Heterogeneous Catalysis and Catalytic Processes
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Lecture – 32

So, good morning in the last lecture I was talking about Catalytic Deactivation and I told that catalytic deactivation is the lost in the activity of catalyst big time.

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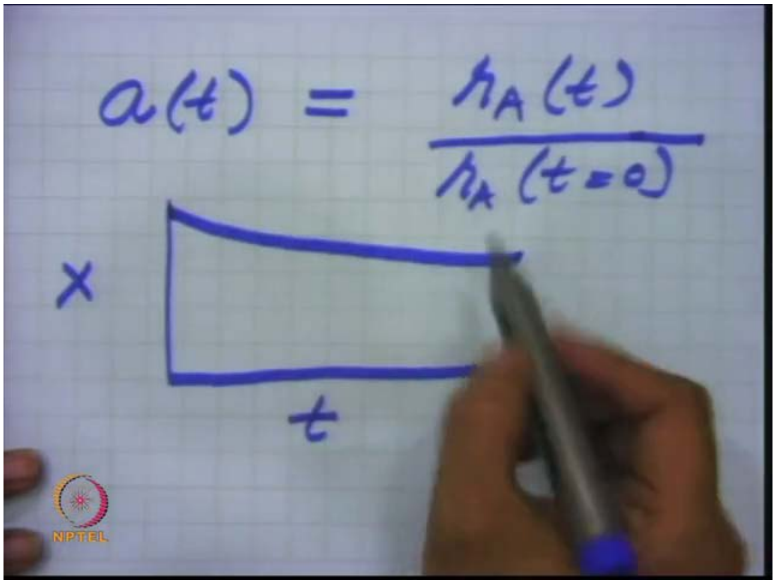

So, we define the activity of a catalyst and then this activity which is define edge the rate at any time t divide by initial rate that is the rate at t is equal to 0 and, rate can be calculated from conversion verses time data. So, one can have the conversion verses time data so if the catalyst deactivate then the conversion will drop like this. This can be calculated in terms of the selectivity of the product also these are product and rate. So, activity of a catalyst will drop with respect to time and a stream. But, I decided discuss last time and that will depend on the order of deactivation also. So, experimentally one can find out the deactivation order also.

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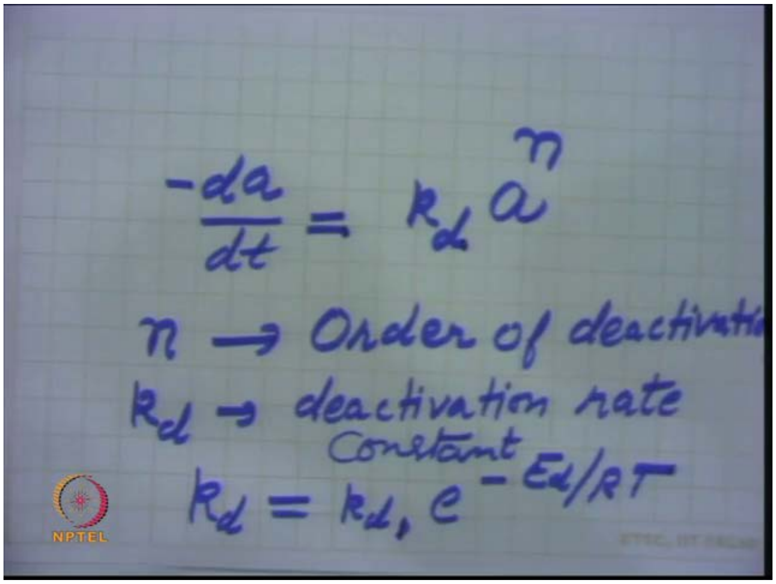

$$-\frac{da}{dt} = k_d a^n$$

$n \rightarrow$ Order of deactivati

$k_d \rightarrow$ deactivation rate constant

$$k_d = k_{d_1} e^{-E_d/RT}$$

So, in general one can write minus da by dt that is drop in activity function of time some constant which may be your deactivation constant and will be a function of temperature. And, times what about the activity to the power n where, n is known as Order of deactivation. So, this can be find out the deactivation rate constant kd, kd is known as deactivation rate constant and will be given by Auranious equation is a function of temperature. So, kd is a function of temperature can be given kd at 1 temperature kd1 or, kd0 e to the power minus Ed divide by RT. Where, Ed is the activation in a, d for deactivation reactions.

So, one can use that differential method of analysis or integral method of analysis to find out the rate data bit time on a strain and, can then activity can be calculated as a function of time on a strain. And, then by using that differential method or interial method of analysis what is generally done for determination of order of reaction. And, a activation of generate constant one can find out the deactivation kinetics or deactivation order of reaction and activation energy also. So, in general when, you write the rate of a main reaction by knowing this function.

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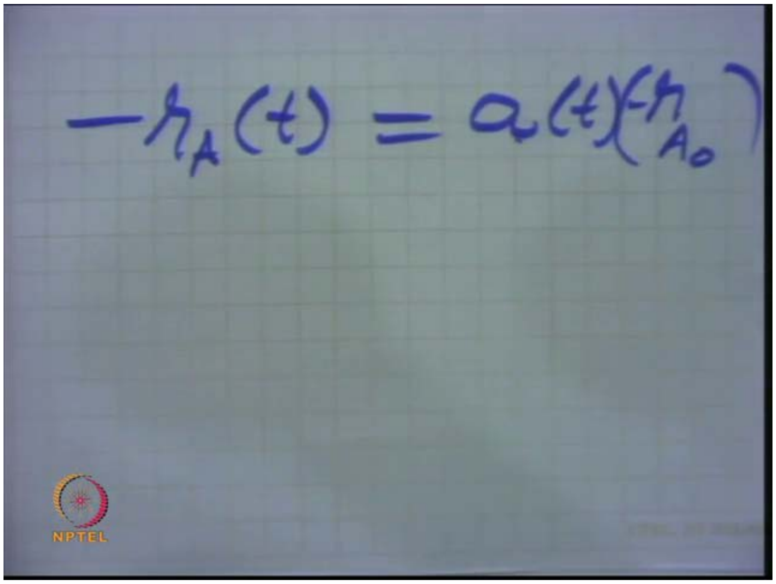

$$-r_A(t) = a(t)(-r_{A_0})$$

That how activity drops for a given reaction as a function of time then one can correlate this net rate or, rate at any time t which can be a function of activity which is a function of time. Times the rate which is a first catalyst rate or minus rA disappreance of reactant for the fresh catalyst that is initial rate. So this, a t is calculated from the deactivation kinetics and then the rate at any time can be used for the design of the reactor.

