Heterogeneous Catalysis and Catalytic Processes

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Lecture - 01

This course is on heterogeneous catalysis and catalytic process, the catalytic process which is one of the most important reactor applications for transformation of reactants into products. The basic of this course will involve that, different type of catalysts used in process industries, whether it is a pharmaceutical industry or a hydrocarbon, petroleum, refinery industry and their selection some design and some reactor design applications.

And, then finally, the some catalytic process which are commercially used in industry and then some environmental aspects of this. So, today's lecture will mainly talk on introduction on basic concepts of green catalysis. Because now, every transformation process of reactant into product is related to the environment sustainable development of environment that is ecological and but where the environmental concerns to deal that deals and that concept is known as green chemistry.

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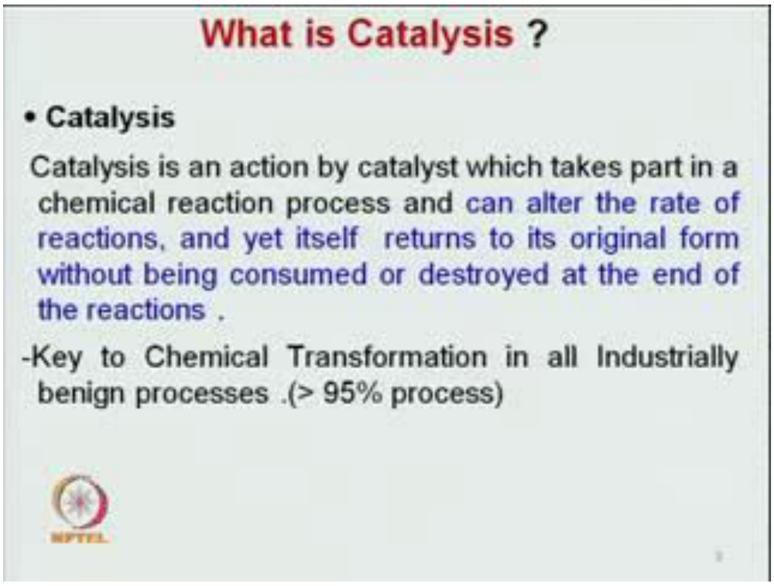

What is Catalysis ?

- **Catalysis**

Catalysis is an action by catalyst which takes part in a chemical reaction process and can alter the rate of reactions, and yet itself returns to its original form without being consumed or destroyed at the end of the reactions .

-Key to Chemical Transformation in all Industrially benign processes .(> 95% process)

What is catalysis? That is the first question in mind that how a catalyst works and the basic principle is; so the definition there are numerous definition if you look at the literature lot of definitions are available on catalysis. But the basic definition; if you look at the catalysis is an action by a catalyst, which takes part in a chemical reaction process and can alter the rate of reaction. And yet, itself returns to its original form without being consumed or destroyed at the end of reactions so, this one definition of catalysis. So, catalysis is basically the application of catalysts for transformation of reactants into the products.

So, catalysis is a process and catalyst is a substance which reacts during the process, but at the end it immerse as an un-reacted raw material. So, that does not mean that catalyst does not take part in the action it does take and definitely due to the course of time there are several reactions and secondary reaction which take place on the surface of the catalyst and because of that its activity or life or the property also detoriates.

But the definition wise, if you look at it is a substance which does not take part in the reaction. So, basically the purpose of using the catalyst in the process is to speed-up the reaction; because the thermodynamics is one, where you look at the equilibrium kinetics and the rate of reaction can be increased in the presence of catalyst, but the final or equilibrium conversion; what you call the maximum conversion that cannot be changed. So, basically when you have a catalyst in the process you are trying to (((Refer Time:03:18)) the rate of reaction in one way what we say it is the energy or the activation energy which is required to activate the process or to make a; the complex during the reaction that is reduced.

We will talk on that; so, presently if you look at it is a key to chemical transformation in all industriallibiline processes. So, whether you look at any fertilizer industry, refinery, petrochemical, pharmaceutical the catalysts are beings used right and more than 95 percent or I will say 90 to 95 percent process are generally being run in the presence of catalyst.

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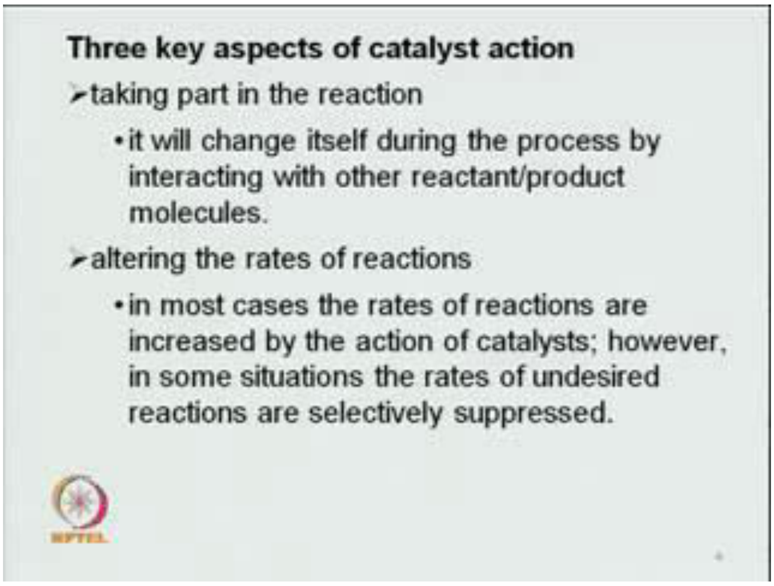

Three key aspects of catalyst action

- taking part in the reaction
  - it will change itself during the process by interacting with other reactant/product molecules.
- altering the rates of reactions
  - in most cases the rates of reactions are increased by the action of catalysts; however, in some situations the rates of undesired reactions are selectively suppressed.

The important aspects in catalytic process, if you look at the as I said before also that, it will change itself during the process by interacting with other reactant product molecule. So, this thing I will discuss in detail later, but basically it is something on a surface of a catalyst the reactant molecule; molecule come to the surface of the solid and then it transform into the secondary reaction, what you call mechanism of the reaction. So, that we will discuss in detail later, but basically, when we see here that, the reactant is adsorb on the surface of the solid and then, transform it to a some intermediate and that intermediate transforms into the product.

So, there is, if you look at net change in the Gibbs ((Refer Time: 04:45)) free energy that is from thermodynamic that does not change; because it is nothing but based on reactant and the product side. So, this is the first thing here, that this will change itself during the process by interacting with other reactant or product or molecule and it can alter the rate of reaction, right.

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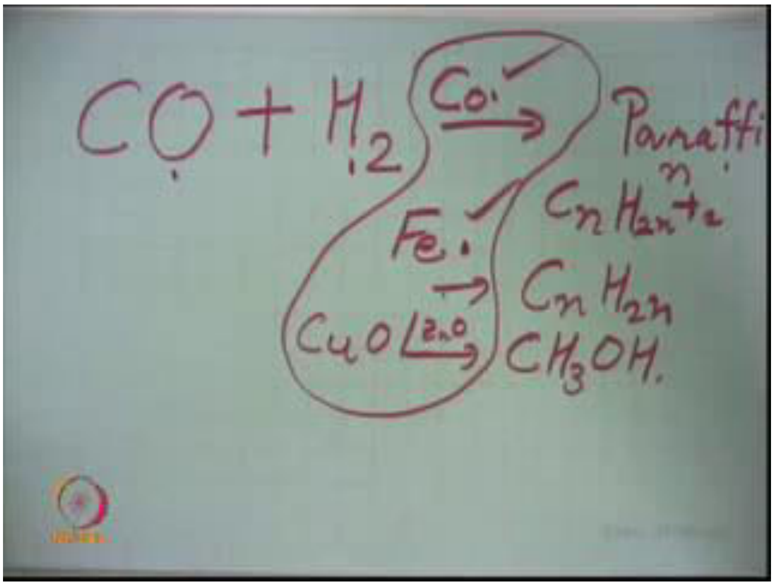

So, that is another important aspect suppose if I just say that a reaction you have the carbon monoxide, if you just look at this CO plus hydrogen on a metal substance it can give you a paraffin. Suppose, if I have a metal something like so this is a paraffin hydrocarbon which is a state change hydrocarbon which will have molecular formula of C n H 2 n plus 2 something, like this so, C n H 2 n plus 2 and if the metal is something like your cobalt.

So, a metal cobalt can transform this, these two reactants carbon monoxide and a hydrogen to a paraffin which is your diesel range of hydrocarbon. If you have something on iron as a catalyst or metal then this can give you oliphinn C n H 2 n and which can be isonised or hydro-isonised and you can get from this the gasoline or petrol range of hydrocarbon. If you have something like a different metal which is copper oxide then, it can give you some time in zinc oxide also; then, you can get alcohols from this like methanol.

So, you can say very clearly here, that by same reactant carbon monoxide and hydrogen but with different metals; the product distribution or products are different and this is the key here the selection of a metal for a given reaction. So, it means the same reactant can be transformed to different type of products depending upon the catalyst; so, this is the key here in the reactor application or process application for a catalytic reaction. So, one can control these reactions, in order to get a desired product. So, this means that, in most of the cases if you look at the rate of reactions are increased by the catalysts however, in some situations the rate of undesired reactions or selectivity suppressed.

So, this is what I was talking in this reaction that we know how a carbon monoxide and hydrogen it can give you alcohol, it can give you alphins, paraffin, napkins and a series of hydrocarbon. But what is your requirement; basically, according to that you have to select a definite combination of metal and support and of course, not optimization of the process condition. So, this becomes a key in the selection of a metal, selection of a support and then, application of these metal supports for a given reaction.

