

Chemical Reactions Engineering II
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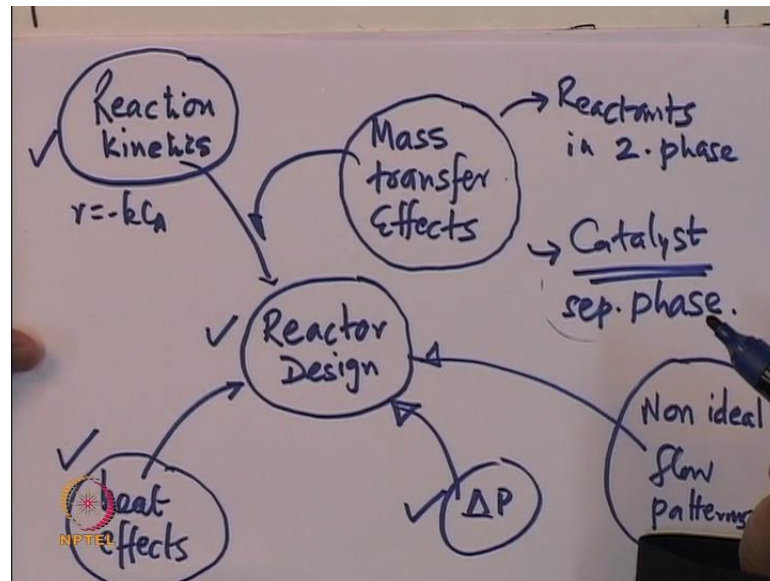
Lecture - 1
Introduction to Catalyst and Catalysis

Good morning. We are going to learn some advanced topics in reaction engineering are part of this particular course. You have already learned basic aspects of reaction engineering, where we talk about what is reaction kinetics; what is its role in reactor design or simulations. Then, how to come up with a rate law base on the laboratory data that is given? What are the effects of heat transfer? Like for example, like the reaction exothermic or endothermic. So, how the temperature would change and accordingly how the reactor design will get affected. So, many basic aspects of reaction engineering that we have learned in the first part of this course.

So, in the second part we are going to look at we are going to go next step, where we talk about what is a role of catalyst and if catalyst is in solid form, how the reactor design will get affected. What are the different procedures to taking into count effect of the presence of a catalyst? Then, if the flow patterns are non-ideal how you deal with them right. The many other possibilities, where one reactant is sitting in one phase that is say gas phase. The other reactant is in liquid phase. They going to react either it liquid or gas phase. Then, in that case how do it do the reactor design like for example, we have a multi-phase case, where to reactant sitting in two phases like a how to a count for something called as mass transfer effects.

So, in this particular course we have going look at all these additional effects that will come in while dealing with reactor design. So, let me go back and talk about what is reaction engineering. So, now, normally what we deal with the reactor design?

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So, that is a decent reactor design or it can be simulation adsorption well. So, reactor design needs some input and where it comes from the main input is the reaction kinetics is reaction kinetics. Now, this reaction kinetics, we can derive it from laboratory data or it can be based on some theoretical aspects like for example, density function theory. Then you have some additional effects; so this reaction kinetics if the reactions are taking place in multi-phase systems. This is reaction kinetics that is normally r is equal to say minus $k c a$ or something, which will not remain as it is because it will be affected by something called as mass transfer effects.

This is something that you have not done in reaction engineering part one. Then, apart from this you may have heat effects as well. So, you may have energy effects or heat effects, where the reaction is effected by the heat boiler or heat absorbed. So, the temperature the reactor may change and as you know rate of the reaction increases exponentially with temperature. That is, why I need to take in to consideration the change in temperature. So, heat effects what else then they can be pressure drop. So, the pressure drop in the reactor especially, in the case of gas phase reactions if there is change in pressure drop, and then the change in concentration and that will again affect the rate of reaction.

So, ΔP is again very important what we need to do here is. So, write is a momentum balance take into consideration of the pressure drop and so on. In the case of gas phase

reactions is very important anything else; we have something called as non-ideal flow patterns. This is what you going too learned at later stage in this particular course, non-ideal flow patterns. Now, most of the reactors that we have studied in the part one of reaction engineering course; they are ideal reactors. So, that is CSTR or plug flow reactor, where we assume certain flow pattern and accordingly define the concentration the reactor.

For example, CSTR concentration is uniform everywhere; it is constant does not change with respect to special coordinate whereas, in plug flow reactor it changes from inlet to outlet, but it is no back mixing that we have assume. We have assumed that the concentration profile or the velocity profile along the radial direction is uniform. So, these are the assumptions which make the reactors ideal in sense; we assumed that the behavior is specific, but in the reality it may not be that way. So, in reality the flow patterns may be non-ideal depending on the internals for example, in the part bent reactor you have channeling in CSTR you may have stagnant pockets.