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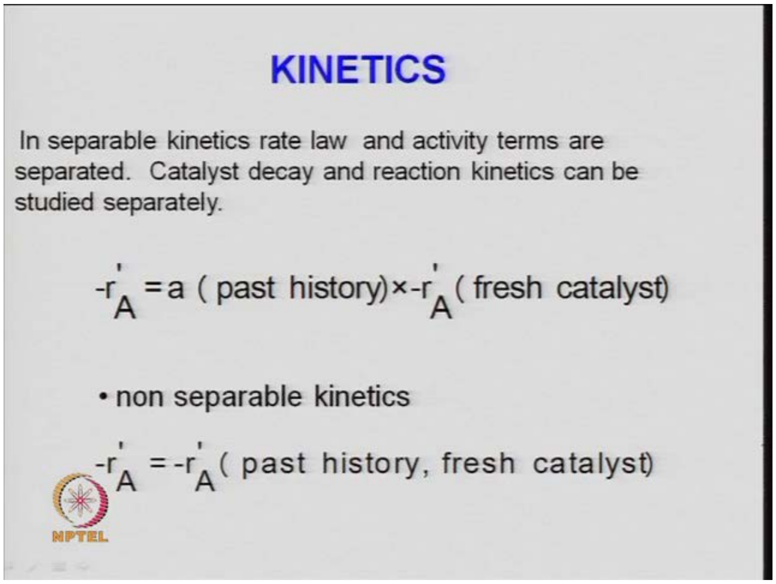

KINETICS

In separable kinetics rate law and activity terms are separated. Catalyst decay and reaction kinetics can be studied separately.

$$-r'_A = a\text{ (past history)} \times -r'_A\text{(fresh catalyst)}$$

- non separable kinetics

$$-r'_A = -r'_A\text{(past history, fresh catalyst)}$$

So, the rate expression engine can be define by two ways one in known as Separable Kinetics so where this deactivation concern it independent of the geometric of the catalyst for property of the catalyst. In the second case when the deactivation concern is related to the property of a catalyst then it should be a kind of non separable kinetics. So, in this case most of the time we talk only a deactivation concern separately and the kinetics of a main reaction separately and then we analyze. Otherwise, in this case one needs to find out the surface property of the catalyst with time on a stream and then correlated with the activity of the catalyst.

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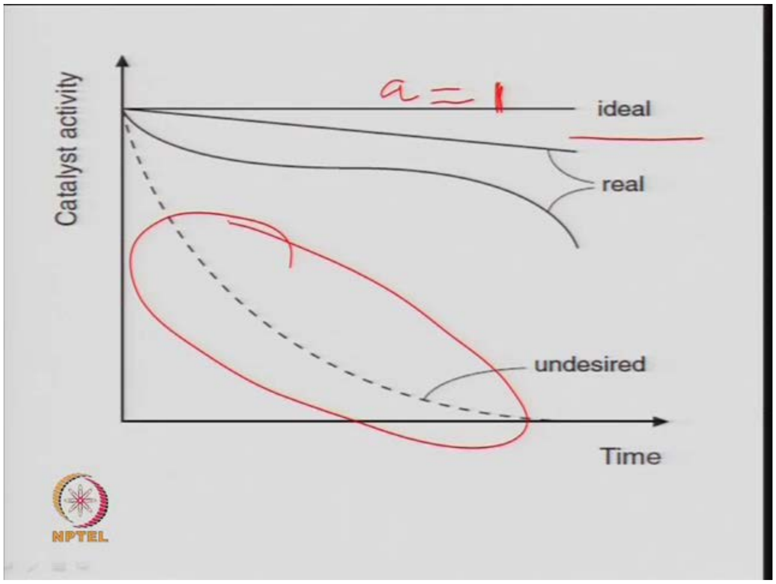

So, as I said that ideally the activity should be wall that is the catalyst should not deactivate. So, this is the ideal case there should not be any deactivation in a good catalyst. But, if you look at the practical catalyst there activity decrease big time. So conversion decrease, portal selectivity decrease, or decrease productivity decrease with time on extreme. So, this can be like a real catalysis this is drop like this can go like this also. Or, this is a severe deactivation of the catalyst between the odd design actually this you consist the activity become 0 after a certain period of time. And, the drop it much faster a kind of exponential decay with very high order of deactivation so that it not recommended in a good catalyst.

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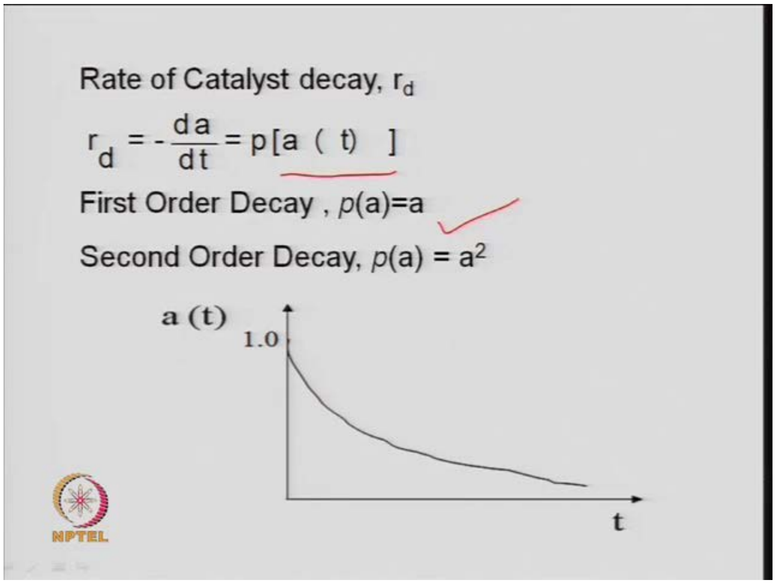

Rate of Catalyst decay, r_d

$$r_d = -\frac{da}{dt} = \underline{p[a(t)]}$$

First Order Decay, $p(a)=a$ ✓

Second Order Decay, $p(a) = a^2$

So, as I said now that the deactivation order or deactivation rate minus da by dt is a form concern of activity of a catalyst. And, this activity of a catalyst can be something like a First Order Decay if the deactivation is known as first order decay.

