state; this is the energy level at the product state and for a reaction to occur. There is a activation energy, let us say F forward from if you are going from A 1 to A 2.

Catalyst by interacting with our reactant in variety of different ways, In fact, reduces this activation energy or in other words the activation energy in presence of catalyst is lower than the activation energy in absence of catalyst that is without catalyst. Now, by whatever extend is activation energy is reduced by the catalyst E f that is for the forward reaction, the same thing must also apply to the reverse reaction. So, reverse reaction activation energy is also reduced by the same extend. The main use or main idea behind using catalyst is to increase the rates of reaction. And this is well known, we all know this, but there are several side effects of using a catalyst, which are not necessarily well appreciated. So, let us take few examples and see what those are.

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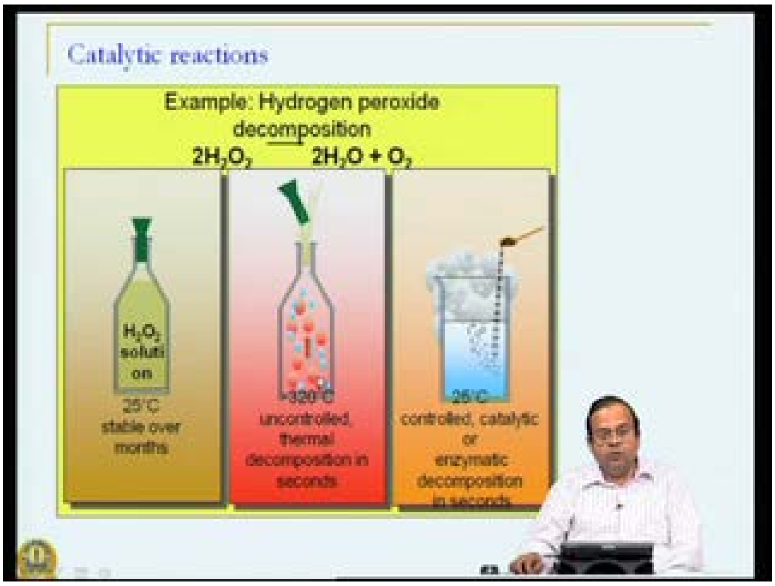

Catalytic reactions

Example: Hydrogen peroxide decomposition

$2H_2O_2 \quad 2H_2O + O_2$

What we do know? For example, if you have a catalytic reaction, let us say hydrogen peroxide decomposition giving rise to water and oxygen. Then, if you take hydrogen peroxide solution keep it in a bottle, keep it in a brown or dark colored bottle. Why, because you do not want it to expose it to sunlight. if you do that then this solution may remain stable or with rather remain stable at 25 degrees over months, nothing will happen to it.

But the same solution, now you heat it up at 320 degree centigrade. So, you supply energy there will be suddenly uncontrolled decomposition of H 2 O 2 in a matter of seconds. Or in other words, our H 2 A 2 O 2 hydrogen peroxide will completely disintegrate into water and oxygen, if you heat it at 320 degrees. But to the same hydrogen peroxide at 25 degrees, if you add an enzyme or a biological catalyst called peroxidase, then again once again the hydrogen peroxide will decompose in matter of seconds. So, this first for example, this implies that something which takes place for months stable at for months at 25 degree centigrade will disappear in matter of seconds, if we heat it to, if you rather add an enzyme or catalyst to it. So, we have increase the rate of this decomposition, so that at 25 degrees we can carry out these reactions.

The other option is also there, that is at 320 degrees, and we can also heat it up to 320 degrees and bring about the same reaction. But look at the temperature difference 25 degrees, with a catalyst or 320 degrees, with a without catalyst by simply enhancing the temperature.

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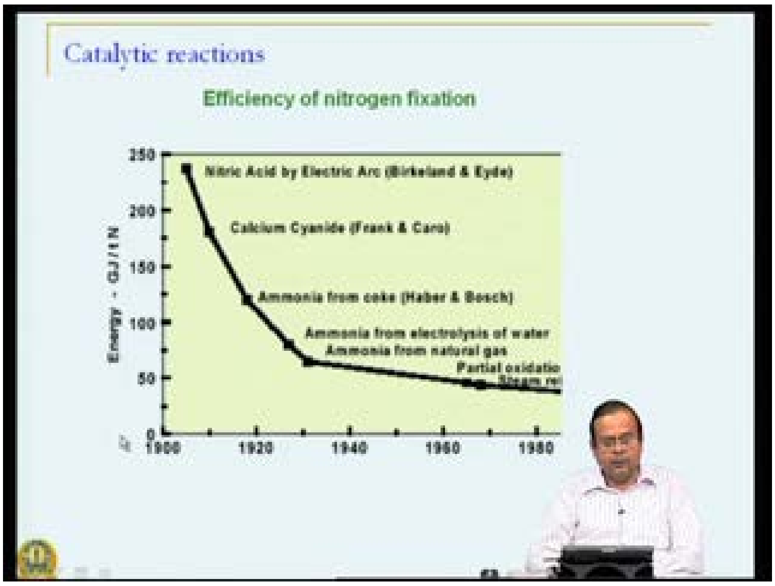