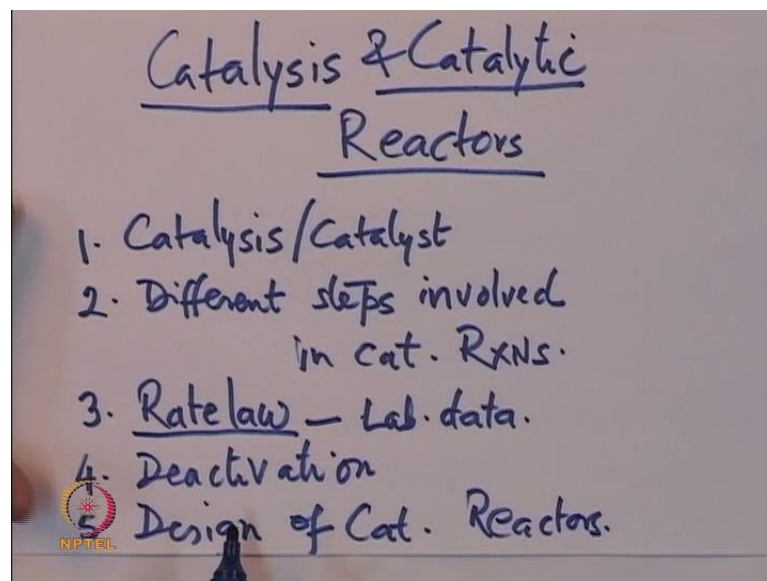
So, all these effects are to be considered while designing the reactor. So, if you see reaction engineering it is all reactor design and around which we have so many effects. What you learned in reaction engineering one is, the reaction kinetics for simple reactions for say homogeneous reactions r is equal to minus $k c_a$ or $c_a c_b$ and c_a raise to n c_b raise to m and so on. So, this is what you have learned; what reaction kinetics is all about. How to design an ideal reactor based on the reaction kinetics is given. Now, you may have multiple reactions also you may have the heat effects also. So, this is what you have learned to some extend in part one.

Then you have learned in this one also in part one and to some extend how to design reactor for these particular cases. But very of course, probably the pressure drops constraints. These three things you have already taken into a count while designing the reactor you know the procedure how to design the reactor. But, now what you going to do look at is the effect of mass transfer if the reactants are sitting in two different phases or product comes out of the reaction phase; so multi-phase effects or if this catalyst that you using is in solid phase or any different phase. So, you have mass transfer effects then you may have the flow pattern effects where there is a non-ideality. So, it does not follow ideal CSTR or plug flow reactor.

So, these are the things that we have going to learn in this particular course. Now, in case or in the case of mass transfer effects, you may have the reactants sitting in two phases or you may have even the catalyst sitting in a separate phase. This forms almost twenty five to thirty percent of this course, the catalytic reactions and catalytic reactors. In fact, you see industrial reactors almost all of them are catalytic reactor; very few reactions are uncatalyzed reactions. In these catalytic reactors, most of the reactors are where the catalyst is used in the solid form.

So, which is which form the separate phase most of the time reactions are taking place or the reactants and products or in other gas or liquid phases whereas, the solid catalyst phase is a solid phase. So, we need to consider those mass transfer effects apart from that there is, so many other aspects to be learned in catalysis.

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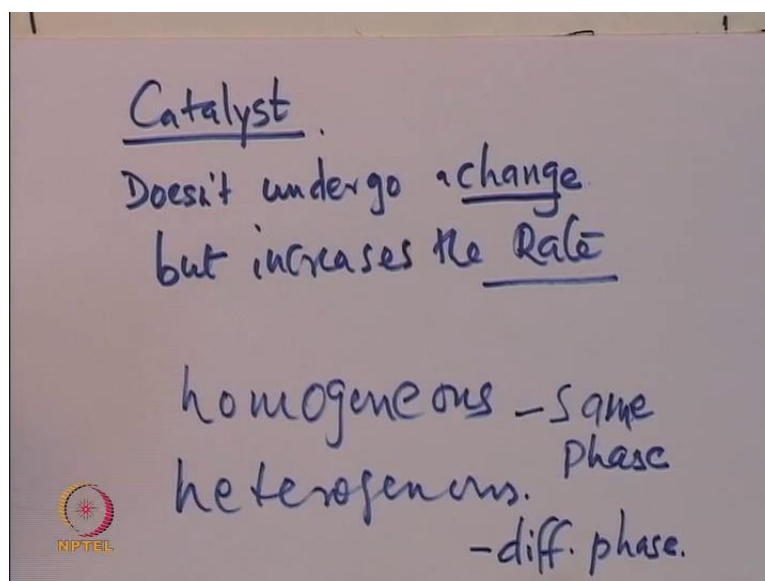


So, what we going to start now in today's lecture is the first part of this course that is catalysis and catalytic reactors. What to be learned in this course, first we know what we tried understand, what is catalysis and what are catalysts; something that you already know, but I will just stand review that information in context of reactor design. Then, different steps involved in catalysis, when a reaction takes place on the catalyst. What else? Rate law from the data laboratory data, now again this is something like you learned before as well, but now the rate law will be different if you are using a catalyst.

The rate law will have a different expression and normal expression is r is equal to minus $k c_a$, whereas in the case of catalytic reaction, then so many steps that are taking place while the reaction is happening. So, in that case the rate law would have a different form. So, you going to spend some time understanding, what kind of rate equation one can encounter in catalytic reactions especially when the catalysis solid. Then, catalyst has again very important, I would say property or it is not a property such, but then there is something that is undesired where when the catalysis happening.