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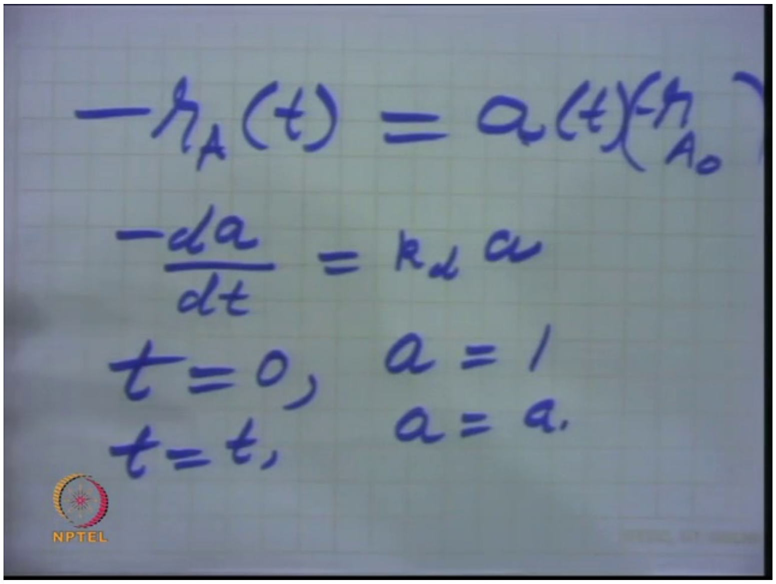

$$-r_A(t) = a(t)(-r_{A_0}$$

$$-\frac{da}{dt} = k_d a$$

$t=0, \quad a=1$

$t=t, \quad a=a.$

So, in the first order decay one can very easily like minus da by dt is equal to kd times a. So, this is a kind of first order decay and one can very easily integrate because time t is equal to 0 the activity is 1 and t is equal to any time t activity a each a. So, one can use the separation of very variable and take the limit from 1 to a and time 0 to t kdt and the integration can be done in this form. So, exponential decay of activity for the first order deactivation if it is second order then one can write to this is a first order decay.

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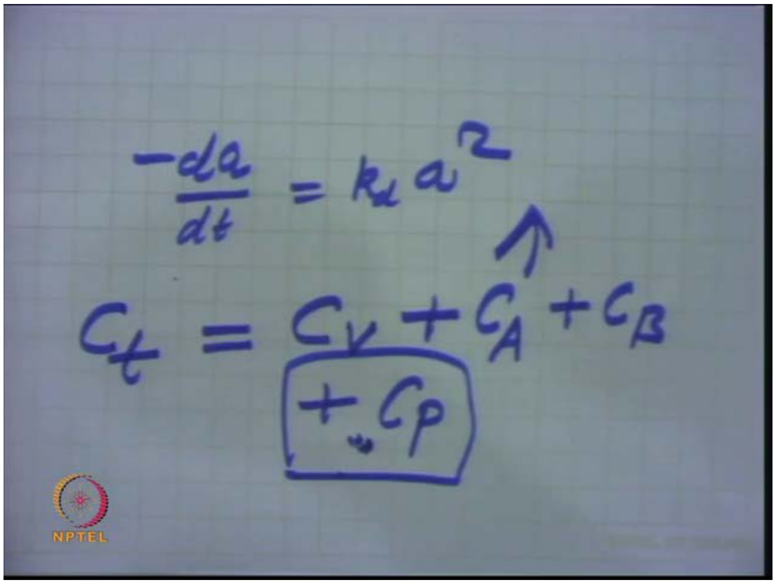

$$-\frac{da}{dt} = k_d a^2$$

$$C_t = C_V + C_A + C_B$$

$$\boxed{+ C_p}$$

Second order minus da by dt will be written as kd times a square and again the separation of variable. So, minus da upon a square is equal to kdt and then you integrate it from the limit 1 to a is equal to kdt. And, then 0 to it dt and one can again solve this equation activity can be correlated as a function of time. So, whether it is first order decay or second order decay so one can very easily write the exponential lesson of the different kind of decay rates.

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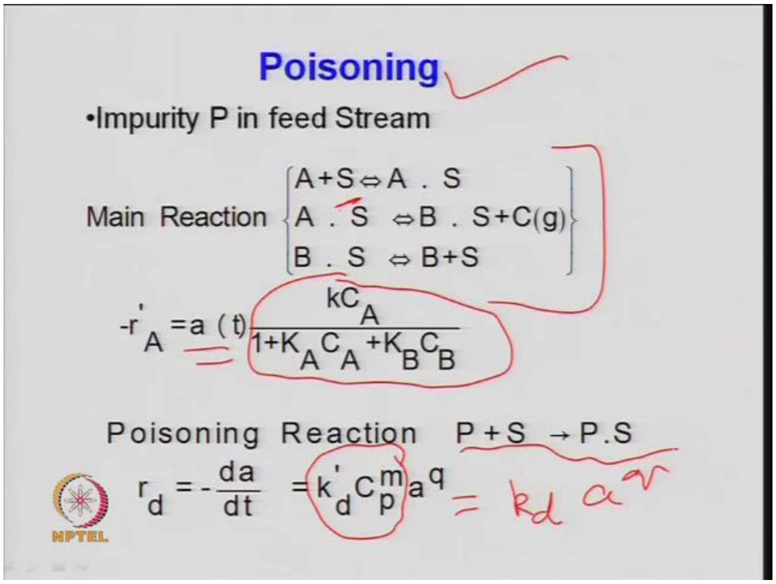

Poisoning

- Impurity P in feed Stream

Main Reaction
$$\left\{\begin{array}{l} A+S \Leftrightarrow A\,.\,S \\ A\,.\,S \Leftrightarrow B\,.\,S+C(g) \\ B\,.\,S \Leftrightarrow B+S \end{array}\right\}$$

$$-r'_A = a\,(t)\frac{kC_A}{1+K_AC_A+K_BC_B}$$

Poisoning Reaction $P+S \rightarrow P.S$

$$r_d = -\frac{da}{dt} = k'_d C_p^m a^q = k_d a^q$$

Now, as I said that the deactivation mechanism may be different type it can because of bowling that is the deposition of the pope. It can be because of the poison precursor the so the rate drops because of the concentration of the poison precursor. Or, it can be kind of sintering where the surface area of the catalyst may be affected because of the relists ligation. So, the grain size increase and because of that the surface area or active surface area of the catalyst decrease this can be because of the blockage of the pour because, when the heat constant heating at high temperature then the pours miss the sink. So, depending upon that the pours I distribution change and the surface area of the catalyst may be affected because of the sintering.

So, this is what here the kinetics of deactivation for a poisoning type of reaction. So here a poison precursor which is available in the feed stocks itself and absorbs on the surface of the catalyst. So, as I said that when poison pickers absorbs on the surface then number of active sides available for catalytic reaction that decrease and, once this happens then the activity of catalyst will drop permanently. So, we end it will because the poison precursor if it present in the feed then it will keep on absorbing on the catalytic active side and it will damage the catalyst. So, this is the main reaction what we are assuming that a, absorbs which is a reaction respective it absorbs on the active side of the catalyst as. And, gives a intermediate kind of complex which we all discus A S. And, this A S this is your surface reaction so transforms into which is B S and some C which, is a product task. And, then B S gives you product B and the side it is free. So, A gives you B plus C this is the main reaction. But, since the feed contain a poison precursor like sulphur as I said it can be sulphur componective minitrogen compound or any feed stocks may be oxalate compound. So that absorbs on the surface of catalyst and makes it P S which is can be jobbed poison precursor.