Catalytic reactions

Efficiency of nitrogen fixation

So, this then points out to an important effect of catalyst. Which is a direct consequence, because it increases the rates of reaction by reducing the activation energy. Therefore, reactions can occur at lower temperatures, but with a higher rate. if you look at the history of nitrogen fixation, that is how to as you will know nitrogen is an important constituent of all living beings. It occurs in proteins and several other bio molecules.

We have plenty of nitrogen. Now 79 percent in fact in air. But unfortunately, that nitrogen is of no use to living being, because it is inorganic nitrogen. We have to somehow fix that nitrogen and several different ways had been attempted. And what you see here in this particular figure is the progress of these reactions over almost a century and the energy required for this nitrogen fixation. And you can nicely see the almost exponential decrease in amount of energy. The energy we are talking about is giga joules per kilo ton of or per ton of nitrogen fixed. From roughly about 250 to which to about 40 which is now is the energy that is required.

And what is who is responsible? The main reason for this is the catalytic reaction for combining nitrogen and hydrogen to form ammonia, at much lower temperatures and at much higher rates.

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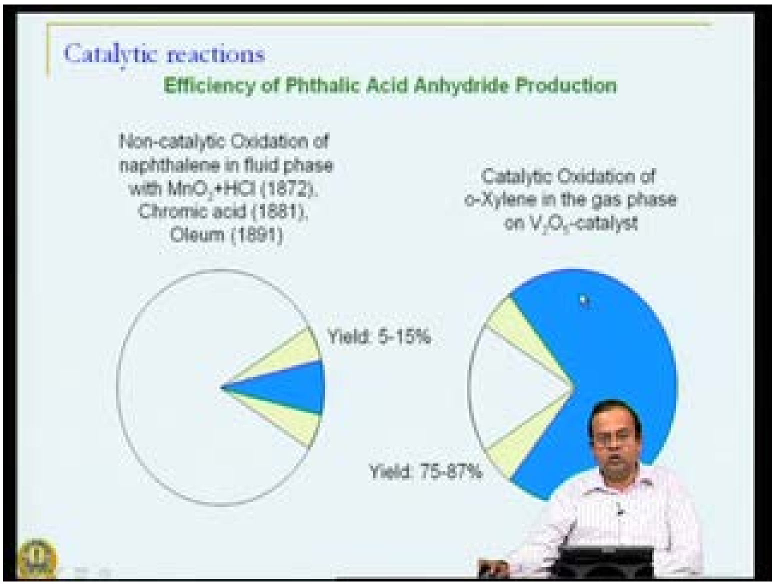

Catalytic reactions

Efficiency of Phthalic Acid Anhydride Production

Non-catalytic Oxidation of naphthalene in fluid phase with MnO_2+HCl (1872), Chromic acid (1881), Oleum (1891)

Catalytic Oxidation of o-Xylene in the gas phase on V_2O_5-catalyst

For example catalyst, therefore, then saves energy, apart from increasing the rates of reaction. Catalyst also improves the yield of a given reaction. That is, if you have several reactions that are possible and some of these reactions are favorably influenced by the catalyst, then you can expect the yield of the desired compound will be higher in presence of catalyst, as compared to in absence of catalyst. The example here shows the phthalic as an acid anhydride production, which was initially done by non-catalytic oxidation of naphthalene with chromic acid with oleum and various different compounds in 19th century, which give an yield of about only 5 to 15 percent yield of only about 5 to 15 percent no more. But the same reaction, now carried out by ortho-xylene oxidation in presence of validium pent oxide catalyst gives you almost 75 to 87 percent yield of phthalic anhydride. So, yields of desired reaction are inner.