What is that? It is catalytic deactivation or is a catalyst deactivation if catalysis solid then the catalytic sites, they are deactivated during the course of the reaction. Many reactions, where the deactivation the rate is much faster than the actual reactions in that case how to deal with deactivation, so catalyst deactivation. The last one of course, is the design, design of catalytic reactors. So, these are the different things that we have going to learn as part of this particular chapter. So, let us start with what is catalyst very simple most of you know about it.

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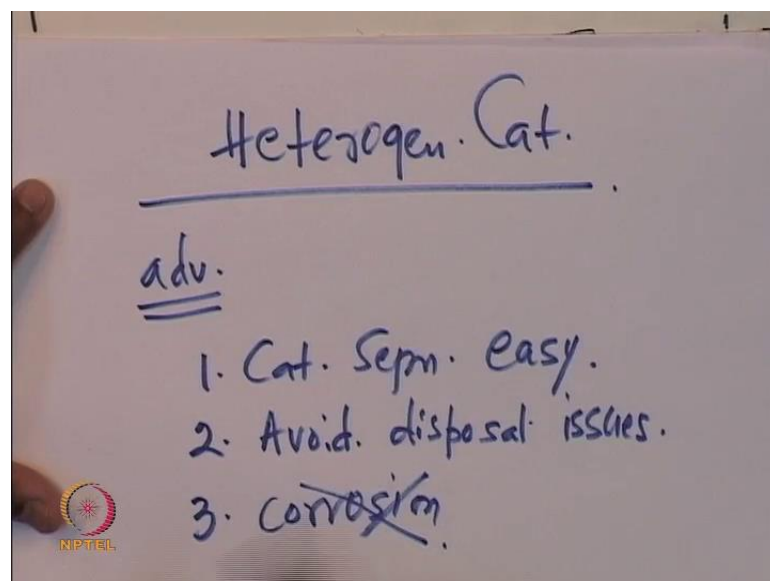
What is catalyst? Catalyst is a substance that increases the rate of the reaction, but is not consumed during the reaction does not undergo a change, but increases the rate, it may undergo change temporarily. But at end of the reaction you see the catalysis coming out in the form that you all already started. Of course, deactivation is a different thing, but otherwise if the deactivation is not taking place, the catalyst comes out of the reactor as

such. Catalyst remains in the reactor as it is in the form that we have already taken. So, what is it doing it is increasing the rate of the reaction and that are many types of catalyst it can be homogeneous and it can be heterogeneous depending on what is the phase in which it is.

If it is in the same phase as the reaction mixture same phase, then this homogeneous; if it is in different phase then it is heterogeneous. So, as an example if you have solid catalyst, which is catalyzing the reactions of the reactants which are present in gas solid liquid phase; say for example, ion exchange resin for esterification reaction which is the liquid phase reaction; fluid catalytic cracking zeolites they are used for catalyzing hydrocarbons cracking, which is a gas phase mixture. So, that is heterogeneous reactions.

As I said before the heterogeneous reactions quite common chemical industry; there are many advantages of heterogeneous reactions. What do the advantages, why for heterogeneous catalyst over homogeneous. Of course, not that see there are many other reactions also still practice in industry with homogeneous catalyst, but the drive is towards developing a heterogeneous catalyst for a given reactions; because they are many engineering benefits if you use heterogeneous reactions. So, before we going to details of the catalyst just let us try understand, what are the advantages of heterogeneous catalyst?

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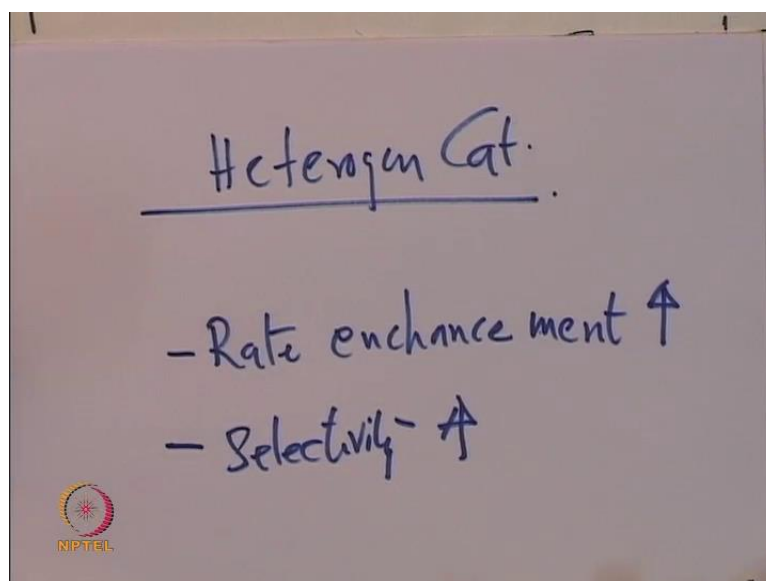


As I just said it is mostly in the different phase and most of the reactions it is solid and reactants and products are sitting in either gas or liquid phases. So, the heterogeneous catalyst the advantages are first of all you do not need catalyst separation or the catalyst separation is easy; if it is a fixed bed reactor the catalyst remains in the reactor. We do not need to separate it whereas, in the case of homogeneous catalyst it goes with this reaction mixture and we need to separate it. So, you have disposal problems also in the case of homogeneous catalyst.