So, this is the kinetics of the main reaction which we have already discussed earlier. So, minus rA that will depend on your rate of absorption of a rate of surface reaction and rate of desorption. So, any sub may be rate controlling and one can determine the rate of main reaction which is here. kCA divided by 1 plus K A C A plus K B C B plus so this rate of the main reaction can be different but here we have written it in this form assuming this a controlling. So, and absorption and B they are fast A and B they are equilibrium. So, the rate is first this is the rA 0 first catalyst rate and this is the activity function when the catalyst is deactivating with time. So, activity is decreasing with we called there are the sides which are been blocked by the poison precursor. So, in this case if you look at the rate of deactivation rd is minus da by dt that is decrease in activity of the main reaction with respect to time because of the poison precursor absorb on the surface.

So, this is written here in the form of kd dash times concentration of this poison precursor p to the power m times d activity to the power q. So, generate the poison precursor concentration and this whole term can be combine together because this is present in the feed itself. So, we can very easily write sometime here kd times a to the power q where q is the order of deactivation and a, is the activity. And, k d is the overall rate of deactivation because Cp is the concentration of the poison precursor present in the feed which is taken as a constant here. But, sometimes this may that is the power to the by which the catalyst deactivators suppose the sulphur precursor so the deactivation in must faster and basically this kind of deactivation when you write. Then, you total site Ct if you calculate that is nothing but the concentration of vacant site plus whatever the site absorbs by A you write CA site absorbs by B and sites which are absorbs by poison precursor.

So, this is the term which is decreasing the activity of the catalyst these are recovered because this A S gives you whatever the A plus S and B S gives you B plus S but, this Cp it is a kind of irreversible reaction. So, this Cp remains in the denominator of the main reaction if you write the expression in terms of the absorbs species concentration so that is generally not known. So, we write it in terms of some activity function that is how much the rate is lowered because of this poison precursor with time on extreme. So, this is what actually the rate is decreasing because the poison concentration which covering the active side of a catalyst so the available vacant side are continuously decreasing with time on its stream. So, this is Ct 0 now in this case but with time this Ct is decreasing because this Ct continuously blocking the active site of the catalyst.

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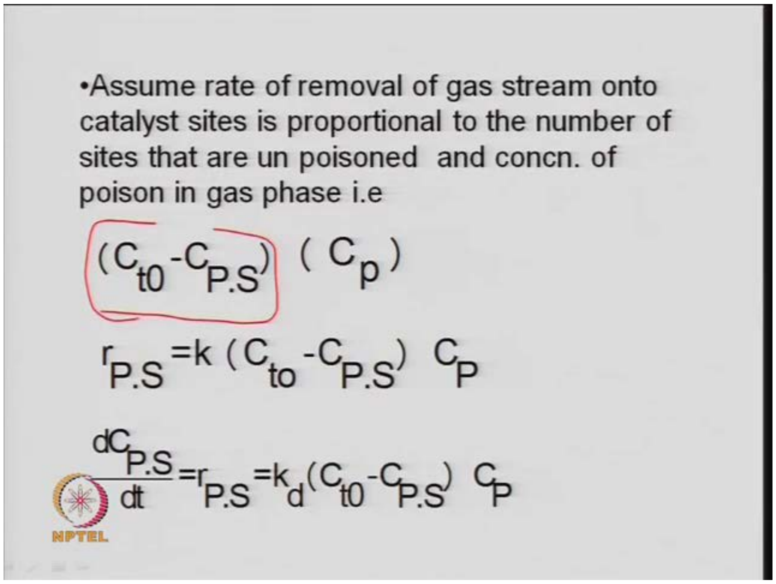

- Assume rate of removal of gas stream onto catalyst sites is proportional to the number of sites that are un poisoned and concn. of poison in gas phase i.e

$$\boxed{(C_{t0}-C_{P.S})}\ (C_p)$$

$$r_{P.S}=k\,(C_{to}-C_{P.S})\ C_P$$

$$\frac{dC_{P.S}}{dt}=r_{P.S}=k_d(C_{t0}-C_{P.S})\ C_P$$

So, this they written here if you look at Ct 0 minus Cp as basically the same expression which we are written in terms of activity. Or, how this rate it changed because, what we have written here deactivation but same can be written in the form of this concentration of the poison precursor. Which, is written here and the concentration of the weekend side C S that has been written here in terms of the concentration of poison precursor Cp times Ct0 minus CPS. Because, CPS is permanently blogged or damage sites so, Ct0 minus CPS the concentration of the vacant site which is available and change bit time on its because CPS it is increasing big time. So, this concentration total sites which are available that will decrease.

So, rPS can be written in the form of k times Ct0 minus CPS times Cp. So, this is the rate of formation of poison precursor which is written here assume the rate of remove all gas extreme on to the catalyst side is propositional to the number of sides that are un poisoned. And the concentration of the poison precursors in the guest just like when define the rate it propositional to the concentration of the poison precursor. Or, partial pressure of the poison precursor multiplied by the concentration of the vacant side where the poison can absorb or on the surface of the catalyst.

So, this rPS can be written in terms of dCPS by dt that in how your catalyst is deactivating with time will depend how the poison is absorbing on the surface of a catalyst. So, rate of absorption of poison precursor on the surface of the catalyst is equal to some constant which is kd, which is here kd time Ct0 minus CPS time Cp. This, is based on the surface reaction which we are assuming in terms of mechanism here for the poisoning. And, one can directly correlated in this form also by just doing the experiment and calculate the rate bit time on a stream. And, then calculate the order of deactivation and rate constant decaled rate constant. So, this kind of mechanism that in the poison precursor mainly in the petroleum refined. If you look at the sulphur precursor nitrogen in a, feed or auction comparison in the feed like, phynolic compound there absorb on the surface of the catalyst. And, the mechanism of this catalyst needs to understand in order to develop. Or, design a normal catalyst system for a given process hydro treatment just like an example I am talking here.