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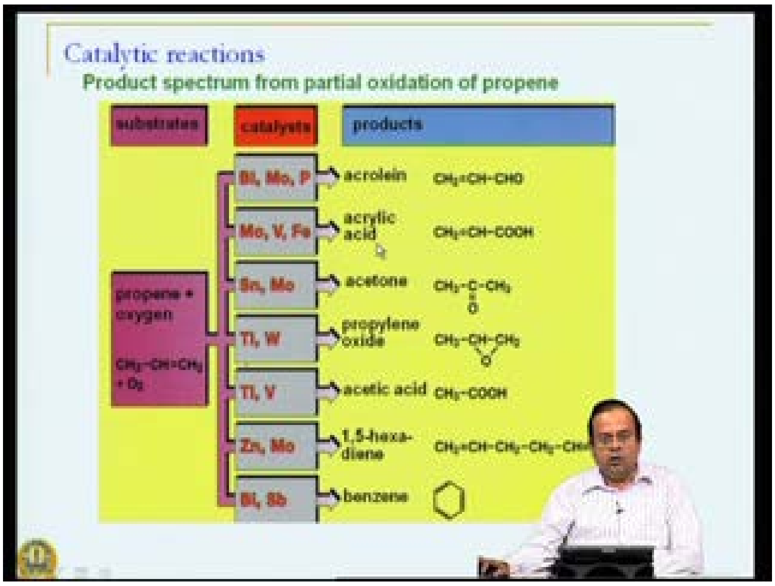

Catalytic reactions

Product spectrum from partial oxidation of propene

substrates	catalysts	products	
propene + oxygen $CH_3-CH=CH_2 + O_2$	Bi, Mo, P	acrolein	$CH_2=CH-CHO$
	Mo, V, Fe	acrylic acid	$CH_2=CH-COOH$
	Sn, Mo	acetone	$CH_3-\underset{\underset{O}{\parallel}}{C}-CH_3$
	Tl, W	propylene oxide	$CH_2-CH-CH_2$
	Tl, V	acetic acid	CH_3-COOH
	Zn, Mo	1,5-hexa-diene	$CH_2=CH-CH_2-CH_2-CH$
	Bi, Sb	benzene	

The energy of course, is another aspect we saw, but there is also an interesting side effect, if you like to call it of a catalytic process. Take for example, propene and oxygen. We have propene and we have oxygen and these two chemicals together can give us a spectrum of product acrolein, acrylic acid, acetone, propylene oxide, acetic acid, 1 5 hexa diene, benzene and so on.

Now, if you suppose these reactions were to occur all simultaneously, then you could you and let us say acrolein is your desired product, then you can expect not only acrolein, but all other chemicals. Fortunately, these reactions do not occur, unless there is an appropriate catalyst. Now, even in presence of appropriate catalyst, if all the reactions were to occur together we would have the same problem, as in the case of absence of catalyst. lot of effort has therefore, gone into developing a class of catalyst which give you a specific product. For example, bismuth, moledium, phosphorus they give you only acrylene. Zinc and moledium, for example give you only 1 5 hexa diene. Bismuth and anti moni, for example gives you only benzene.

In other words, different catalyst for different products. If we were to use, let us say this first set of catalyst we will get highly selective product acrolein over the entire range of products that are possible. So, catalyst can play an important role in increasing the selectivity of the desired product. And this is important, because as you would realize that focus now is on making highly selective processes. We do not want any side products, so that we do not have to worry about how to separate them, how to get rid of them, and so on. So, selectivity therefore, is an important issue. If selectivity is what you are looking for, then catalyst plays an important role. And therefore, it is not surprising that chemical companies spent enormous amount of money or invest lot of their man power and finances to develop a suitable catalyst. And of course, after doing so, they will try to guard that catalyst, because they do not want a competitor to know about that catalyst. So, you have patenting and all kinds of kinds of issues related with it.