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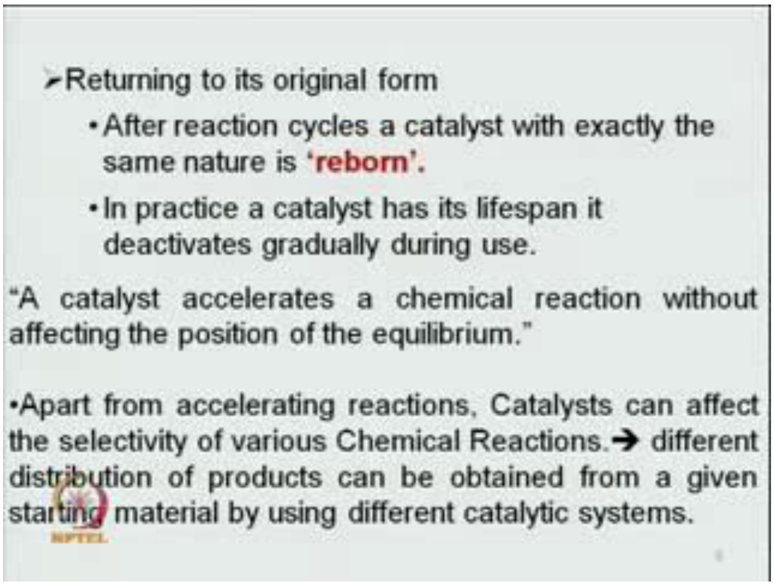

- Returning to its original form
  - After reaction cycles a catalyst with exactly the same nature is **'reborn'**.
  - In practice a catalyst has its lifespan it deactivates gradually during use.

"A catalyst accelerates a chemical reaction without affecting the position of the equilibrium."

•Apart from accelerating reactions, Catalysts can affect the selectivity of various Chemical Reactions.→ different distribution of products can be obtained from a given starting material by using different catalytic systems.

So, again we all seeing that catalysts comes to its original form, which is a general definition; but due to the several secondary reactions on the metal surface the activity of catalyst may change during the course of time. So, that is what you call the deactivation or decrease in activity of the catalyst which we will see later. After reaction cycles, a catalyst with exactly same nature is reborn; this is what the definition of catalyst we said that it does not take part in the reaction, right. In practice the catalyst has its life span and deactivates gradually during use this is what I was talking here.

So, in general if you look at the definition is that, the catalyst accelerates a chemical reaction without affecting the position of the equilibrium, right. But if you look at apart from accelerating reaction catalyst can affect the selectivity of various chemical reactions, right. So, that is what the just like the sin gas application; I told the different product distribution or the different distribution of products can be obtained from a given starting material by using different catalytic system.

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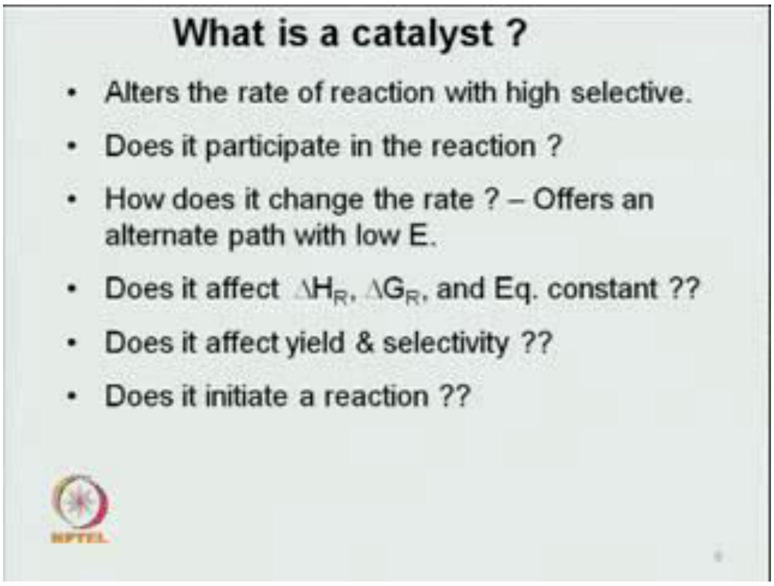

What is a catalyst ?

- Alters the rate of reaction with high selective.
- Does it participate in the reaction ?
- How does it change the rate ? – Offers an alternate path with low E.
- Does it affect ΔH_R, ΔG_R, and Eq. constant ??
- Does it affect yield & selectivity ??
- Does it initiate a reaction ??

So, now what is catalyst? We have seen that it alters the rate of reaction with high selectivity. So, selectivity the definition of selectivity basically, is a nothing but the moles of some desired product divide by moles of undesired product; there can be different definitions of selectivity also. This can be defined the moles of desired product per of mole of the reactant which is reacted, right. Because the suppose gas is reacting and you are getting paraffin and suppose paraffin is the desired product. So, moles of paraffin produced or diesel produced per mole of sin gas reacted or it can be moles of diesel produced divide by moles of all the other hydrocarbon which are produced.

So, there can be different definitions of selectivity and depending upon the requirement or optimization of process condition; we look at that definition and we use it in the process right, during the design. So, basically the catalyst alters the rate of reaction; so, there several other questions when you look at this point then, does it participate in the reaction. So, as I said that yes, the catalyst participate in the reaction because it makes the intermediate and the root of when you have a non-catalytic reaction then, the mechanism may be different. And, when you have a catalyst then, the mechanism may be a different right.

How does it change the rate? Another question; so, we said that it offers an alternate path with low activation energy so E refers here the activation energy I will talk on that. So, basically activation energy is minimum amount of energy required right to activate a reaction. Because when you see a reaction; the reactant products reach to a level of intermediate state right which is called a transition state.

So, when you have a non-catalytic reaction the reaction can happen right just like if you look at that environment has lot of nitrogen and oxygen right; so and luckily it does not react, right. Because the temperature conditions and catalysts is not there right so there may be a some N O formation because of that but it is not in access; otherwise we will have oxygen deficiency.

But if you look at the Ostwald process where you look the nitrogen or oxygen reaction to form the nitric oxide for HNO 3 manufacture; you need a catalyst right. And, there we got the more conversion of nitrogen in presence of oxygen to form more and more nitric oxide and then, reacted with water and give you nitric acid. So, that is again key of the Ostwald process for HNO 3 formation, right so use some catalyst there.

So, I mean to say here is that, the catalyst for a reaction is required to reduce this activation energy. Because when the activation energy is reduced then, at a lower temperature the reaction can be processed that is one thing. Or, if you have same temperature the rate towards that process can be increased. So, this is the key in a catalytic process that it reduces the activation energy for a given reaction.

So, again, does it affect the heat of reaction delta H R refers to heat of reaction delta G R effects the Gibbs free energy right and equilibrium constant. So, these things are generally defined from thermodynamic; so as I said before catalyst can never change the equilibrium right the catalyst can change the rate or approach towards reaching the equilibrium. So, your reaction can be faster.

But your maximum conversion which is governed from the thermodynamics that cannot be changed in presence of catalyst, right. So, basically you know the one they chemical reaction happens it reduces the free energy should be decreased right, it decrease the free energy. And, as soon as the reaction processes the negativity of Gibbs free energy reduces; so finally, it will come to 0. So, when the Gibbs free energy is 0 delta G is 0 no chemical reaction; so, that is what you call system is at equilibrium. So, when you have a catalyst in the process the rate towards that is increased that is one thing and delta G which we are calling Gibbs free energy is related to your delta H minus T delta S.

So, actually this is thermodynamics when you look at a delta G for a given chemical reaction this is known as Gibbs free energy or basically, this is the useful energy is equal to delta H minus T delta S where this term is entropy delta S is known as entropy. So, this is basically the total energy is this delta H R heat of reaction and this is the amount which had been transferred to the surrounding. So, net total energy is this minus this and that your useful energy right. And, for a chemical reaction to happen delta G should be negative.

So, less than 0 then only their chemical reaction will take place and when delta G approaches to 0 then it means speed of the process is decreasing. So, how much you are away from the equilibrium? It means, you are increasing the rate right. So, that is what the key in the reactor design; so, we used in our different concept for reactor design and also like say membrane reactor or separate the product. So, membrane desolation process; so, every process where you are removing the products during the course of reaction so, you are disturbing the equilibrium right in a process.

So, that is what the rate towards that will increase when you have the disturbed the division from the equilibrium. So, catalyst cannot affect these 3 points but the equilibrium constant cannot be changed. So, equilibrium constant is a function of temperature right; so, endothermic, exothermic different kind of chemical reaction. So, according to that your value will change. But otherwise, the catalyst cannot change the equilibrium constant of a given reaction; so, again, does it affect yield and selectivity? So, catalyst can affect, yes. As, I said that different type of metals can be selected; so, the rate towards a given process can be increased, right.

So, yield and selectivity can be affected in presence of catalyst; does it initiate a reaction; so, catalyst can initiate a reaction. So, sometime the reaction cannot happen even at the but when you have catalyst in the system it in a initiate the reaction; so that, that is the key of a catalyst. Sometime, the reaction may not happen in the absence of catalyst; but when you have a metal on the; that reactor proceeds a job and then, it can transform into a product.

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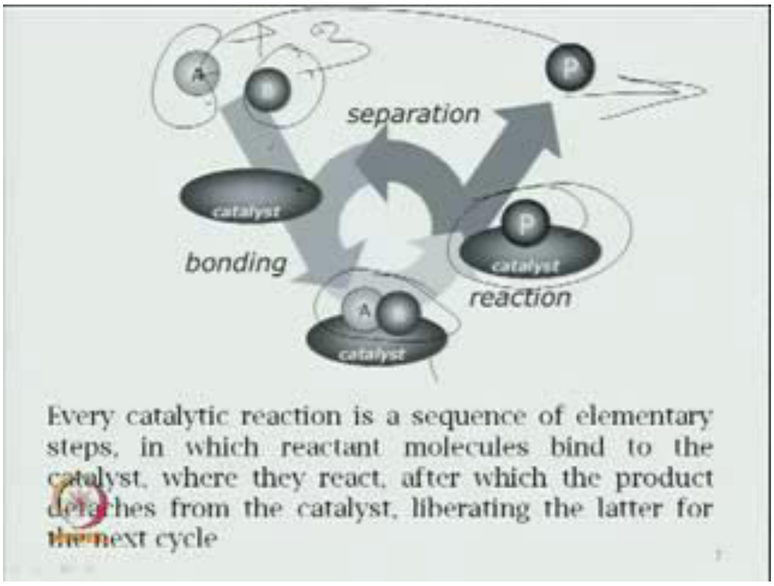

Every catalytic reaction is a sequence of elementary steps, in which reactant molecules bind to the catalyst, where they react, after which the product detaches from the catalyst, liberating the latter for the next cycle

So, if you look at what catalyst does? So, that is what we are talking here if you look at this; so A and B these two reactants. And, they are adsorb on a surface of a catalyst so this is the catalyst; so, something is happening on the surface so it is a kind of bonding of A or B or this can be on the gas, this can be on the gas or both can be on the surface of the solid. Then, they in this case, here A and B both are adsorbed and they are transforming into some complex A B star something like that.