So, this separation is easy sometimes you have you avoid disposal issues; all this is less load on effluent treatment if the catalyst is corrosive for example, sulphuric acid it is liquid phase catalyst it corrodes the material of construction whereas, if you immobilize those acid sites on solids and if you have acid catalyst in the solid form is zeolites or isomerization. In that case, it does not come in contact with the material of the construction, so corrosion problems are avoided.

So, you get rid of corrosion problems and the material cost goes down. Like this the many advantages apart from sometimes you may get enhancement in selectivity and rates. So, these are only practical advantages from process point of view whereas, sometimes you get advantages in terms of selectivity yield all the performance.

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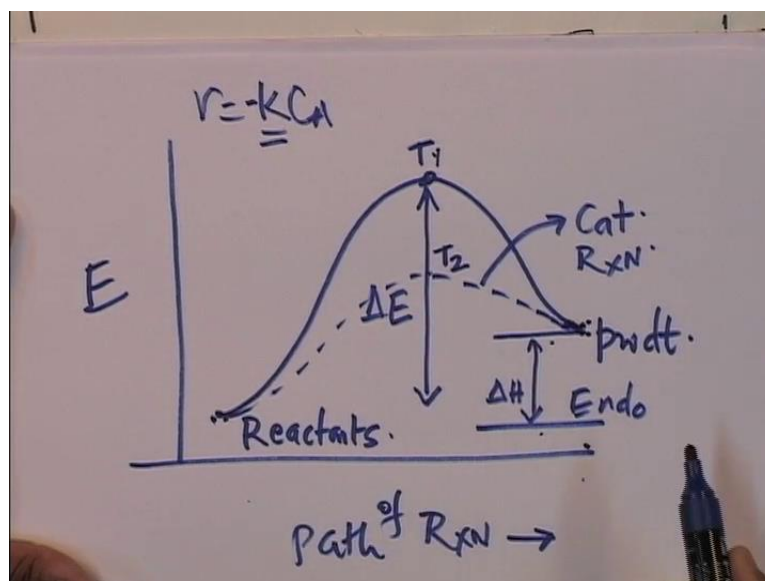
So, in the case of heterogeneous catalyst I just continue, there may be a rate enhancement not always in fact, some most of the times it goes down, but still we prefer it because

they are many other engineering benefits. But sometime, I can increase the rate more than that it is selectivity towards a particular product that goes up. I can design catalyst as per my requirement and get high select will talk about it later more. So, these are the advantages of heterogeneous catalyst. So, I just quickly revise what we have learned. First, I told you what is an importance of learning mass transfer effects and non-ideal flow patterns, which is going to constitute major portion of this particular course; from reaction engineering point of you from reactor design point of you.

Then, I told you the importance of catalyst, most of the times the catalyst is present in another phase. So, which makes it heterogeneous and because of that there are many aspects need to be studied while designing the reactor. So, in this particular chapter we have going to learn, what is catalyst? What are the different steps involved when reaction happens on the catalyst surface? Coming up with the rate law based on the laboratory data, which is a natural extension of what we have learned in a reaction engineering one but now for catalytic reactions.

Then, catalyst deactivation and catalytic reactor design. Now what is catalyst is a substance that increases the rate of reactions, but does not undergo change it and may undergo change during the course of the reaction, but at the end of the reaction it comes out as it is. That is nothing but a catalyst and catalyst can be homogeneous or heterogeneous and heterogeneous catalyst are advantages; because of no disposal problem separation is easy; no corrosion issues. Sometimes may get higher rate and it can be design appropriately to increase selectivity towards a particular component.

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So, let us go ahead and try understanding what catalyst is. So, if you see in normal reactions say path of the reaction on one side you have reactants; on the other side you have products and this is energy it is very famous plot that we have learned long back. Let us try and understand it, again we will start from somewhere here let us were your reactants are, the energy level goes up and then comes down and this is where your product is and this is where you reactants are. Now, it needs to go up and then it comes down what is it. So, it goes through a transition a peak will be obtain at which you have an intermediate form, which has a very high energy it is not stable there.

So, it goes down and attains the stable value where your product is. So, what is this called as this is nothing but activation energy ΔE of the reaction. This particular energy level is very important this particular energy level, this can be either above this point or it can be below this point depending on whether reaction is exothermic or endothermic and the way I shown here this reaction is this reaction is endothermic. Why because this difference energy difference here to here is positive. So, I have this an net absorption of energy by the reactions, because of which it becomes endothermic if this point goes down further compare to the reactants then then it is exothermic.