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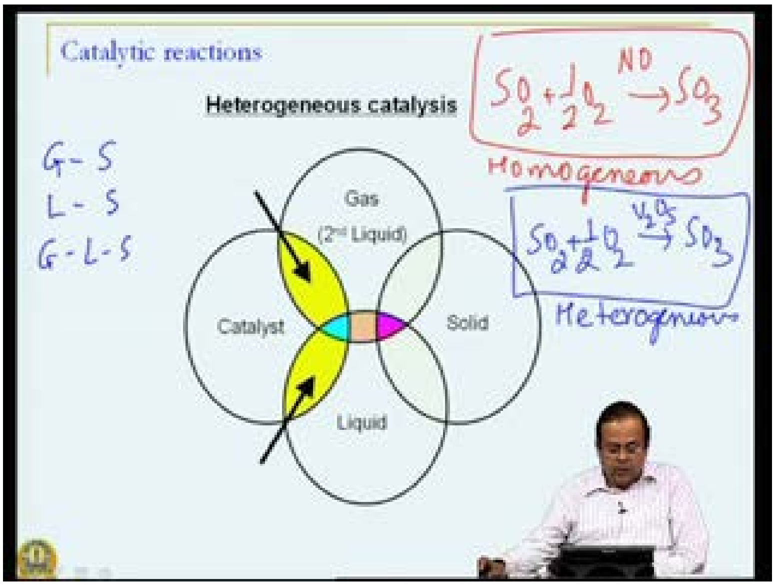

Catalytic reactions

Heterogeneous catalysis

G - S
L - S
G - L - S

$SO_2 + \frac{1}{2}O_2 \xrightarrow{NO} SO_3$

Homogeneous

$SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$

Heterogeneous

So, now let us look at some example of catalyst. And basically, there are two types of catalyst, heterogeneous catalysis and homogeneous catalysis. For example, if we take reaction for generation of SO 3, which when absorbed in water will give you H 2 SO 4, this reaction can take place in presence of nitric oxide. So, when presences of nitric oxide, these two gases combine to give you SO 3, which is also a gas. So, this is an example of homogeneous catalysis. Because both reactants product and the substance which is acting as a catalyst, all of them are in the same phase gas phase.

However, the same reaction can also take place in presence of V 2 O 5. Reaction is same, but the substance now is a solid material valedium pent oxide. And therefore, the reaction now is an example of a heterogeneous catalysis, because we have solid as a catalyst and reactants and products as gases. This is an example of heterogeneous catalysis, so two classes. The role played by that catalyst is similar, but the phase in which it is present is different. We have for example, if you want to look at this, we have a gas phase, we have a liquid phase, and we have a catalyst. So and we also of course, have solid reactions. Typically catalytic reactions become a multi phase process. For example, we could have gas solid phases, because gases gaseous reactant, gaseous products, solid catalyst. We could have liquid reactants and product and catalyst.

So, liquid solid catalytic reactions, we could have gas, liquid as reactants and products with catalyst. That becomes a gas liquid solid reaction phase. So, we have various different possibilities. For example, gas solid catalytic reactions, we have liquid solid catalytic reactions, we have gas liquid solid catalytic reactions.

Now before we, so our objective here now is to see that how do we develop the kinetics of these process or what are the rates of the reactions, which are carried out in presence of catalyst. Now before we go on to looking at the specific example, let us look at what happens when we have a catalyst? Or how do we define the kinetics? So, how do we define the rate of a reaction of a catalytic reaction?

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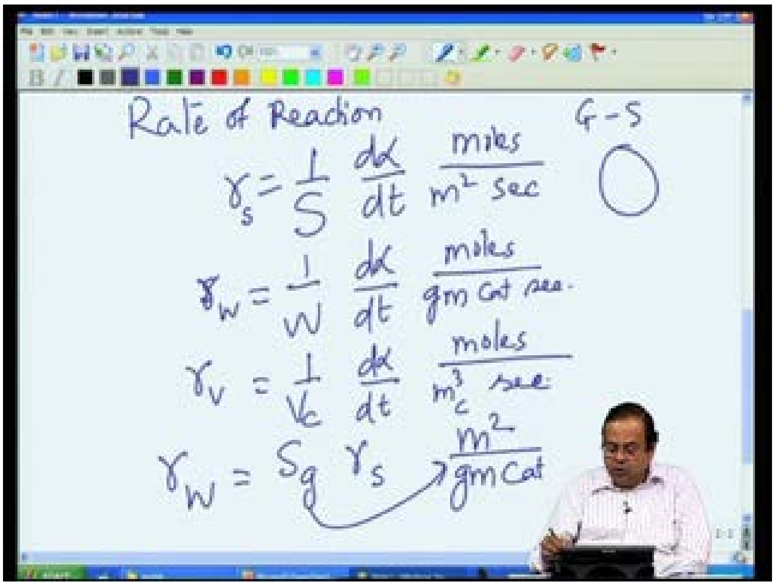