And, that complex again on the surface of the catalyst it can diffuse or it can transform into a product like p so, this is a adsorb p on a surface of a catalyst, right. So, detailed of this mechanism we will discuss; so, these are the keys of the reactor design also. Because how big is your reactor or how small is your reactor will depend on these selections of this metal these and then operations of this, right.

Because the basic idea is that if you have reaction is highly activated right or rate of reaction is very fast; so, size of the reactor can be reduced. So, new concept of this now a days atom efficiency or whatever E factor we call that are the key in terms of the catalyst design and green catalysis concepts also. So, you have A P and you have may have a un-reacted reacted the product.

So, you get it separated or catalyst separation from the product and then finally, you have a product here. So, this is what the overall action of a catalyst. So, if you look at here in every catalytic reaction, this is a sequence of elementary step. So, because here I expect that all of you have the some knowledge of the chemical reaction engineering; so, you know what is the elementary type of reaction and non-elementary.

So, basically the elementary reaction we say that directly, the reaction is in terms of the stoichiometry co-efficient. Then, you talk non-elementary, the rate may not depend on the stoichiometry of the reactants right A goes to B; what is here? It is overall reaction A plus B gives you P right. But this is not the case here, because A plus B gives you something like A B and then, A B transforms to into P star or A B star transform to P star and the P star goes to the product.

So, basically; so, this is the meaning that every catalytic reaction is a sequence of elementary steps every step is now elementary but overall step are non-elementary if you look at overall reaction that is non-elementary type right. So, in which a reactant molecule bind to the catalyst where they react, after which the product detests from the catalyst and liberating the latter for the next cycle. So, this cycle continues so, catalysts are free always or catalyst is free from the reaction

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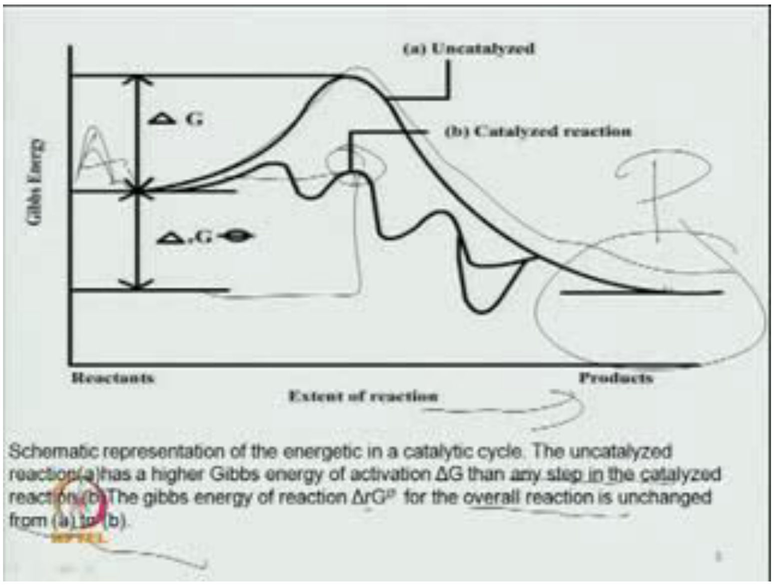

Schematic representation of the energetic in a catalytic cycle. The uncatalyzed reaction(a) has a higher Gibbs energy of activation ΔG than any step in the catalyzed reaction(b). The gibbs energy of reaction $\Delta rG^\ominus$ for the overall reaction is unchanged from (a) to (b).

The same picture, where I was talking about the catalyst lowers the activation energy right. So, sometime that reaction can happen in the absence catalysts; so, this the Gibbs free energy. What is the delta G for a reaction and this is the extent of reaction or some time you call reaction coordinate also, right. So, if you look at here that this is the actual path then there is no catalyst in the system right and when you have a catalyst in the system there are adsorption right, some surface reaction, some desorption. So, reaction is exothermic if it is adsorption basically the something adsorbing on the surface of the solid so, reaction is exothermic that adsorption is generally considered as exothermic reaction and when you have a desorption it is the endothermic reaction. So, these are the peach which are talking in terms of adsorption and desorption so, basically these transition state or some kind of start which has found here, right. So, the catalyst as lower this activation energy for this reaction basically which is something like A plus B which we are talking here a formation of this.

So, this can happen only in the presence of catalyst when you have a; you have no catalyst in the system then it may happen that you may need a large temperature right or some severe reaction conditions. So, the un-catalyzed reactions, that has higher Gibbs free energy of activation delta G and then, n is step in the synthesize catalatia. So, this is the first thing right the Gibbs free energy reaction delta G for the overall reaction is unchanged from A to B because if product is here, right; reactant is here.

So, your net change which you call enthalpy of product minus enthalpy of reactant, that is same. This is just like a point property. So, the total Gibbs free energy for the reaction will not change but for activation energy or free energy which is here compared to catalytic reaction; so, this is barrier is now reduced. So, the reaction can happen at lower temperature or if you have same temperature, the rate of reaction will be higher.

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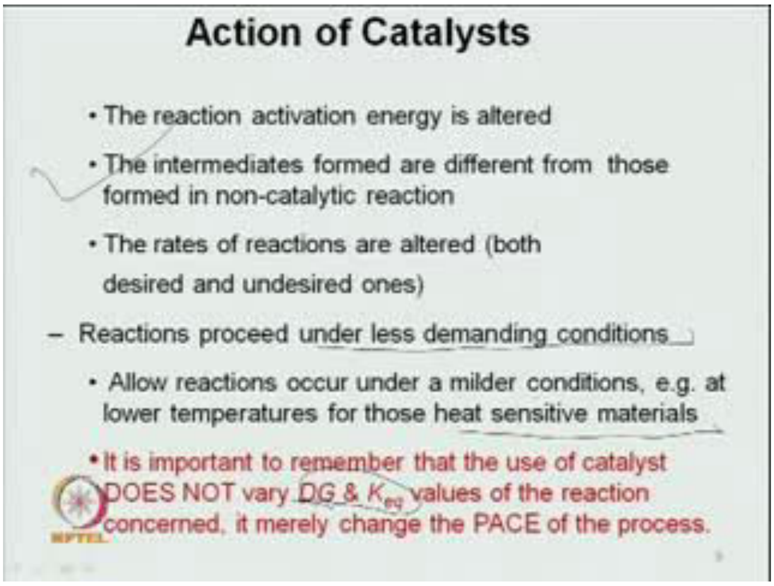

Action of Catalysts

- The reaction activation energy is altered
- The intermediates formed are different from those formed in non-catalytic reaction
- The rates of reactions are altered (both desired and undesired ones)

– Reactions proceed under less demanding conditions

- Allow reactions occur under a milder conditions, e.g. at lower temperatures for those heat sensitive materials
- It is important to remember that the use of catalyst DOES NOT vary DG & K_{eq} values of the reaction concerned, it merely change the PACE of the process.

So, if you look at action of a catalyst now, how does catalyst act; so, reaction activation energy altered that is what the lowered basically. So, when you have a catalyst in the system the activation energy for the reaction is reduced right; the intermediates formed are different from those found in the non-catalytic reaction. Because when you have no catalyst in the system the reaction is a kind of free radical reaction. So, that will be the gas space; but when you have the catalyst in the system the reaction is on the adsorb surface so, it is a kind of adsorption and surface reaction which we will see later in the mechanism.

But the basically, the mechanism is changed when you have a catalyst in the system. So, this is what the intermediates will formed will be of different type though that is what the example which we have given for sin gas or GTL now a day's called. So, sin gas conversion to liquid fuel when you see you can get the series of the product right a simple component if I just say from methane conversion and methane can go to your wax also C 60 C 80 range of hydro carbon very high range right. And, if you have a selected catalyst you can just get a narrow down product distributions something like C 5 to C 10 which is your gasoline or C 12 to C 28 diesel range, right.

So, paraffin can be there a straight chain hydrocarbon right napkins can be there cyclo paraffins aromatics can be there, alcohols can be there. So, series of the product can be obtained when you have a catalyst in the system and that is what you are talking of a selectivity. Because you have you can get series of products but how to narrow down these product to have a valuable product for the reaction or high selectivity for a valuable product that is the key in the catalysis selection.

So, the reaction when your catalyst in the system the reaction can happen under less demanding conditions like temperature, pressure. So, part of the things are governed from your thermodynamics but the rate towards that can be governed in the presence of a catalyst or different type of catalyst will have different kind of rate but equilibrium will remain same just note down that point.

And, the catalyst allow reaction to occur under milder condition is at lower temperature for those of heat sensitive materials. So, if we have something where the component which can decompose at higher temperature where there the reactions need a certain kind of specific action. So, there the catalyst can play a role right; most of the time when you look at the enzyme type reaction where the; they are very much sensitive to p H very much sensitive to concentration of acid or temperature. Then, a suitable catalyst can help to happen the reaction under those ideal condition so, those the selection of a catalyst will be the crucial and this can happen in the presence of catalyst.

And, it is important to remember that, the use of catalyst does not change delta G and equilibrium constant that I have said and that is the catalyst can only speed up the reaction but cannot change the reaction right. So, basically the thermodynamics plays a very crucial role that whether a chemical reaction when you are looking A plus B converting into C plus D the first important thing is that, read the thermodynamics, understand the thermodynamics. Calculate the Gibbs free energy for that and delta G has to be negative; then only, the reaction is possible.

So, you have to look at the delta G which is from your whatever your requisition from delta G minus r t l n of k; k is equilibrium constant; calculate the equilibrium constant which is function of temperature running upon the endothermic or exothermic reaction and then, calculate delta G at different temperatures right. So, when you have to select that temperature minimum temperature required for a reaction so, wherever your Gibbs free energy comes, starts negative then, your reaction will persuade that temperature.