This is nothing but it transition state where you have some intermediate form. So, every reaction either it is catalytic or non-catalytic it has this energy curve or energy diagram, where you have transition from reactants to products through an intermediate stage

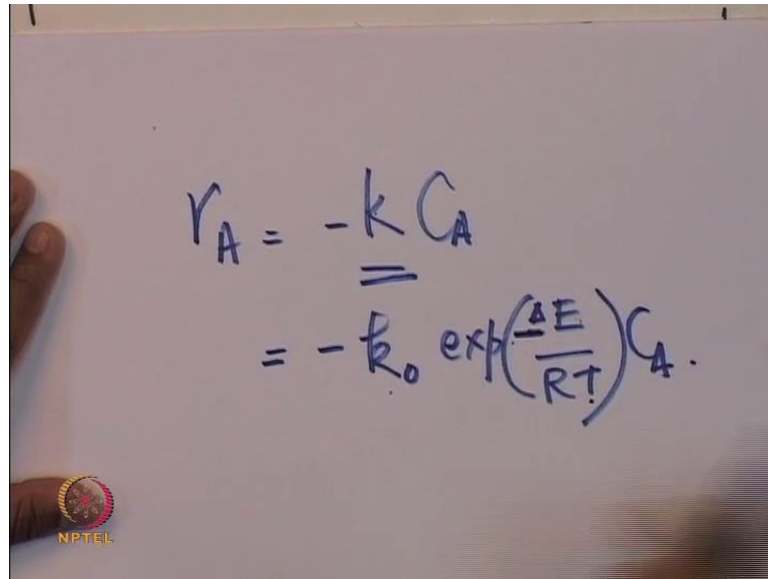
which is at high energy level. So, I need to provide this much energy; so that it goes here and then comes down, so that the reaction takes place. This energy level comes because of some molecules they have this energy that energy comes because of the temperature. Now, if I use catalyst what happens this particular graph or before that the rate of the reaction would depend on which factor it will depend on this activation energy; high the activation energy, lower is a rate as simple as that.

You learned something called as Arrhenius laws or Arrhenius equation, where we say that r is equal to $k c^a$ or $\text{minus } k c^a$. This k the rate constant depends on temperature. We will talk about it more later, but this rate constant depends on temperature is temperature increases; then the rate constant increases and high the activation energy higher is the sensitivity of this rate constant to the change in temperature. So, if you increase temperature the rate increases and for higher activation energy the rate would be lowers. So, now you tell me if I use the catalyst what happens to this particular graph; if I use catalyst this activation energy is goes down because the rate increases.

So, you have different graph for a catalytic reaction. So, what is catalyst doing catalysts changing a path? So, now the transition state here is different from a transition state here; the intermediate formed here that may be T_1 and this is different from T_1 . So, you have different intermediate which has less this compare to the earlier one and because of that the activation energy has reduced. So, the rate increases what will happen to this catalyst cannot change this. Always remember that most of the time just concentrates on this, but forget this comes out of thermodynamics; this comes out of thermodynamics and this is not decided by the catalyst, this means this energy level.

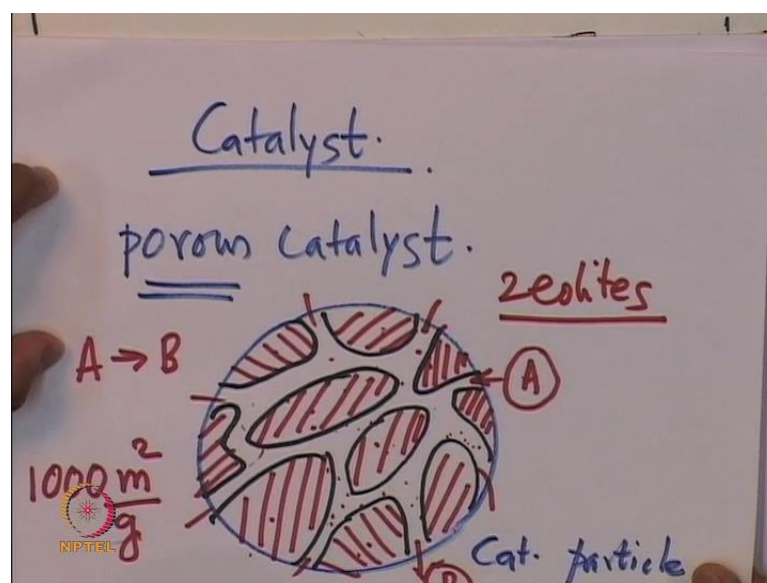
The heat of reaction catalyst cannot change the heat of reaction catalyst cannot make endothermic and exothermic reaction. So, that is the property of the reaction catalyst only changes the path it only changes the activation energy and it only changes the rate; it will not change the equilibrium always remember that. So, the rate of the reaction is change by the catalyst by virtue of reduction in activation energy. So, we have learned what catalyst is.

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So, in this we had considered the rate law which is nothing but r_A is equal to minus $k C_A$; the C_A can be C_A raised to and C_B whatever depending on the type of reaction and the stoichiometric. Now, this k is a rate constant. So, let us have a closer look at the rate constant. This is nothing but $k_0 \exp(-\Delta E/RT)$ or ΔE by RT into C_A . So, what is this k is equal to $k_0 \exp(-\Delta E/RT)$ this is Arrhenius equation. So, as you see from this equation this is minus. So, from this equation the rate is proportional to temperature let me see increase a temperature rate increases it appears an denominator, but this is negative and sensitivity of the rate constant depends on this factors that is ΔE , activation energy and this is what you already learned Arrhenius law.

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Now, let us back to the catalyst at I was telling you about the types of catalyst the different types of catalyst homogeneous and heterogeneous. Most of the times the homogeneous catalyst like whatever learned, so far like we can directly extend that analysis to homogeneous catalyst whereas, for heterogeneous catalyst the things may change. Now, what are the different types of heterogeneous catalyst? Heterogeneous catalyst again they come in different forms. So, one of them is a porous catalyst. Now, what is porous catalyst is very important concept we need to understand it at in detail.