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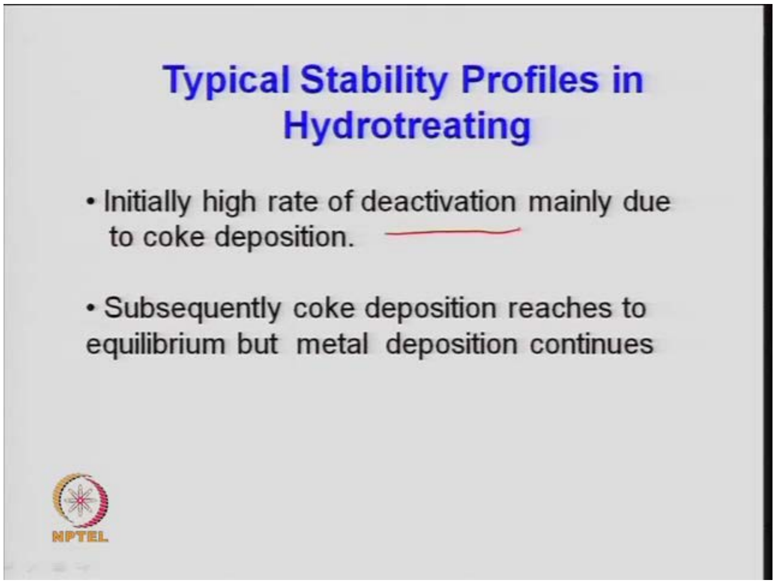

Typical Stability Profiles in Hydrotreating

- Initially high rate of deactivation mainly due to coke deposition.
- Subsequently coke deposition reaches to equilibrium but metal deposition continues

So, testability profile then only if you look at the high rate of deactivation in mainly due to the coke deposition in the case because, initially your concentration if you look at here even for coke deposition or poison initially this concentration or vacant side concentration is very high. So, the rate of poisoning will be high and finally it will reach two kind of poisoning rate. So, finally the rate will decrease as the concentration of the poison side decrease the vacant side decrease. So, coke depositions finally reach to the equilibrium but metal depositions if the metal is there absorbing on the surface of the catalyst irrespective to the fraction of the vacant side. So, that in case so if you look at this graph in case of hydro treatment reaction which I was talking for example for hydro treatment. So, the activity of catalyst drop like this. So, this is the activity profile.

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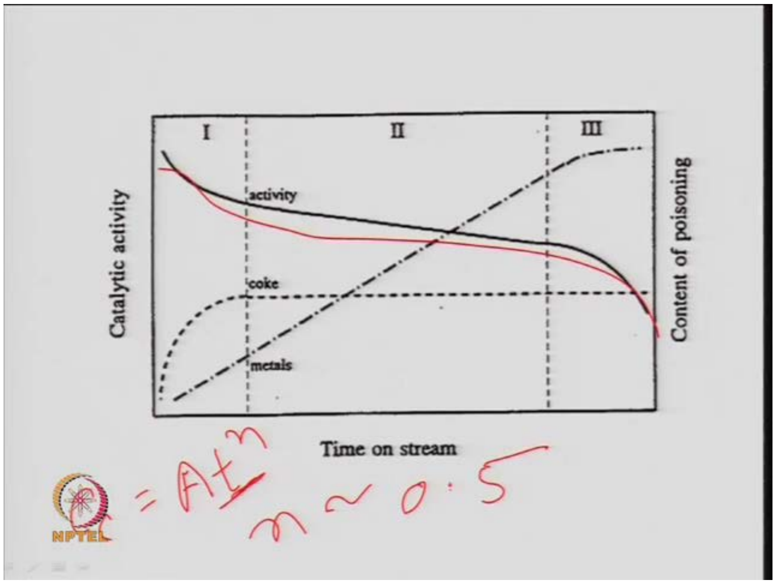

So, catalyst activity which is calculated with respect to the conversion with time on a stream so that decreases with time. If, look at the coke so coke deposits on the vacant side active sides of the catalyst so this is a kind of assumptive coke in road. So, initially it increase something like it may be Cc the coke formation it can be related to A times t to the power n. So, in that t is the time and intimate and A is a constant n is the order of deactivation. And, Cc may be the concentration of carbon deposited on the catalyst which, can be define in terms of gram per unit area of the catalyst or gram per gram of the catalyst so either units can be used. So, just a coking coke formation rate which can be written in the concentration of the coke precursor also so, that can be related edentates of t. So, generally this is where here n is roughly 0.5 that is kind of order of deactivation in terms of these equation. So, n is roughly 0.5 here so this is a kind of assumptating coke in road.

But, metal formation increase continuously that is the hydro demetallization is to be done in order to remove the matter from the catalyst. So, some metals concentration increase continuously but this coke formation is a kind of assumptating coke in rate an activity of the catalyst drop because of the combine in fact. So, that is what the content of poisoning which has been shown here in this graph.

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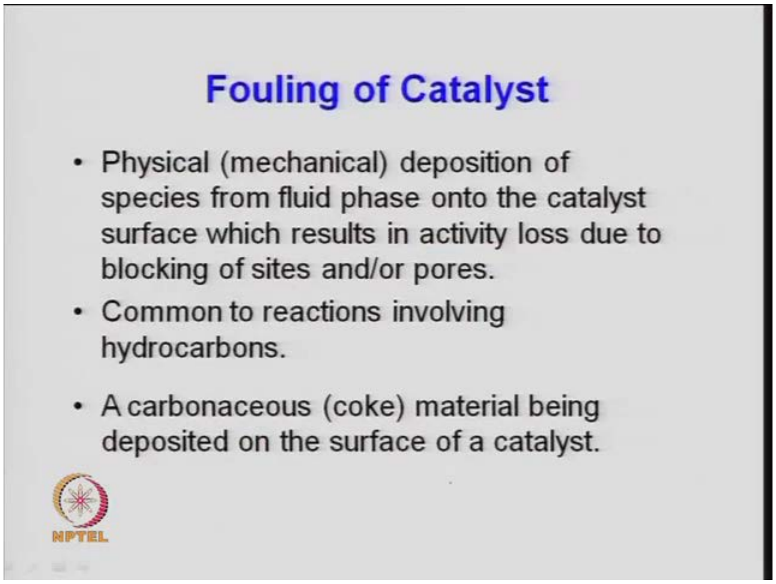

Fouling of Catalyst

- Physical (mechanical) deposition of species from fluid phase onto the catalyst surface which results in activity loss due to blocking of sites and/or pores.
- Common to reactions involving hydrocarbons.
- A carbonaceous (coke) material being deposited on the surface of a catalyst.

So, Fouling that is first thing is a poisoning and second is a fouling. Fouling as I said is a carbon or dolt so deposition of the carbonization material on the surface of a catalyst that is known as fouling. So, it can be Physical deposition of mechanical deposition of species from the fluid phase. So, sometime the feed stock may contain the coke precursor just like as I said aromatics if the feed contains more amount of aromatics then on the carbon on the catalyst will be more. So, that is because of feed stock some time it may be because of the carbon or the catalytic activity that the acidic catalyst. So, as a catalyst have more tendency to form coke so coke formation from the acidic catalyst will be more. So that is if, the feed stock itself is a more problem to coke formation then the catalyst assenditration is should be reduced accordingly. So, one is to identified like the zeolite catalyst silicon like catalyst are highly acidic in nature.