Rate of Reaction

G – S

$$r_s = \frac{1}{S}\frac{d\alpha}{dt} \quad \frac{\text{moles}}{m^2\ \text{sec}}$$

$$r_W = \frac{1}{W}\frac{d\alpha}{dt} \quad \frac{\text{moles}}{\text{gm Cat sec}}$$

$$r_V = \frac{1}{V_c}\frac{d\alpha}{dt} \quad \frac{\text{moles}}{m_c^3\ \text{sec}}$$

$$r_W = S_g\, r_s \qquad \frac{m^2}{\text{gm Cat}}$$

Now, if you recall our definition of a reaction rate, we said that the rate of a reaction is 1 over V d alpha d t, where alpha is the extent of the reaction and V is the volume of the reacting mixture. Now, if you think of gas solid catalytic reactions, let us see. Catalyst is solid; gas is my reactants and products. Now if I use volume of the catalytic volume of the reacting mixture namely of that of the gas this rate of reaction does not make much sense, because it is the interaction between the gas and the solid which is what is causing the reaction to reaction to proceed.

So, volume of the reacting mixture is not an appropriate quantity to normalize the change of extent of reaction. In this particular case for example, we use surface area of the catalyst. Let us say that we have this catalyst and let us make it a round one. We use the surface area, now what surface area? We will come talk about it little later. So for example, the units of rate in this particular case become moles per meter square per second. Rather than moles per meter cube per second, meter cube of reacting mixture.

So this is how we define rate. There are of course, alternate ways. For example, I could define my rate by normalizing it with the weight of the catalyst. So, I have moles per gram of catalyst per second as the rate of my reaction. Or I could have it normalized with the volume of the catalyst, let us call it V C, not that of a reacting mixture, but that of a catalyst and I could have moles per meter cube of catalyst. So, I will put and per second.

Now, as you can see from this various terminologies. Let us call this as rate defined per unit surface area, rate defined per unit weight of the catalyst, rate defined per unit volume of the catalyst. And as we can see that all these are not independent of each other. For example, I could write r w, as r s into S g, where this S g is, what is this S g? It is S g is meter square per gram of a catalyst.

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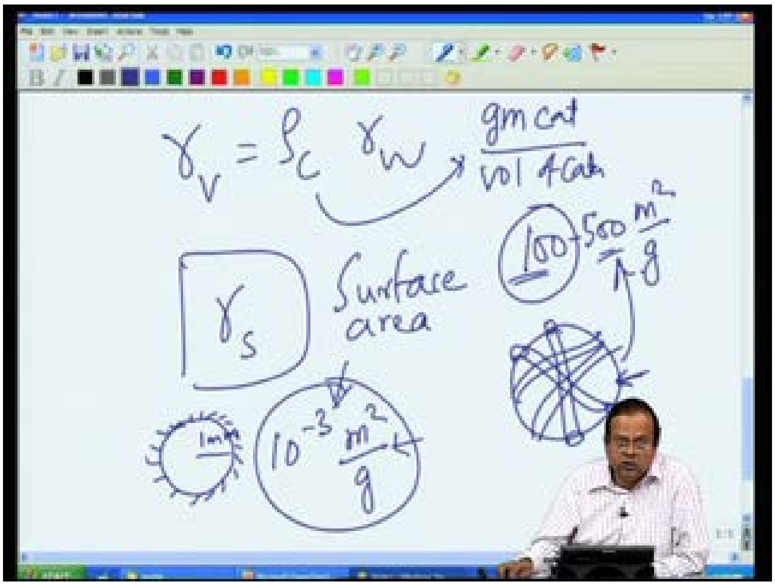

So a gram of catalyst, how much surface area does it allow for reactions. That is my S g. I could also write for example, my rate in terms of volume, related to rate in terms of weight into the apparent density of the catalyst. What is rho c? Rho c is gram of catalyst per volume of catalyst.

So, these all these rates are related to each other. Typically, we take r s as the basis of our definition that is surface area per surface area. Now, question arises what kind of surface areas does this catalyst provide us? You will be surprised to know that it is not uncommon to see catalyst which 100 to 500 meter square per gram of catalyst, surface area. When we were using micro scale catalyst, when nano was not in fashion may be last decade or so, this range was more common 100 100s. But now, because our catalyst itself can be nano size and you know that surface area will increase, as the radius of the particle decreases. So, you could have significantly higher surface areas. Now, where do we get this surface area? If we were to have us, let us say spherical by the way how big is 100 or 500 meter square per gram catalyst, how big is this area? This area is as big as the football field, a typical football field, the surface area that you see. That is how much area is available for catalyst, so that the reactants can interact.