Now, if I see a single particle of the catalyst it is a catalyst particle. Now the size or dimension of this particle can be the order of one millimeter or even less than that can be observed order of few microns is very small one millimeter. This small particle itself will have large surface area within it large surface area; how I have got the surface area. Now it is a porous catalyst. So, it will have pores inside now what are pores let me draw that. Now, this red ones are the solid the solid phase this is solid phase this is sold the phase and the space between these rate matrices; these are nothing but pores.

The typical pores size can be of the order of few angstroms say ten angstroms twenty angstroms or it can be nanometers one nanometer also. So, this is open this is open the reaction mixture. So, what happens to these reactant molecules say A is a reactant let goes inside through this pores. Then, so much surface available inside a catalyst particle and on this surface there are catalytic sites, which are responsible for catalysis on which

the reaction takes place and in the product will come out say B. You may have reaction taking place A going to B. So, A goes inside it diffuses through these pores there are catalytic sites present will talk more about the catalytic sites on which the reaction takes place.

So, I was talking about its transition state intermediate and all that will happen inside the catalyst or other in inside pores and products will be formed here. So, this has small tiny reactors on where in the reaction will take place and there product will come out. So, slowly I am we developing a picture about how the catalysis happens. What are the different steps I am not told you all the steps, but you can understand diffusion, reaction and product coming out. But more than that there are other steps as well will come to that now. So, what is happening here now you as I said the, so much surface area available; can you imagine the order of magnitude of surface area? This surface area can be as high as say one thousand meter square per gram.

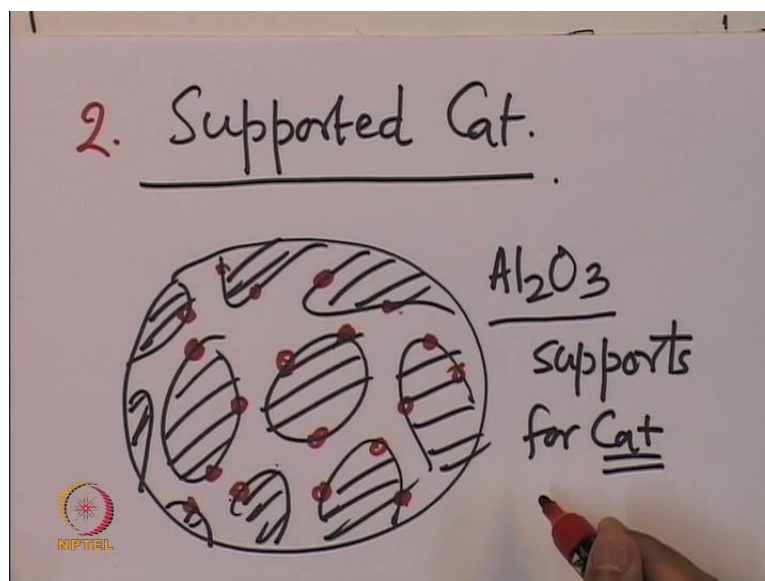
Can you imagine? One thousand meter square per grams gram is very small quantity try and get a field for this number trend get a fill for this number one gram is very small quantity. What is a surface area? One thousand meter square thirty by thirty meters it is like a gram such a high such a large surface area in such a small amount of the catalyst, it is all because of these pores. So, and not necessary that every time will get this much surface area depends on the material. But just give you some idea I wrote this number, it can be five hundred; it can be two hundred; it can be even ten also.

But a porous catalyst are the materials, which provide very large for surface area in the small amount in the small volume and that is a main advantage of using porous catalyst for catalysis. Now, where are the sites presents sites are inside? So, if you take example of zeolites which are alumina silicates the sites are inside. So, say acid catalysis by zeolites h plus are photons are present here of course, there are small amount of sites on the external surface as well, but these sites the number is much, much lower compare to what you have inside. So, the surface area is mainly inside external surface area is much smaller compare to inside is the catalyst particle size of the order of few millimeters.

So, if you go to nano level then that case external surface area also increases and it becomes comparable with the surface area inside a pores, would you have not talking about that surface area or that particle size. Most of the times, the catalyst particle size is

of the order of few millimeters or probably less than a millimeter, but not less than 0.1 or 0.01 millimeters. So, in that particular range it is the interior surface area, which is important. So, the best example of the porous catalysts is zeolites and which are used in many applications say catalytic cracking of hydrocarbons in refinery. So, this is one type of catalyst porous catalyst.