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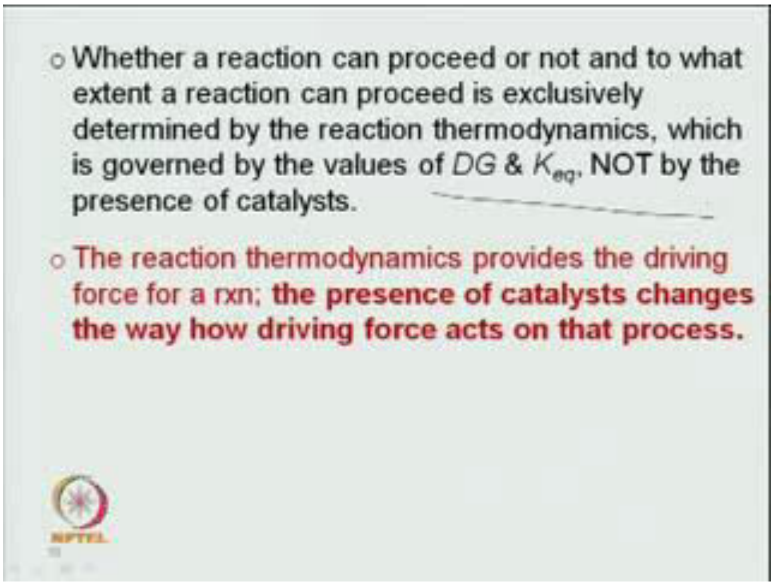

- Whether a reaction can proceed or not and to what extent a reaction can proceed is exclusively determined by the reaction thermodynamics, which is governed by the values of DG & K_{eq}, NOT by the presence of catalysts.
- The reaction thermodynamics provides the driving force for a rxn; **the presence of catalysts changes the way how driving force acts on that process.**

So, that is the first thing; so, the catalyst cannot do anything in that regard, right. So, reaction thermodynamics provides a driving force for a reaction, the presence of catalyst change the way how driving force acts on that process. So, I am just speaking the reverse repeatedly because the thermodynamic is the first part for a chemical reaction to happen right you have to just look at that that whether a reaction is possible from thermodynamics or not.

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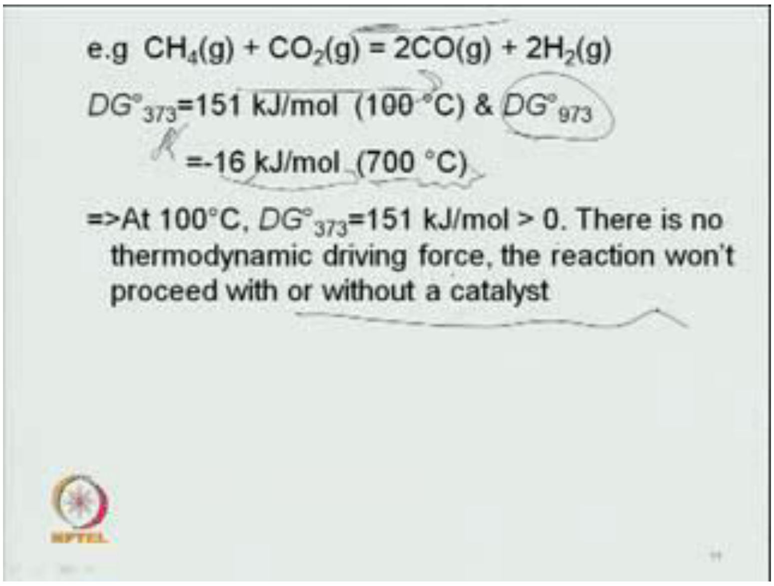

e.g $CH_4(g) + CO_2(g) = 2CO(g) + 2H_2(g)$

$DG°_{373}$=151 kJ/mol (100 °C) & $DG°_{973}$ =-16 kJ/mol (700 °C)

=>At 100°C, $DG°_{373}$=151 kJ/mol > 0. There is no thermodynamic driving force, the reaction won't proceed with or without a catalyst

Just as an example, I have shown you here the dry reforming ((Refer Time:24:51) is forming basically this reaction has lot of have importance now a days; because these two green house gas methane and carbon dioxide they are available and cause the green house effect. So, methane and carbon dioxide can be converted to carbon monoxide and hydrogen; so, this is very important process we got this gives the oxy-alcohols this gives the sin gas in the ratio of 1:1 and that can have the application in the production of either di-methyl ether or alcohols right or this can be used as a power generation system also.

So, if you look at the, this step; 373 degree Kelvin, this is the temperature at Kelvin the Gibbs free energy 151 kilo joules per mole, right so, 100 degree centigrade means the reaction is not possible, right. If you look at Gibbs free energy at 973 Kelvin minus 16 kilo joule right so, it means that 700 degree centigrade this reaction is possible because the delta G is negative. So, when delta G is negative the reaction is possible; so, if you inverse the temperature this will still go towards the negative side right. So, and then it will come as the reaction proceeds this is delta G value will decrease and finally it will come to zero level so it means the reaction is at equilibrium now.

So, that time the does not mean that equilibrium does not mean that reaction is stopped; there is a reaction but the rate of forward reaction is equal rate of backward reaction. So, the reactants are converting into products, products are converting into reactant at the same rate so, effectively there is no additional conversion, right. So, at 100 degree centigrade the delta G value which is greater than 0 so, there is no thermodynamic driving force the reaction one proceed with or without a catalyst so this is very important here, to understand.

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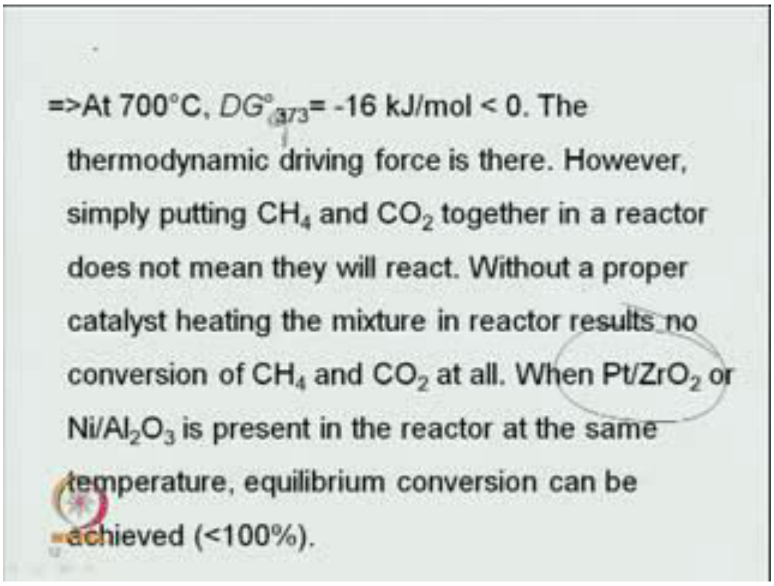

=>At 700°C, DG°_{373}= -16 kJ/mol < 0. The thermodynamic driving force is there. However, simply putting CH_4 and CO_2 together in a reactor does not mean they will react. Without a proper catalyst heating the mixture in reactor results no conversion of CH_4 and CO_2 at all. When Pt/ZrO_2 or Ni/Al_2O_3 is present in the reactor at the same temperature, equilibrium conversion can be achieved (<100%).

Same thing here, at still 700 degree or 973 Kelvin thus, a 973 so, 973 Kelvin delta G is minus 16 kilo joule per mole. So, thermodynamic driving force is there. However, simply putting methane and the carbon dioxide together in a reactor does not mean they will react this is very important. Without a proper catalyst heating, the mixture in the reactor results no conversion of methane and carbon dioxide, right. So, a catalyst is results so in this case of platinum, zirconia or nickel alumina these catalysts can happen the reaction at faster rate, right. So, these are the key for the reaction of drive reforming of methane right that is known as drive reforming of methane or methane carbon dioxide will form.

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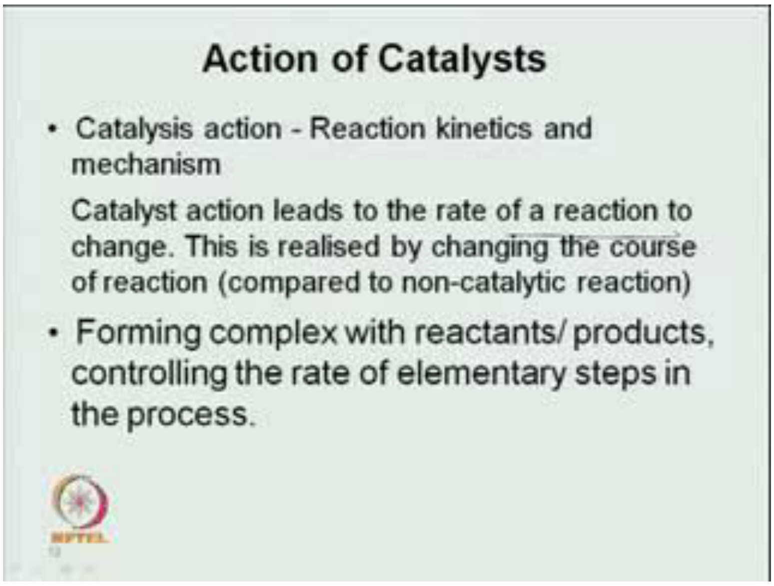

Action of Catalysts

- Catalysis action - Reaction kinetics and mechanism

  Catalyst action leads to the rate of a reaction to change. This is realised by changing the course of reaction (compared to non-catalytic reaction)
- Forming complex with reactants/ products, controlling the rate of elementary steps in the process.

So, action of catalyst what we have read so far is that, catalytic action reaction kinetics and mechanism very important right. So, what is the kinetics of a reaction that you call overall kinetics; but how that overall kinetics appear in terms of rate determining step for a reactor design that becomes important. So, we need to understand how methane is absorbing on the surface, how carbon dioxide absorbing on the surface of a catalyst and then, how these two absorbs ((Refer Time: 27:49)) reacts and transform into a sin gas right and then how the product dissolves. So, that that will be the key in terms of inversing the rate towards equilibrium or increasing the rate and that will help in reactor design. So, catalytic action leads to a rate of reaction to change right; this is realized by changing the course of reaction compared to the non-catalytic reaction.