Now, where does this area come from? Let us say that we have a solid block of catalyst, a material solid as a rock. And let us say that if we have a size, let us say 1 mm 1 millimeter. Fairly small, you can we can see it with the naked eye, but fairly small. Now, for this kind of material with a solid material, this surface area will work out to be only about 10 raise to minus 3 meter square per gram, if you take the typical properties of a solid material density and so on.

Where is 100 meter square per gram and where is 10 raise to minus 3 meter square per gram. There is 5 orders of magnitude difference between, what we want and what we can get, if we use a solid block as a catalyst. So, where does this area come from? This area comes from the inside pores of the catalyst. That is catalyst is never a solid block, recall I said spongy ions spongy platinum rather, when ammonia oxidation took place fairly rapidly why spongy, because lots of pores the entire material consist of a network of these pores. So, that reactants can interact with the catalytic active sides on the in the catalyst. And this is the kind of thing that leads to these high surface areas. So much so, that the actual surface area, as we know that is if you have a solid block, the surface area is what surrounds it. That surface area, that is the real surface area is practically negligible compared to what can happen, I mean you can look at this number and what you actually get.

This is insignificant. So, the reaction occurring on the surface of the solid is practically negligible. What is happening is, most of the reaction is taking place inside the catalyst.

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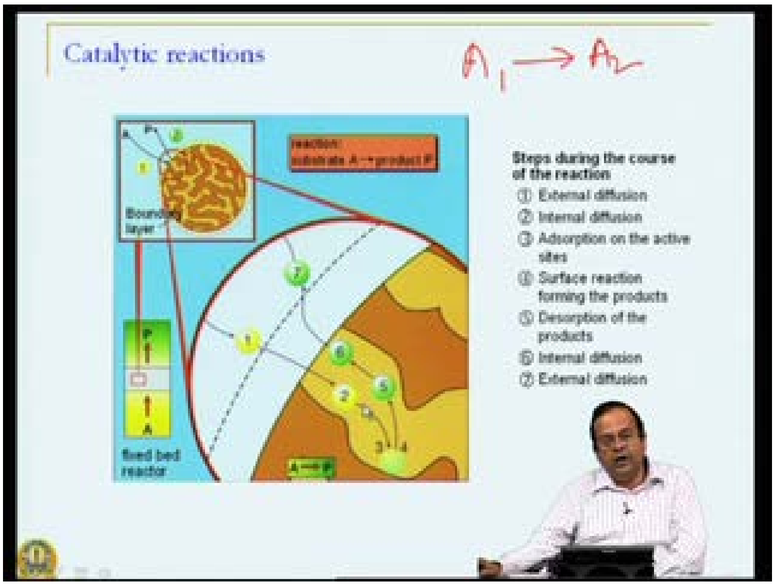

Catalytic reactions

$A_1 \rightarrow A_2$

Steps during the course of the reaction

① External diffusion
② Internal diffusion
③ Adsorption on the active sites
④ Surface reaction forming the products
⑤ Desorption of the products
⑥ Internal diffusion
⑦ External diffusion

Now, how does for these two occur. What should the happen or what are the key steps for this catalytic reaction to take place. So, let us look at what are some of the important steps that this catalyst must under undergo. So, that the reaction takes place. Let us say that we have a reaction A 1 going to A 2.

And this reaction is taking place in the presence of pore porous catalyst. And these are all the pores, that is these light shaded ones are, let us say all the porous network inside the catalyst. The dark material that you see here is a solid real solid material. And together they make a porous catalyst. So, for this reaction to take place what must happen? We can visualize this process as follows.

This solid is surrounded by the gas. Let us say this light blue colored thing is the gaseous reactants and product. So, for this reaction to take place, what should happen? The first and foremost thing that should happen is from this gaseous phase, which I am going to call it as bulk phase that is where most of the I mean the gas is present. So from this bulk phase, the material must come to the surface of the catalyst. What we see here, is an expanded portion of this. So from the bulk phase, the material should come to the surface of the catalyst.

Then once it comes to the surface, it must pass through the pores of this catalyst. Somewhere along this porous boundary line is some active material which is really acting as a catalyst. Incidentally, catalyst is not all active material. Now, if you imagine that you are making your solid ball porous and you go on drilling holes or pores, pretty soon the structure will just crumble, because it would not have the physical integrity that you want.