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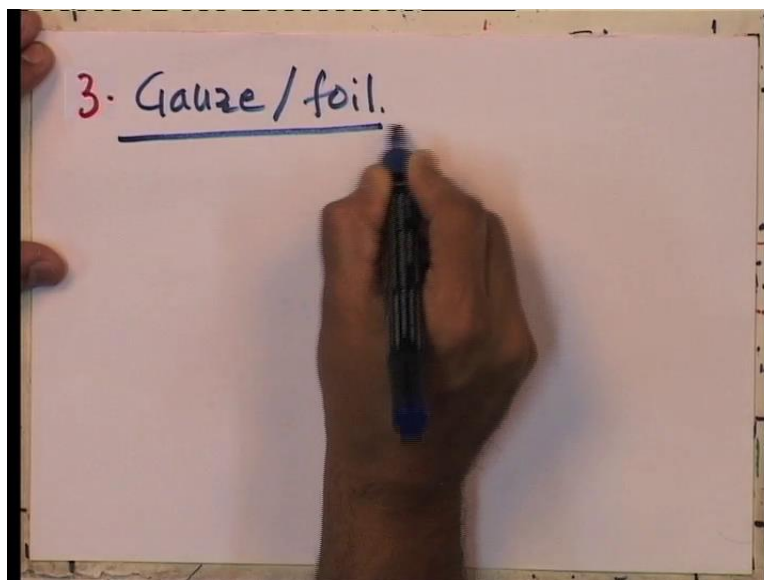
Then, there are other forms of catalyst there supported catalyst. Now what is supported catalyst, the same thing a porous material, which is non-catalytic in nature; otherwise same porous material, but that is not acting as a catalyst. Now the main catalytic species the component is different and not this material. Say for example, alumina or silica, activated carbon these are the materials which are porous in nature, but may not be the good catalyst for the reaction. But I still use these materials because they have the property to provide, so much surface area. Now, I use them as supports I use them as supports; supports for what supports for the catalyst.

Now for example, I have platinum being used as a catalyst. What I will do is, I will dispose I will put this platinum on the support at various locations. So, how is this catalyst different from the earlier one; the earlier one was the porous material itself access a catalyst the sites are part parcel of that material itself. Now, what I am doing here is I am putting catalyst on a support; that means, the material which is porous in

nature is support; otherwise non-catalytic on which I am putting this catalytic species. How do it is, something not of concern a present.

But then if I am able to put this catalytic species on the surface, say platinum, ruthenium, nickel whatever cobalt, iron, which are all good catalyst see the d block elements transition metals the good catalyst because of their variable balance see that we know. So, we are able to put them on the porous support and because of which I gets. So, much surface area and many items of the catalytic species are available for the reaction. So, these are supported catalyst and quite common in industry; many supported catalyst as I said like all this metals when supported on alumina, silica and carbon they are all supported catalyst.

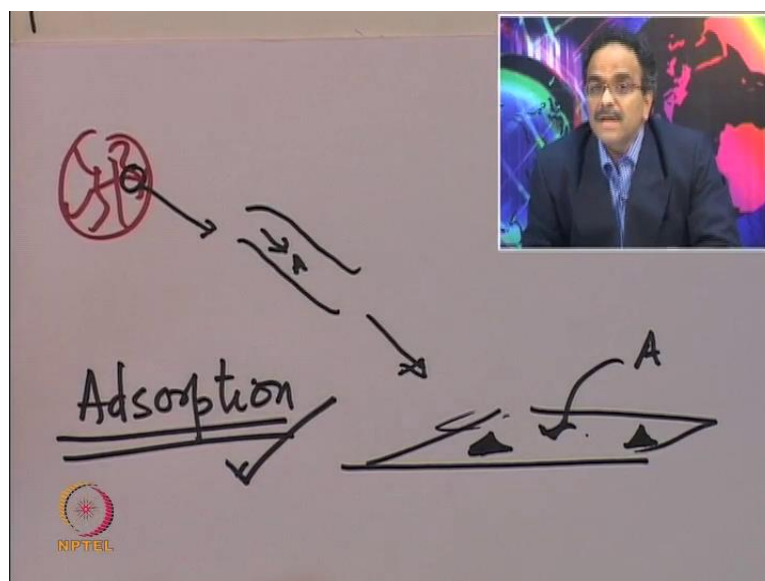
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Third type of catalyst gauze or foil; the reaction is, so fast that I do not do not need to expose the metal lines to that extend. See, even if I take a wire or gauze that is good enough to catalyze a reaction the catalysis. So, active that even the external the atoms present on the external surface of the catalyst; they are able to catalyze a reaction fast. So, I do not need to go for a porous material, these are called as monolith catalyst. So, example is of course, the oxidation of ammonia to nitric acid use the platinum gauze oxidation of ethanol to acetaldehyde they use silver gauze, why gauze and why not supported on something; because I do not need very large surface area.

Catalyst itself is very active only the atoms, which are present on the external, surface of the wire or gauze or good enough for catalysis. So, monoliths these are non-porous and non-supported. So, these are different forms of catalyst. So, how do you define catalysis or how do you compare different catalyst. How does a reaction take place on the catalyst surface when the reactant molecule approaches the catalyst; let us something we have to learn now. Now, let us look at the catalyst surface what I am going to do is I am going to just magnify that pore on molecular level.