So a complex forms, right. So, forming complex with reactants or products controlling the rate of elementary step in the process so a particular step of reaction controls the rate not all the steps will be rate controlling. So, generally it is something like a rate driving or whatever the; this closest system of that rate will be the controlling step. So, we have to find out the kinetics for each rate of reaction for each term their activation energy and then rate constant, the lowest or slowest step of that reaction will be called either rate governing. So, it means these are kind of resistance which are offered during the course of reaction and we have to look at; when we design the reaction we just focus on our slowest system because that is controlling the total efficiency of the process right.

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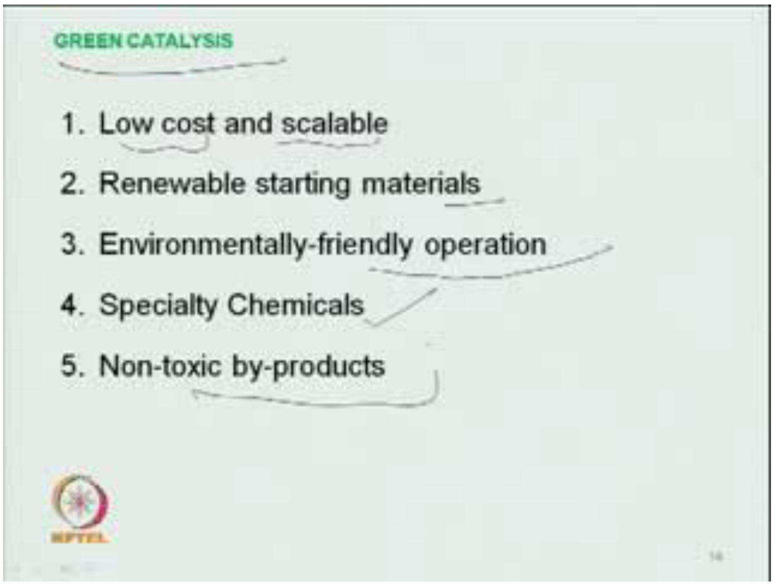

GREEN CATALYSIS

1. Low cost and scalable
2. Renewable starting materials
3. Environmentally-friendly operation
4. Specialty Chemicals
5. Non-toxic by-products

The concept of green catalysis now a days is very common; so, everybody is talking in terms of green technology, green chemistry and green environment, sustainable environment. The meaning of this, is that; the whatever the technology which is being developed or whatever the old technology that should be rewind in such a way that the waste production should be minimum right and the environment should not be affected.

So, there in all if you look at the catalyst plays a very important role and that is why the catalyst is now a days a billion dollar business, right. The new catalyst novel; catalyst in terms of selectivity, in terms of their efficiency for the process and in terms of the waste minimization in novelty is to be developed or lot of R and D scope is available in terms of catalyst development or new process development using the catalyst or using the concept of green catalysis, right.

So, basically the meaning of green catalysis is that the technology which we are developing that should be of low cost right, cost should be low and can be easily scalable, right. Because sometimes, the; when you look at the large scale plant the technology may not be successful right, in a small scale or lab scale the data may be generated their results may be excellent but when, you try to scale-up the process it fails. So, that is the meaning is that, the technology or catalyst which is developed that should be scalable.

Renewable starting material; so, new concept is again, that the source because the like just like as an example crude oil sources are limited right the life of crude oil is expected to be just 60 years. So, now the new the concept is that use some kind of renewable crude fuels or renewable energy like biomass L G biomass, solar, wind; so, these kind of ((Refer Time: 30:54)) nuclear so, these kind of energy sources may be useful to fulfill the demand of the future.

So, new the starting materials should be used environment friendly operation; so, the technology which is to be developed being developed that should not affect the environment. So, the carbon dioxide say that is what the carbon taxing or the carbon dioxide causing the green house global warming potential; so, the amount of carbon dioxide in the environment should be reduced. Similarly, the toxic gases which are produced during the process should be at its minimum level.

So, environmental protection at or the euro norms these should satisfied when the new technology or the new catalyst is being developed or is to be used in a process. So, this is a eco friendly approach for a given process. Specialty chemicals the catalysts widely used for the fine chemical the specialty chemicals right; so, there the waste production is very because the; when you look at the specialty chemicals especially the pharmaceutical industry the purity designed in the 99.99 percent. So, in that case when you have a good catalyst if you design a good catalysts like then, you can minimize the waste right. Because otherwise, the production each efficiency, what I talking is that not the waste should be minimum.

So, that can happen only when your process is optimized, well optimized or the catalyst which is developed or which is used for the process is highly effective, right. So, that is again, the for a special specialty chemicals and pharmaceutical industry the application of these; this is very important and green catalysis concept is being used now a days. Non-toxic by-products; so, by-products should be reused in the process or by-products should be reused for some other process so that is again the process concept of the green catalysis.

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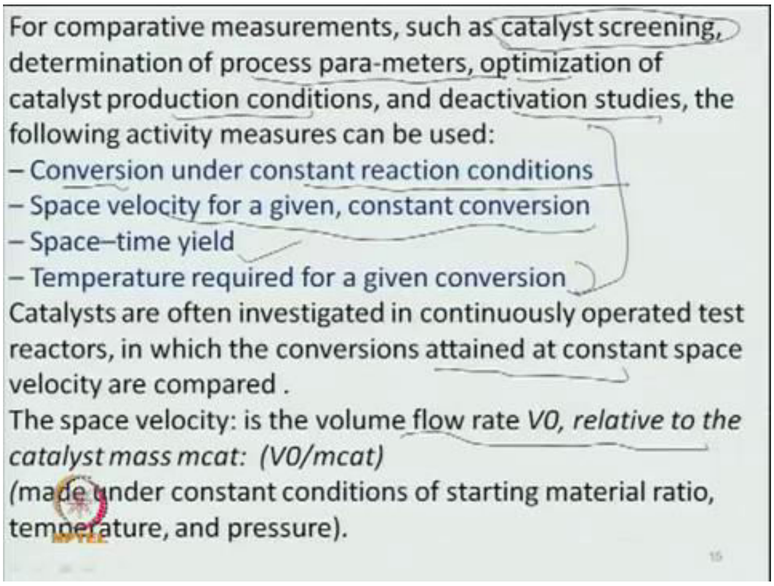

For comparative measurements, such as catalyst screening, determination of process para-meters, optimization of catalyst production conditions, and deactivation studies, the following activity measures can be used:

- Conversion under constant reaction conditions
- Space velocity for a given, constant conversion
- Space–time yield
- Temperature required for a given conversion

Catalysts are often investigated in continuously operated test reactors, in which the conversions attained at constant space velocity are compared .

The space velocity: is the volume flow rate *V0, relative to the catalyst mass mcat: (V0/mcat)*

(made under constant conditions of starting material ratio, temperature, and pressure).

You just look at the comparative measurements, right; when we look at the selection of a catalyst that is the first thing which is the bus catalyst so, catalyst screening, right. Then, determination of the process parameters like when you optimize the process you need to learn the kinetics and then, you have to find out the optimum process variables for the catalyst process or catalyst products in condition. And, then, simultaneously stability of the catalyst, because for how much time that catalyst can be used. Because if, you look at the refinery petrochemical industry, the feed stocks are heavier now a days atmospheric residue, vacuum residue they are being used for tracking operation right or for production of gasoline F C C process for catalytic cracking process.

So, the deactivation catalyst may be very significant right. So, novelty is that catalyst should be successful and should be used for a longer period or should be reused for some other process; if it deactivates after certain period of time. So, these are the new challenges in terms of the green catalytic process. So, when you look at the catalytic selection or screening; so, conversion under constant condition. That is the first thing compare all the catalysts besides A B C; three different catalysts suppose you have. So, first thing is that understand from the chemistry side which for a given reaction which catalyst will be good, so some metals may be good, right metal oxides may be good. So, and once you have selected these metals; so molecules will come on to the surface and then their orientation so design of that, right the support metal support structure which you are designing the preparation methods are very important, very crucial.

Because the molecules comes on to the surface and adsorb; so, how does a molecule adsorb it is very strongly adsorbed, it does not work if it is very weak adsorb then also it will not work. So, a suitable kind of tuning is designed between the reactant molecule and the metal support; so, that is the crucial point in the catalytic reaction. So, we compared the different catalyst that is in the terms of conversion so, you make the identical condition based on either design of experiments right or some optimization tool like a small surface methodology; you select that these kind of methods that the catalyst can be tested in terms of temperature in terms of partial pressure, so concentration.

So, all these are identified the parameter and test the catalysts, all catalysts under the same condition and then look at the conversion, right. Same thing for a given space velocity as I said and make the conversion constant and then again compare the performance right, for a given space velocity your conversion will decrease right so, try to mention that if balance between them and then compare. Space time yield again that is with space time; how the product is changed so, that is again a crucial factor because the you are looking in terms of the product distribution so selectivity may change right. Temperature required for a given conversion; so, all these parameters need to be selected for the selection of a best catalyst or design of a catalyst.

So, basically catalysts are generally investigated, based on a given reactor it may be a fixed reactor, it may be fluid or batch C H T or so depending upon the reaction you select a reactor and then, test the conversion at constant space time and then compare the performance in terms of conversion, right. So, basically the space time, space velocity I hope you know all these terms; so, basically space time is nothing but a kind of W by F A naught.