So coke on those, kind of catalyst will be higher if the feed stock itself is a form to coke formation arrow matrix feed is storm at I said atmospheric gas oil vacuum gas oil. So, they are prom to coke formation because they contain the larger molecular we talk condense polio metric because, coke is nothing but it condenses polymeric hydro carbon so I talk on that little later. So, this is nothing but again when the coke or carbon deposit on the surface of the catalyst that will either blocked of the sites of the catalyst for block the pour of the catalyst.

So, basically distribution phenomena will change when the pour side of the catalyst is decreased. So, when you are more diffusion resistance in the pour of a catalyst because they transport limitation if you look at again it will take mass transform then diffusion and chemical lesson. So, diffusion limitation if you look at the pours are block so your diffusion resistance will be removed. It may happen that because of coke formation the diffusion may be a rate controlling step in that case rate. So, one need’s to check all these things when you look at the deactivation of the catalyst. So, this is very common when you look at any hydro carbon reaction because these hydro carbon are from to coke formation. So, carbonation material being deposited on the surface of the catalyst and they decrease that the activity of the catalyst and that they known as howling.

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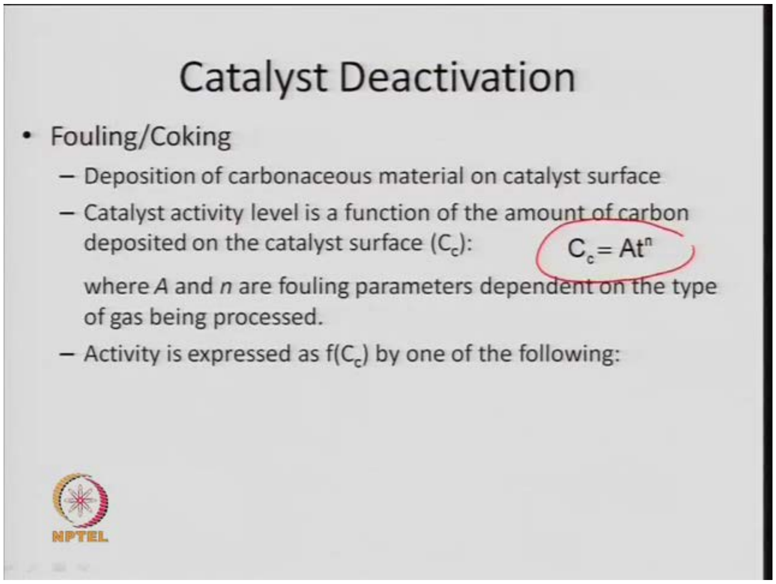

Catalyst Deactivation

- Fouling/Coking
  - Deposition of carbonaceous material on catalyst surface
  - Catalyst activity level is a function of the amount of carbon deposited on the catalyst surface (C_c): $C_c = At^n$

    where *A* and *n* are fouling parameters dependent on the type of gas being processed.
  - Activity is expressed as $f(C_c)$ by one of the following:

So, as I said earlier also so the amount of coke deposition can be repotted. So, basically that determination of coke can be detent because coke is a kind of a material which can be burnt off.

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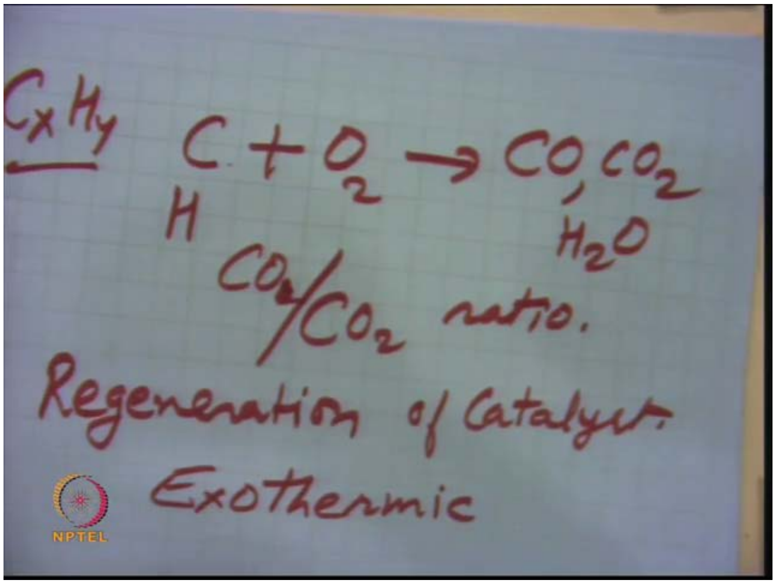

C_xH_y $C + O_2 \rightarrow CO, CO_2$

H H_2O

CO/CO_2 ratio.

Regeneration of Catalyst.

Exothermic

So, one can remove the coke from the catalyst just by burning and that is known as regeneration of the catalyst. So, this basically when you burnt in terms of controlled oxygen so this gives you CO, CO2 and you have water also CxHy some water also. So, you get this because coke may contain your hydrogen or CxHy ultimately you may get these things. So, one needs to control the CO, CO2 ratio in the few gas especially, when we talk Regeneration of the catalyst. Because, this purses it Exothermic so exothermic process so it generates.

So, one needs to control because if the catalyst is being burnt in presence of oxygen at around a 550 degree centigrade this is the generally that the temperature required for resignation. And, if temperature exceeds if 700 or 800 then your catalyst may damage. So, zeolite say they have they cannot subtend a temperature more than 5 fitters or 600 so they are not stoppable with respective to high temperature. So, one needs to control this in order to control the extability of catalyst or otherwise the crystals will grow inside or the catalyst will get sintered. So, one needs to look at that regeneration what I mean to say that. Regeneration, of the catalyst is possible.

But, for that one needs to find out how coke forms. So, compound of carbon formed as a function of time so this will be a function of time temperature also because, higher the temperature more will be the severity of reaction. So, generally it will known as assumptating coke in rate so this will be a kind of profile which is related as a function of temperature. And, one can very easily calculate it at different temperature so increasing the temperature the coke on the catalyst will increase and this is known as assumptating coke rate formation. So, this can be related some function t to the power n which is given here in this form of expression. So, these are a kind of imperial expression which can be determined experimentally by doing the experiment with different catalyst and different qd stop and one can use this expression.

So, in the case of fowling as I said that deposition of carbonation material on the surface and, this related to as a function of amount of carbon deposited on the catalyst. So, that is the catalyst of the Cc so that is the coke deposited which I told you that it can be reported gram per meter square of catalyst it can also be reported gram per gram of catalyst also. So a, and n are known as fouling parameter and depend on the type of gas being processed. So, once this they known then the rate of coke formation dc by dt can be calculated or, that can be correlated in terms of the activity. How, the activity is related with the coke formation because was more coke is forming then activity will drop.