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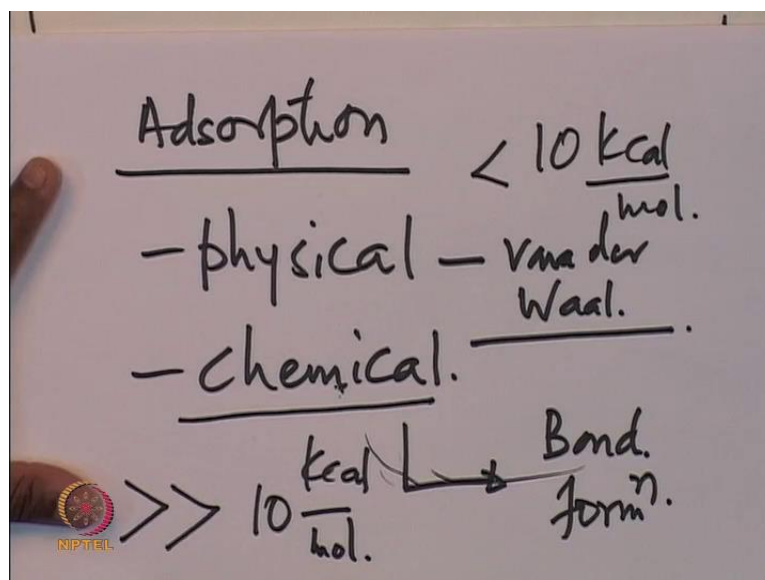
So, as I said like we have this pores inside a catalyst these are the pores inside a catalyst I am going to just magnify this. So, I will have pore through which the reactant is flowing. Of course, the products are also flowing; flowing in the sense through diffusion, there is no velocity inside. Because the concentration gradient they would be flow. Now this if you just look at this surface now I am going to magnify this further I am just going to open this. So, I will have a surface over which A is going to react because it will come in contact with a surface rather a will come in contact with surface.

On surface what you have on surface you have catalytic sites. What are these sites? Remember, I had shown those metals supported on the catalyst. So, typically if you have a supported catalyst then you will have sites present; if you have wire gauze or if you do not have supported catalyst the porous material itself acts as catalyst in that case which what are the sites. So, it is hypothesize that in such cases sites are nothing but those

places where there are defects or irregularities over which the activities very high compared to other atoms. So, these are the sites, so in general whether the catalysis is porous or non-porous; supported or non-supported.

On the surface, I have some places where the catalytic activity is more and that are where the reactions going to take place. So, A is going to get adsorbed it has to be adsorbed on the surface. So, that you have intermediate form under then the reaction takes place. So, adsorption is a very important phenomena as per as heterogeneous catalysis is concerned catalysis, which solid is concerned. We need to understand adsorption in detail in a normal reaction without a solid catalyst adsorption is not important whereas, for heterogeneous catalyst this is an important step in catalysis.

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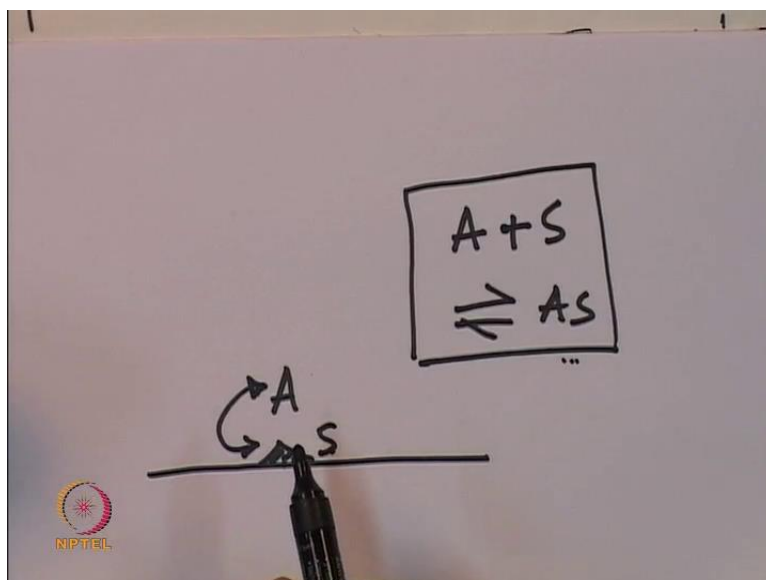


Now, we have learned what is adsorption; adsorption is a two types, it can be physical adsorption; it can be chemical adsorption. This is because of van der Waals forces and other long range forces and this is mainly because of strong interaction bond formations is more like a reaction whereas, this is a kind of affinity is more like condensation a gas molecule is going on solid changing its phase. So, whatever heat is released heat of condensation is a heat of physical adsorption whereas, in this case it is much more than that. It is more like a reaction is the bond formation.

So, heat evolved here is say less than ten kilo calorie per mole whereas, in this case it is much higher than ten kilo calorie; it can be even of the order of hundred kilo calories.

This is chemical adsorption and what we are looking at as far as catalysis, which solids is concerned is the chemical adsorption, where the substrate on the reactant will form a bond with the catalyst we form a bond with catalyst. So, these are two types adsorption physical and chemical.

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So, what is going to happen on the catalyst surface is for example, I have a catalytic site and is a reactant which is coming to the surface. So, it is going to get adsorbed on it; it is going to get adsorbed on it. So, it is going to form a complex. So, this is S, it is going to form a complex. So, there is reaction can be represented or the step can be represented at A plus S gives AS adsorption. There is this interaction through the bond formation of course, it may be unstable and may break with no time. So, it is possible that it is just transition state or intermediate state and further reaction will take place to form a product which is say B or C whatever.