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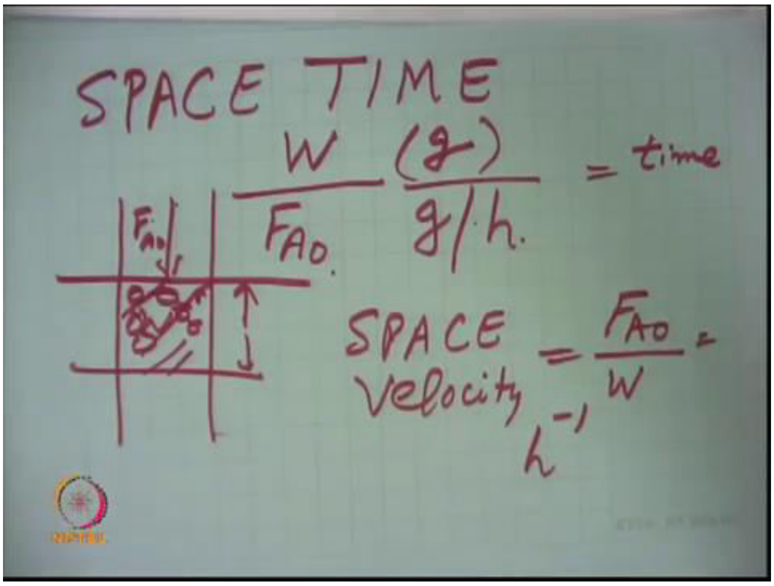

I can just define it here, space time; so basically we define for a catalytic reaction in terms of the mass of catalyst divide by the feed rate of a limiting component, right. So, W is the mass of catalyst so this can be in gram, this can be in kilo gram right feed rate can be different unit; so, generally it can be gram per hour something like this right or gram mol per hour. So, that is the feed of a limiting component so, basically it has a unit of time right so, idea is that when you have a fixed reactor; so this is your mass of the catalyst W and the feed is coming from here F A naught.

So, how much time the reactant precise is spent in a catalytic bed, in this bed right and depending upon that you will have a conversion. So, for a fixed condition you are calculating or comparing the conversion and the space velocity is opposite of this; so, this is basically F A naught by W so, it will have a unit of time inverse, right. So, basically it is giving that, how many reactor volumes can be treated in a given unit time rather right so, both are or both terms can be used interchangeably, when you look at that catalyst performance or reactor design.

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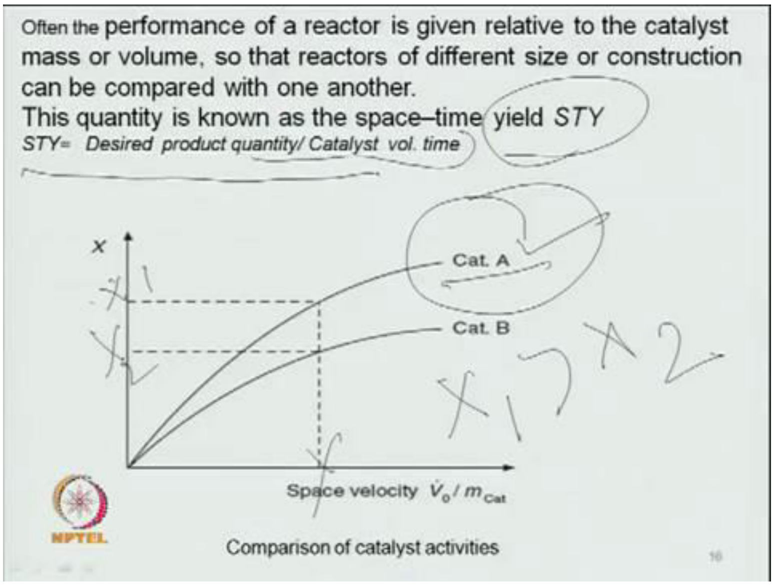

Often the performance of a reactor is given relative to the catalyst mass or volume, so that reactors of different size or construction can be compared with one another.

This quantity is known as the space–time yield *STY*

STY= Desired product quantity/ Catalyst vol. time

Comparison of catalyst activities

This is just an example, for comparing a catalyst; so, space time yield I have already defined desired product quantity per unit mass of the catalyst or per unit volume of catalyst per net time; so, that is another term of space time yield. So, when you look at a chemical reaction you are comparing the conversion as a function of space velocity which is either in terms of hydride divider mass of catalyst in terms of volumetric hydride or molar field hydride of gram field hydride so a catalyst a which has conversion like this X 1 here this catalyst b which has conversion X 2 at the identical condition, right.

So, basically in this case if you look at X 1 greater than X 2; so, you can say that this catalyst is better but this is not a correct understanding because the conversion high, does not mean that the catalyst is good. So, simultaneously, you have to look at this thing also yield of that the desired product, right. So, because suppose if I have a aromatic hydrocarbon or if I take the atmospheric gas oil crack it everything can go to the carbon; because you have very high space, time very high temperature these molecules will react and give you some kind of poly-condense aromatic hydrocarbon right, coke. So, you need a gasoline right; so, in that case you are desired product what you call space time yield or moles of the gasoline produced per unit mass of the catalyst per unit time is very low right that is space time yield.

So, in that case the conversion is high but desired productivity is low; so, that catalyst is not good, right. So, sometimes the high conversion does not mean the catalyst is good; that catalyst will be good if at the same conversion level the product quality or amount is also high. So, that is why we talk in terms of space time yield; so, something like that the carbon formation should be minimized when you look at atmospheric gas oiled cracking and gasoline should be high, right. So, you have to optimize or you have to tune when you select a catalyst for a given reaction.

So, now when I said that that conversion may not be very important the selection of a catalyst becomes a challenge right; on what basis you select a catalyst for a given process right. As, I said that you optimize the process condition you look at the do the desired experiment but for what right you have to look at that you have to compare from the leisured from thermodynamics right and look at the desired product yields, desired product selectivity, right.

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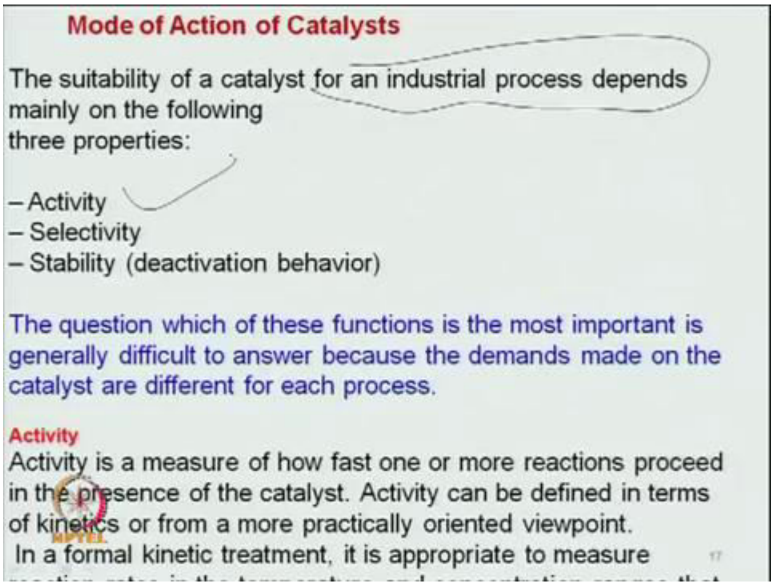

Mode of Action of Catalysts

The suitability of a catalyst for an industrial process depends mainly on the following three properties:

- Activity
- Selectivity
- Stability (deactivation behavior)

The question which of these functions is the most important is generally difficult to answer because the demands made on the catalyst are different for each process.

Activity

Activity is a measure of how fast one or more reactions proceed in the presence of the catalyst. Activity can be defined in terms of kinetics or from a more practically oriented viewpoint.

In a formal kinetic treatment, it is appropriate to measure

So, this is what the suitability of a catalyst when you look at for any industrial process this will depend on activity of catalyst; activity is something like conversion, right, how fast is the conversion in the presence of the catalyst, right. So, catalyst is transforming into a reactor this species ((Refer Time:41:01) into product; so, how fast that catalyst can work so because faster this activity of catalyst the smaller will be the size of reactor but you have seen in your W F A naught effect, right.

So, this is what the size of reactor can be reduced if you have very active catalyst. So, the commercial reactors will look at industrial reactor they are very large in size. So, now the nutrient when you look at the desired active catalyst in such a way that would be highly activate, right. So, if is the catalyst is more active the size of the reactor can be reduced and these are what your compact type of reactors right just like a heat exchanger, onboard reactors. So, they can be useful right space consumption is less and the same design the critical conditions of design that will be reduced when you size is lower. So, all these things lead they are very viable when you look at a novel catalysts are that technology in terms of the total economy of the process that can be reduced, right.

So, activity is very important first thing; then, selectivity which I told space time yield or desired product, stability is related to that deactivation behavior. Because sometimes the catalyst maybe very active in the initial period, right. Just for say your design developed a catalyst for 10 hours the activity maybe very high right but after 10 hours the activity drops faster and becomes zero after 15 hours right catalyst B the initial activity is low but it can last for say 100 hours. So, you have to find out which catalyst is good, right; in that case the stability that we need a catalyst which should be stable also. So, a good catalyst when you look at from green catalysis process because when your catalysis deactivated, you have to dispose it right and disposal of these type of solid base is also a challenge, right.

You need to find out that what are the process which can be used for the disposal or save disposal or the use of these catalysts. So, if you have a catalyst which are longer live for a given conversion or given activity or selectivity of a product can it is good. So, we need to select a catalyst or we need to design a catalyst as per these terms and conditions. So, the question which of these function is most important a generally difficult to answer as I said right because demands made on the catalyst are different for each process. So, sometimes you talk in terms of selectivity, very high selectivity, sometimes we talk in terms of stability or you tune it in terms of the process selectivity and stability designed in a our reactor, right.

You can do a few right you can have a moving bioreactor so the catalyst deactivation is very faster but conversion is high, selectivity is high; so, you transfer in a given time into second reactor is generated and take it back, right. Just like in a fruit catalytic F C C reactor; they are based on that right, so, reactor regenerated combination that can also be taken or considered but this depends on the demands or for a given catalytic process in terms of economy or reactor desire calls; definition by you have already discussed. So, activity generally measure of how fast one or more reaction proceeds in the presence of catalyst.

So, how fast the reaction transform reactant transform into product that is related to the activity of a catalyst; so, basically conversion also you can say that right. So, activity can be defined in terms of kinetic forms right that is basically, in terms of more practicable or oriented viewpoint that is the rate of reaction. Generally, what we call the moles of a reactant transform into the product per unit time per gram of catalyst right or just moles of product form per gram of catalyst per unit time or moles of reactant reacted per gram catalyst per unit time. So, any definition can be used to define this activity of catalyst right; so, just most of the time it all the reactant reacted per unit time per gram catalyst or related to the rate.