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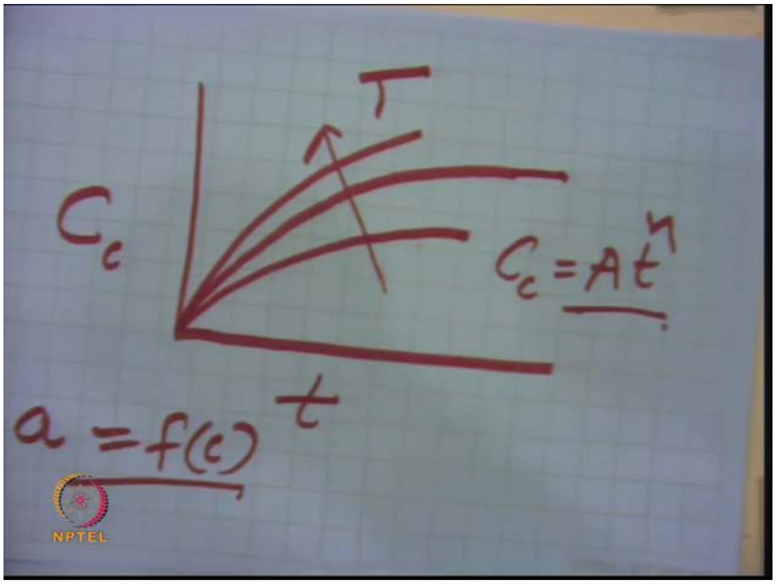

So, A will have some concern of coke and this will decrease. So, activity will decrease when the coke is forming on the catalyst because active sides are blocked and there can be different coalitions like this. So, there is 1 collation imperial collation where it is shown that the activity drops 1 over 1 plus the amount of carbon per gram of catalyst to the power p it can be written in terms of times also which is written here. So, it can be given like this also it can be exponential drop also. So, activity return e to the power minus alpha Cc where again Cc is the gram of carbon per gram of catalyst it can be written in this form also 1 over one plus alpha 2 times it is. So, these all empirical constant which can be determent an experimentally so, one needs to do experiment like this at different conditions of temperature and vision the carbon deposited on the catalyst with respect to time. So, carbon deposited on the catalyst can be determine by TGA of operators.

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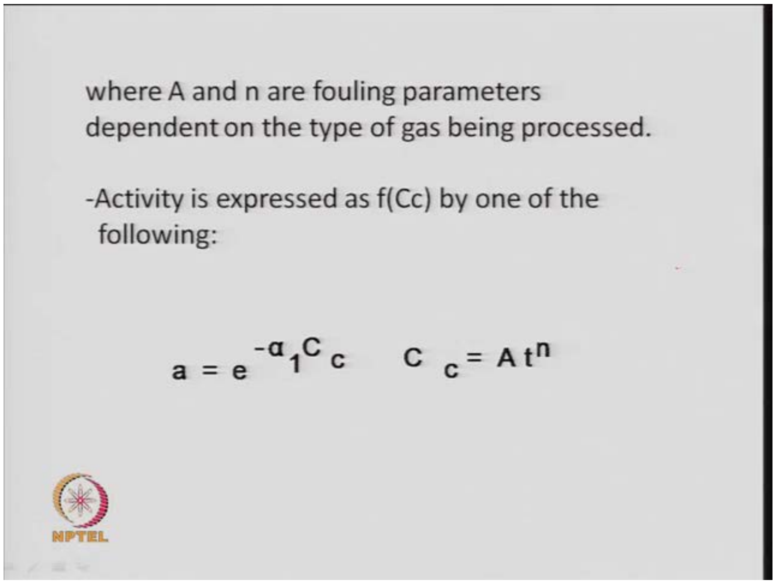

where A and n are fouling parameters dependent on the type of gas being processed.

-Activity is expressed as f(Cc) by one of the following:

$$a = e^{-\alpha_1 C_c} \qquad C_c = A t^n$$

So, one can determine the carbon and then can cord late the expression like this and depute the activity in terms of the concentration of carbon deposited on the catalyst. So, activity will drop continuously like this. So, this activity concern can be added with the main reaction rate and then design can be done.

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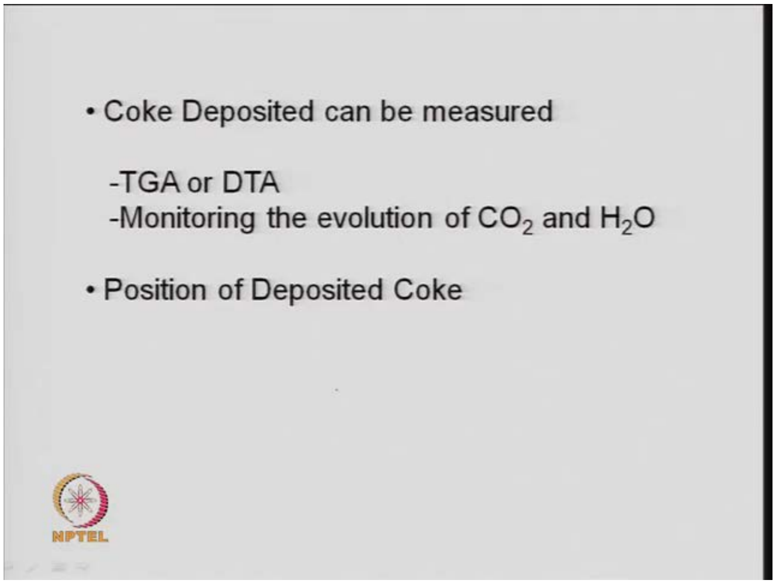

- Coke Deposited can be measured
  - -TGA or DTA
  - -Monitoring the evolution of CO_2 and H_2O
- Position of Deposited Coke

So, the Coke Deposited as I said can be measured by thermogravatic analysis which we have discussed that we heat the sample the non amount of mass at the catalyst you take in a pan. And, then heat it with different temperature rate at different temperature rate and up to a temperature say 1000 degree centigrade’s. Because, the nature of coke may depend on the temperature it may be a grow fight type carbon it may be type it may be kind of carbon nano tube nano fiber. So, needle type of coke that is a production process by atmospheric gas oil or vacuum gas oil.

So, dilate coke in unit which bracket unit so these are the units where the coke it being produced in order to make them cormassally for some other process. So, that can be done so one can measure the amount of carbon deposited as a concern of time and at different temperature. So, how much coke when you removed when you burnt it in TGA one can find out and can cogitated again or you can understand the mechanism of coke formation also, so this falling of coke in mechanism itself a complex phenomenal. So, one you look at a commercial process where you do that or find the operation of packing hydro privation the coke formation it should be removed or minimized.