So, what we do? We add binders, we add supporters or more often the material is deposited on to the porous support structure, the catalytic material, so that the reactions can take place. Now, solid material cannot move into gas so, it is all the gas, who has to do all the travelling. So now, once the gaseous material enters the pores of the catalyst, it must interact. Interaction, we call it as adsorption of the gaseous reactant molecule on the catalyst surface or the pores of the catalyst. Now, once the reactant molecule sits onto this active side, it must undergo some chemical transformation give rise to the product. Product, which is still bound to the active side of the catalyst. So, what must happen next? This active now product which is formed, but which is still bound to the catalyst must desorp. It must desorped into gas phase, travel now through the pores of the gas phase to the surface and from the surface to the bulk of the catalyst.

Or in other words, when we have a gas solid catalytic reaction, this is not a single step affair, but it is a multi step process. Once again let us recap and put a formal terminology to various steps that we just now described in words. The material or the gaseous reactant has to diffuse from the external bulk to the surface of the catalyst. So, all this process takes place by diffusion and we call this step number 1 over here as external diffusion. Then it must defuse inside the pores internal diffusion step number 2.

Step number 3 is the adsorption of these material gaseous reactants which have diffused inside the catalyst onto the solid material or the active component that is going to bring about these conversions. So, that is step number 3 adsorption. Now, reactants which are adsorbed onto the solid must undergo chemical transformation. So, they become the product, still adsorbed onto the solid. So, that is surface reaction which is step number 4. The material or the products which are adsorbed onto the surface must disorp so, step number 5. This disorp material must diffuse through the pores step number 6, internal diffusion of products.

And step number 7, when it comes to the surface, it must diffuse back into the bulk, so that is external diffusion of products. Or in other words these steps, we can now look at into three broad categories of steps. There are total seven steps, but we can group them together. Number 1 and 7 both referring to the diffusion of material either from the bulk to the surface or from surface to the bulk, so external diffusion. Steps 2 and 6 are internal diffusion steps. That is material either reactant or products flowing through the pores of the catalyst. And step number 3, 4 and 5 which actually bring about the chemical transformation from a reactant side that is A 1 to A 2. So, that is the reaction, mainly the reaction or the kinetic part of it.

So, in the first as a first step, we are going to focus only on the reaction part of it. That is the rate as determined by 3, 4 and 5 steps. Now later on, we will worry about what is the rate of this diffusion, inside the catalyst internal diffusion, as well as outside the catalyst or external diffusion. In short now the rate of this conversion of A 1 to A 2 is not governed by the kinetics of the process alone that is not just by steps 3, 4 and 5. Why is that going back to the rate determining step concept. At that time, I gave you an example of relay, a relay team passing by turn from one member to another. The slowest of this team member is going to determine the performance. How is this situation in a different than that you can view this as a 7 member or if you group them together as a 3 member unit external diffusion, internal diffusion, chemical reaction.

So, the idea that is which of this processes is the slowest among this will therefore, determine the rate of conversion of A 1 to A 2. And not just the kinetics of the process which are these 3 steps in particular.

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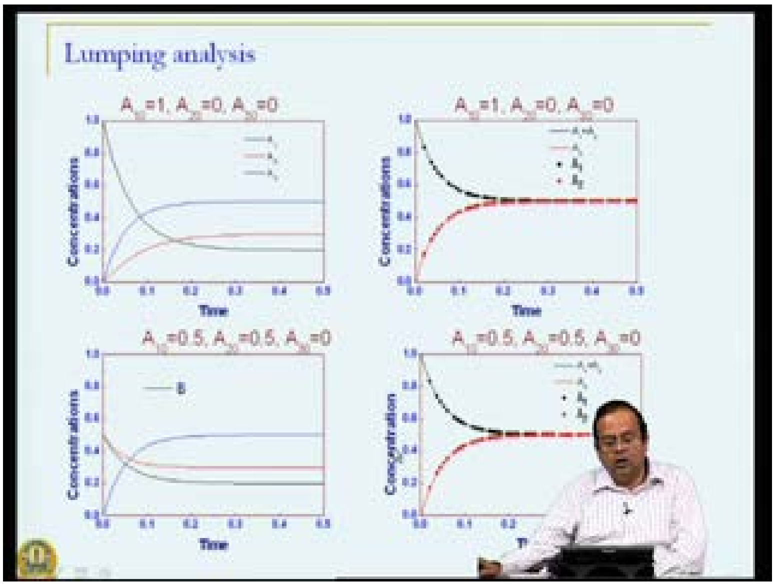

Lumping analysis

So, it is important that we understand the rates of the transport processes as well. And this is where the role that transport processes play in chemical reactions becomes apparent. We will start our discussion with this, but before we conclude for today session, a word about this transport processes.