So, how this rate change with time or temperature that can also be defined in terms of activity; so, in general one conversion what I defined moles reacted divide by whatever the fact right into 100 so, that is known as percentage conversion; so, percentage conversion can also be defined in terms of the activity. The different catalyst when you select for a process right they may have different activity, they may have different selectivity but when you select the catalyst.

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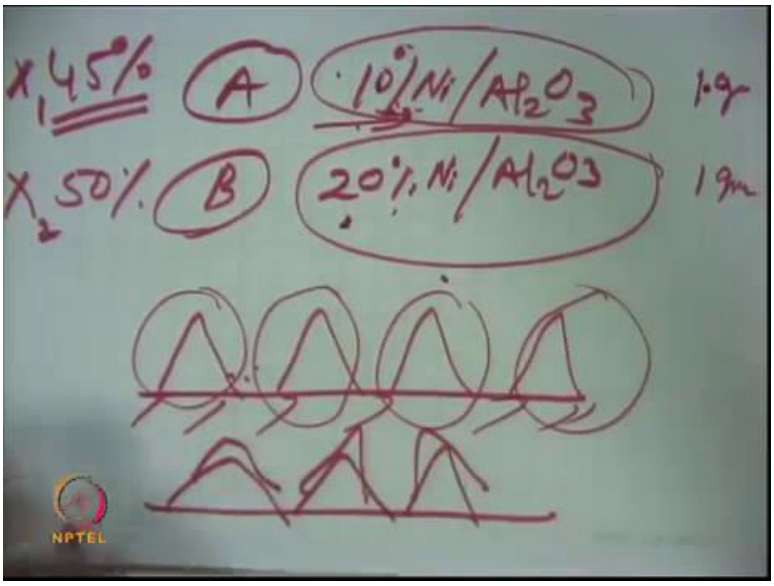

Suppose, I have taken different mass so suppose I am taking catalyst A catalyst B right this is say 10 percent nickel on alumina; so, generally we defined catalyst like this a combination of metal and a support. So, this is 10 percent nickel on alumina; it may total weight is hundred gram and out of that 10 gram is the nickel so alumina maybe 9 right. Same thing suppose if I taken another catalyst this is 20 percent nickel on alumina; so, you are comparing these two catalysts so, obviously suppose if I get with this catalyst 50 percent conversion and with this catalyst say 45 percent conversion, right.

So, you have 2 values of conversion X 1 and X 2; so, how to select which catalyst is good; so, we define a term which is known as turn over frequency. So, basically what is turn over frequency? That is not related to the mass of the catalyst you are taken the same mass of the catalyst here 1 gram here also say 1 gram. So, we are comparing now based on some active centre because what I said on a metal support this is your alumina support and on that you have nickel metal.

So, does not mean that higher amount of nickel when you load it gives you higher selectivity higher conversion; what is important is, that these active centers how they are deposited on the surface or distributed on this support, right. So, that is known as metal dispersion; so, the good definition instead of defining the rate because conversion when I am saying it is basically related to rate, right the moles of area per gram of catalyst per unit time. Here, what I can do I we can define definition in terms of per gram of nickel reactant or per gram of nickel which is active for the reaction; how many molecules of that reactant is precise converted, like something like if I am talking the phenol reforming; so, how many molecules of ethanol reactant per gram of nickel.

So, this can 1 gram of this catalyst if I am taking, right in total mass so the total concentration which is see here is just 0.1 right total mass of the catalyst so, this 0.1 this here it is 0.2 right; and out of that how many are active? Does not mean that suppose in 1 gram catalyst this is 2 gram of this a 0.1 gram here 0.2 gram here does not mean that all 0.2 gram if you calculate in terms of number of gram molecules which are available on surface, right. That may not be same because the molecules may have deposited like this, nickel atoms have become like this, accelerated like towards right one is sitting on the other got a very good design of a catalyst. So, we compare the catalyst activity in terms of this turn over frequency, right.

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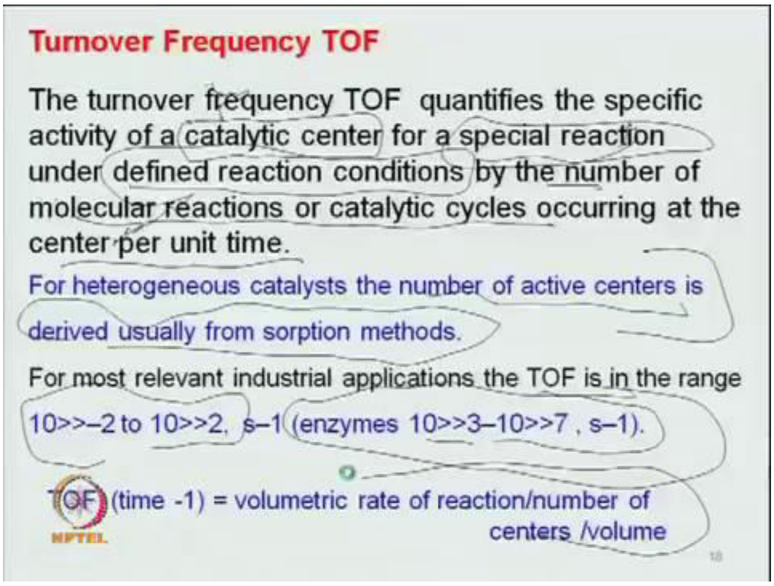

Turnover Frequency TOF

The turnover frequency TOF quantifies the specific activity of a catalytic center for a special reaction under defined reaction conditions by the number of molecular reactions or catalytic cycles occurring at the center per unit time.

For heterogeneous catalysts the number of active centers is derived usually from sorption methods.

For most relevant industrial applications the TOF is in the range 10>>–2 to 10>>2, s–1 (enzymes 10>>3–10>>7 , s–1).

TOF (time -1) = volumetric rate of reaction/number of centers /volume

So, turn over frequency which is actually quantifies the specific activity of a catalytic centre for a special reaction under defined reaction conditions, right. So, when I say this catalytic centre these are these nickel sites which are available on the surface site; so different this active centers because on this the absorption of the molecule takes place, the molecule A comes and absorbed on these active centers right, not on the support site. Because it is a kind of specific reaction so, that is what the meaning is special reaction here right this word had importance here special reaction under defined reaction condition; very important term because I told catalyst is very specific in the reaction.

So, if I have a ethanol molecule it can absorb on nickel but if I have some molecule like say carbon dioxide it may not absorb on nickel, right. So, that is what the when you say the specific reaction so a specific gas molecule will adsorb on specific substrate or metal right. So, that is a key and that deposition will take place only on the active sites so we call them active centers here; so, the word which is written here the catalytic centre is also known as active centre which is nickel basically but not nickel the active nickel there maybe you can a have a 100 gram nickel the reaction may not take place right because we have not activated it properly, right.

They have made a cluster they have exonerated. So, that is why the concept of nano-particles or nano-crystal site is important right the smaller the size, it will have larger such space area per unit volume right, more exposure to the surface right alumina. So, what I am talking here, the turn over frequency is generally quantifying the activity of a catalyst and take given condition of temperature reaction condition for a given reaction, right. So, by definition it is number of molecular reactions or catalytic cycles occurring at a centre per unit time. So, how many gas molecules adsorb on nickel surface per unit time right per unit active centre. So, now it is not the 10 percent nickel it is not the 20 percent nickel it is the active amount of nickel which is available on the surface right.

So, how we calculate the; how we define this active surface available on the surface; we measure the dispersion. So, another definition is known as dispersion which we will see later; but basically, the dispersion is the fraction of the surface which is expands for chemical reaction or available for chemical reaction right and that take just measure in terms of the fractional concentration, right. So, if I say that dispersion is 10 percent so that means out of this 10 percent nickel only 10 percent nickel sites are available for chemical reaction. So, rest is a waste right you have 10 percent dispersion 90 percent is a waste because it is exonerated like this one over other.

So, this site is not available for chemical reaction now which is on the lower site. So, this is the meaning of dispersion; so, we need a catalyst support or good catalyst support on which the dispersion is like this, right. So, that is again a very important concept or key for catalyst preparation how to get good dispersion; and that is what I told the concept of nano science or nano material, right.

So, catalyst is related to your material science right and the concept is known as nano-catalysis also where talked it in term nano-catalysis also where we want high dispersion, right. The platinum; if you take nano particles of platinum it can have the oxidation of CO even at room temperature but the problem is that the nano particles are not very stable they enumerate faster; so, how to make them stable is again an issue right.

And, so this is what the R and D or research work that we need to develop each kind of nano particles, nano catalysis for the reaction where the activity becomes very very high, right. A low concentration of the metal will be effective; so, you are not consuming that my 10 percent 20 percent or 50 percent of the metal right so, they are very precious.

So, some of the values this type of values if you look at for heterogeneous catalysts the number of active centers is derived usually from the adsorption method. This is what I was talking for measuring the dispersion in a catalyst; so, will talk on this term later in different lecture. So, basically now by definition the turn over frequency is nothing but the number of molecules which are absorbed on the surface right per unit active site per unit time, right.

So, if you look at the value so molecules divided by molecules divided by time, right so, units will have something like time inverse. So, if you look at for most of the heterogeneous reactions the turn over frequency comes in the range of 10 over minus 2 to 10 power 2 right so per second. And, if you have something like enzymatic reaction it has the value of 10 to the power 3 to 10 power 7 per seconds. So, very high value for the enzymatic reaction that is why they are been considered right the turn over number of molecules which are absorbed in per unit time per unit site is very very high right turn over frequency turn over number is very high, right. So, this talks in terms of the catalytic life cycle also; so, faster reaction can happen on this right. Same thing here, but turn over frequency is generally the volumetric which are defined volumetric rate of reaction divided by number of centers divided by per unit volume of the total sites.

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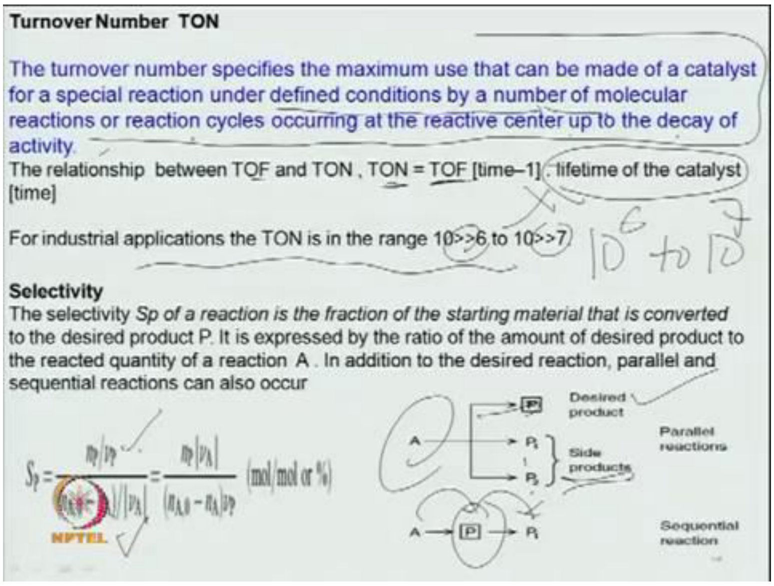

Turnover Number TON

The turnover number specifies the maximum use that can be made of a catalyst for a special reaction under defined conditions by a number of molecular reactions or reaction cycles occurring at the reactive center up to the decay of activity.

The relationship between TOF and TON , TON = TOF [time–1] . lifetime of the catalyst [time]

For industrial applications the TON is in the range 10>>6 to 10>>7 10^6 to 10^7

Selectivity

The selectivity *Sp of a reaction is the fraction of the starting material that is converted* to the desired product P. It is expressed by the ratio of the amount of desired product to the reacted quantity of a reaction A . In addition to the desired reaction, parallel and sequential reactions can also occur

$$S_P = \frac{n_P/\nu_P}{[illegible]/|\nu_A|} = \frac{n_P|\nu_A|}{(n_{A,0}-n_A)\nu_P} \quad (\text{mol/mol or } \%)$$

Another definition is, turn over number which is just inverse of the turnover frequency because they are inter-related. So, turnover number basically talks in terms of the life time of a catalyst right; how many time the catalyst can be used for the process? Right. So, the turnover number is specified the maximum use that can made of a catalyst for a special reaction again under defined condition by a number of molecular reaction or reaction cycles occurring at a reactive centre up to the deactivation.

So means, suppose the catalyst as I said that it can reused again and again right but does not mean that throughout it can be reused. Because activity of a catalyst where we talked about stability that decrease with time; now, whether it is a good catalyst or bad catalyst the activity may drop faster activity may drop relatively slower. So, if the catalyst activity drops then, you have to look at that turnover number with time to time right; so, then you are calculating that for how many time this catalyst can be used in a given reaction. So, generally you must have heard that after three year the catalyst has to be replaced right all these designed company or whatever for fertilizer industry or refined generally the catalyst life is very specific.

So, for 3 year or 5 year or 6 month they are unit right. So, the idea is that you have to relate this in terms of the productivity because where the catalyst deactivates its activity drops; so, deactivation does not mean that activity is reduced to just zero right the activity is reduced to a level which is not economical to run the reactor, right. So, suppose the bench mark gives in terms of productivity right you are producing 10 thousand tons per day when the activity is dropped suppose, 70 percent that means you are just produced 7000, right. So, whether this is acceptable to company and depending upon that, that catalyst has to be replaced or some fresh catalysis to be added right. So, this concept of turnover number is that for how many times the catalyst can be repeatedly reused under identical condition, right.

So this is what the very specific definition is that the number of molecular reactions or cycles occurring at a relative centre up to a decay activity, right so, decay activity can be a defined guideline. So, the relationship between turnover frequency and turnover number that is turnover number is nothing but turnover frequency multiplied by the life time of the catalyst, right. So, turnover frequency has the unit of time inverse life time of the catalyst has the unit of time so this is the number of time I can say 1000 time the catalyst can be used right or 50,000 times the catalyst can be used. So, I can compare the two catalysts A and B based on this performance right.

So, for the industrial application generally that the desired is that the turnover frequency should be of the order of 10 to the power 6 to 10 the power 7; so, these are representing the powers right. So, 10 to the power 6 to 10 to the power 7 this should be the approximate reuse of the catalyst in the process right so that is what I said that if the catalyst say highly active it may deactivate also faster so, it may not be good right. FCC catalyst has these kind of problems right; so, they reacts much faster you need a different kind of reactors so flowed by reactor side or moving by reactor side. So, the reactor design is related to the catalyst performance in terms of activity in terms of selectivity and definitely the other reactor optimization process conditions also right.

The definition of selectivity we have defined earlier also; so, their numerous definitions which have been used but most common definition if you look at here; A reactant this can give you p which is the desired product right and it can give you P 1 and P 2 which is your undesired or side product right; a kind of parallel reaction. Similarly, this is a sequential or series reaction where a goes to P and the P goes to P 1 that desired is this one. So, the how do we define selectivity; is just simply the moles of the desired product divide by the moles of the reactant reacted, right. It is a very important special definition generally we but we are writing the definition says that the moles of the desired product divide by stoichiometry co-efficient of that product right. And, divide by moles of the reactant reacted divide by stoichiometry co-efficient of the reactant that when the general definition.

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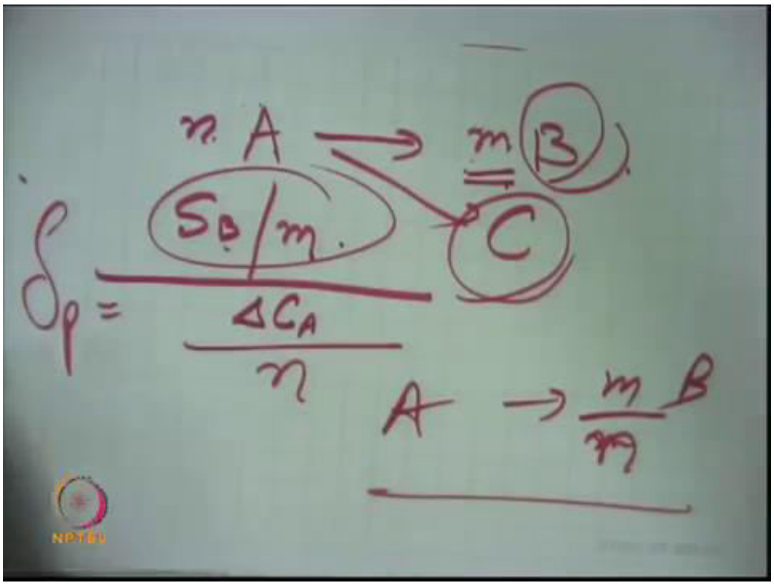

So, the basic thing idea is that here, if I write that n A gives you m B right and then, I write some other reactions also in parallel. So, selectivity generally used for the where these are the multiple kind of reaction; so, what I am defining that moles of the desired product. So, whatever the S of B divide by its stoichiometry co-efficient, divide by the moles of reactant reacted A reacted. So, that is nothing but whatever the delta time concentration difference of a right divide by its stoichiometry co-efficient; so, this is generally a definition for selectivity. But there can be other definition as I said some times its defined as moles of the product B formed divide by moles of the product C formed per mol desired product divide by undesired product.

So, there can be different definition because all of the time when we talk reactor design will relate the reactor concentrations of heat concentration of reactants or products and finally, when we optimize or compare a catalyst we talk in terms of the selectivity. So, different researchers or different reactions definitions of the selectivity may be used; but when we look at your stoichiometry or mole balance equation that will not change right. Because we are talking in terms of the reactants transformed into the products; so, when you write a mole balance it will remain same right. So, here is just a basic that per mole of this if you look at the comparison for because m also we are produced so per mole have been produced how many moles of they are produced, similarly, this is what of the reaction.

So, basically it is nothing but you writing in terms of limiting component a gives you m by n times B; something like this in terms of limiting reactant, right. So, all of you must have been learned this thing before. So, stability definition we have again talked; so, in that case the chemical, thermal and mechanical stability of catalyst determines its life time right for a industrial reactor. So, when you look at the stability of a catalyst then you are talking in terms of activity mainly; so, the definition is generally we define a term known as activity a right.

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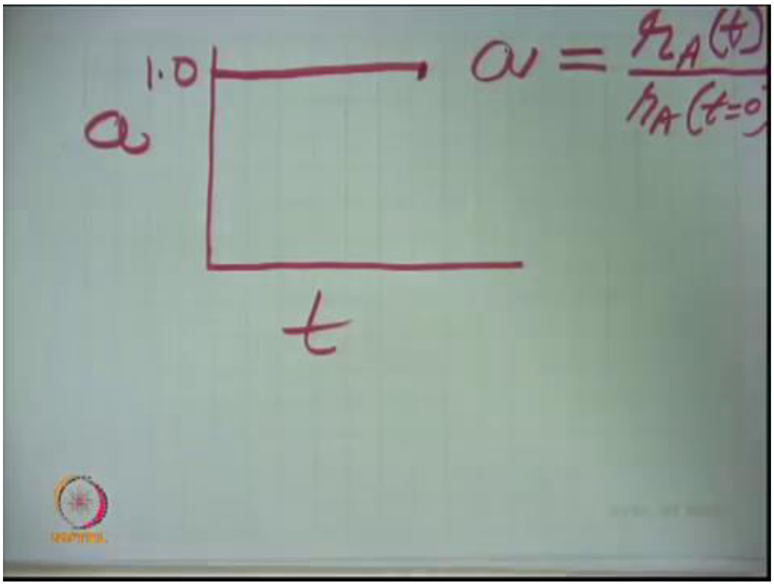

So, activity a is defined in general the first catalyst rate or rate at any time t divide by rate when the catalyst was fresh t is equal to 0 right. So, what is the definition is that catalyst if this is the activity of a catalyst right and when I say that the catalyst is good though my activity a versus time activity should always be 1 it means catalyst is not deactivating for a long time. So, I will continue this part in the next lecture; I think time is up so, I will continue it next time.