And why surface area is important and so on. Before we do that, let me just highlight that since the reaction is going to be or the kinetic part of the reaction is determined by steps 3, 4 and 5. In particular 3 and 5 involve material adsorption onto the surface or desorption from the surface. both term, both times surface is important and therefore, it is not surprising, we define our intrinsic rate in terms of rate intrinsic rate, in terms of rate as one over surface area d alpha d t, that is our true kinetic rate. Going back to the transport phenomena, now transport phenomena is a scale dependent process.

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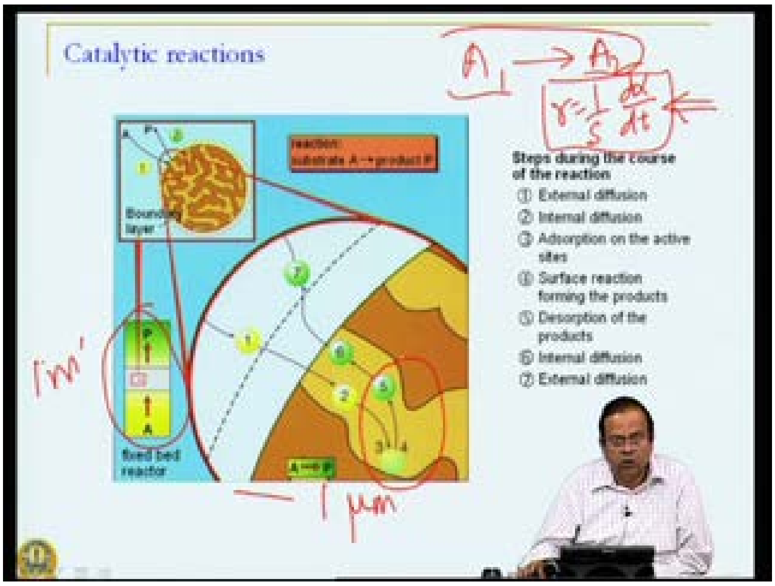

Catalytic reactions

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$\boxed{r = \frac{1}{S}\frac{dA}{dt}}$

Steps during the course of the reaction
① External diffusion
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⑤ Desorption of the products
⑥ Internal diffusion
⑦ External diffusion

The reaction rate is scale independent. Why is it scale independent? Our idea of normalizing itself lends to independence with the scale. What it says is? This is my rate of reaction that is this is how my reactant A 1 changes moles per unit area per unit time, intrinsic rate as we call it. Whether I have a catalyst, which is which is 1 mm dia or which is 1 micron dia or 1 nano dia. my reaction rate per unit area of surface area is same. Now, surface area will be different in different dimensions, but per unit surface area, the kinetics which I would talk about when we talk about chemical kinetics is same. So, that is a scale independent process. Not to be confused with the fact that the rate of these reactions itself is scale independent, overall rate no. because as we just now saw, the overall rate is a combination of transport rate and chemical rate or kinetic rate.

So, what I am saying is the kinetic rate is independent of scale. But the overall rate that is the rate that will actually be present will be determined by which of this process is slow. So, that rate is scale dependent. Why is it scale dependent? It is scale dependent, because depending upon, whether I had one micron catalyst or 1 nano and nano meter catalyst or 1 mm catalyst my surface areas will be different. And therefore, the transport rates will be different the overall rate will be different. The scale dependency does not end here. Typically, we talk about catalysts which are in macron sizes let us say. But the actual reactor is in meters. So, what is happening? In a reactor for example, in which we dump this catalyst. We looked at the example, where ammonia, we saw the cartoon or the photograph of an ammonia reactor where a close to 300 tons of catalyst was dumped in these in this reactor.

So, if you have that much catalyst. What we are saying is that we actually our reactor in which we pass reactant from one end, products come out from the other end of the reactor which is in meters. I am just putting order of magnitude, so 1 meter, but the real reaction is taking place at the scale of 1 micron let us say. So, that is the scale variation also as the reaction is taking place. That is also an important issue to be kept in mind. With that we will close today's discussion and in the next session, we will focus on this adsorption surface reaction desorption processes to get the kinetic rate of a catalytic process. thank you.