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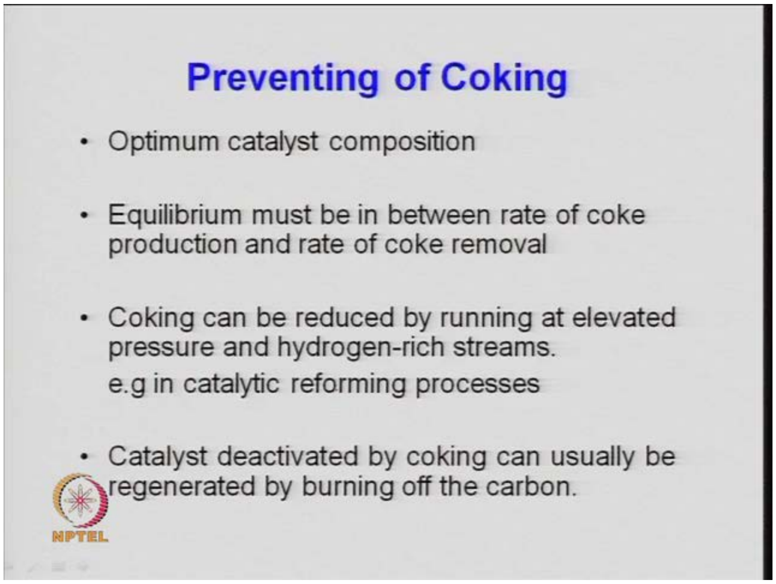

Preventing of Coking

- Optimum catalyst composition
- Equilibrium must be in between rate of coke production and rate of coke removal
- Coking can be reduced by running at elevated pressure and hydrogen-rich streams.
  e.g in catalytic reforming processes
- Catalyst deactivated by coking can usually be regenerated by burning off the carbon.

So, you need to identify the Optimum catalyst composition because I told that when the coke deposits the activity of catalyst stops. So, one can add some promoters in order to reduce the coke formation. So, just like in cracking a small concentration of potassium can be added with the presences of potation in his because the x as a gasified agent same thing does CDI added because they have the exes oxygen in the latish structure.

So, all these kind of materials like potassium ceria as a support basic support kind of basic support zincornia added as a promoter. So, these the basic promote kind of basic promote basically the as I said that more acidic is a catalyst your deactivation will be higher the, because carbon formation will be more on acidic catalyst. So, it mean of one thing that acidity to the controlled I am not saying acidity should be reduced controlled, because the main reaction rate will also decreased when decreased the acidity especially when you have a cracking type of reaction so one needs to find out that. So, means optimize the conditions, so temperature is one thing because high temperature favors the coke formation if you have a higher temperature then more coke will formed during the reaction pressure again has a, some in fact. So, you need to find out high pressure or low pressure so originally high pressure will avoid the coke formation. But, higher hydro carbon will increase the coke formation the concentration coke precursor will increase the coke formation. So, Equilibrium must be in between rate of coke production and rate of coke removal so reactor comes reaction.

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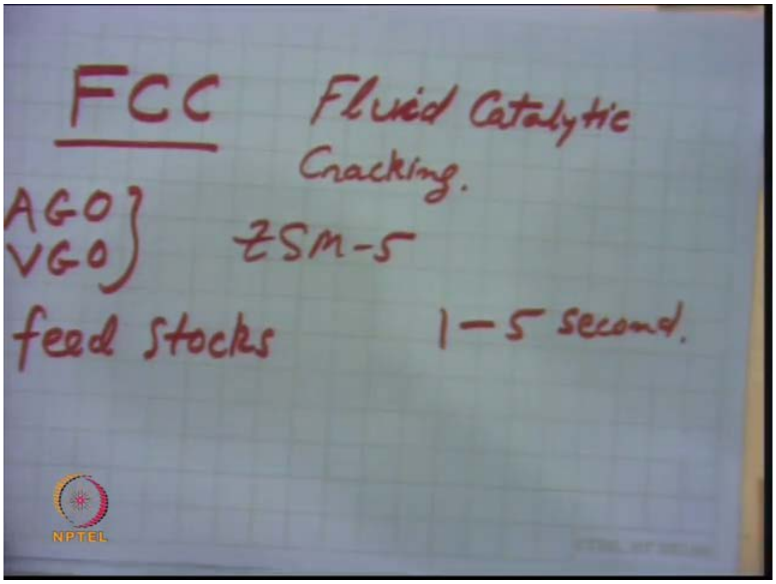

FCC Fluid Catalytic Cracking.

AGO
VGO } ZSM-5

feed Stocks 1-5 second.

So, generally if you look at your FCC cracking just like an example Fluid Catalytic cracking. So, in this case the fluid catalyst cracking the coke formation is server. So, generally celiac alumina type of catalytic are used zeolite catalyst are used. There, are sum five type of catalytic and feed stock is used some atmosphere gas oil or vacuum oil so these are feed stocks. So, all these feed stock contains your higher mono weight compounds and also aromatic. So, this trend to from coke so large amount of coke will for m when you do cracking of these kind of feed stocks with this cracking. So, generally the residence time should be as soon as possible so 1 to 5 second residence time which is kept in the reactor during the cracking.

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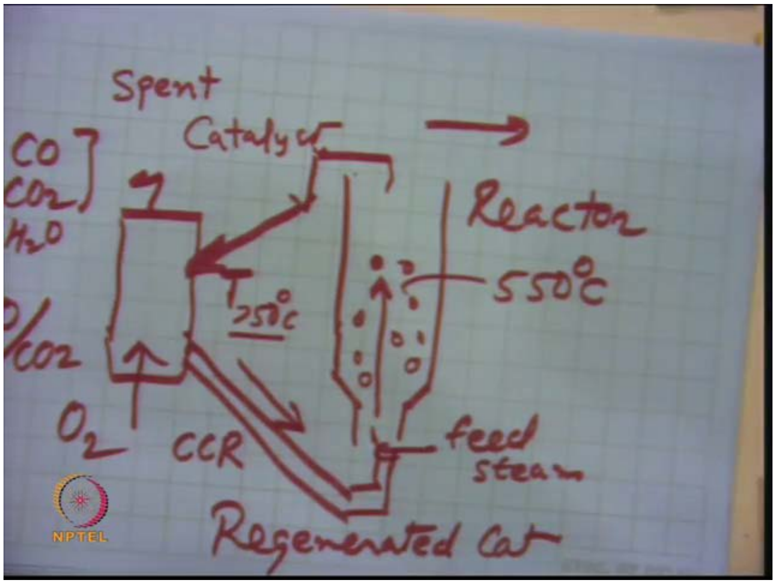

So, the system you look at in that case you need a system when you have continuous feed the catalytic like this. So, feeding of the catalyst is done along with the feed you have the feed say wipers of the AGO along with some say stream. And, you have some that can be used and that fluidizing media or there is steam or feed wrapper itself so these are the wrappers. And, the catalytic is here inside the reactor foodies bed condition. And, this can be a rigor type of cracking because most type of cracking take place in the initial portion. And, then you have here hopper here cyclone separators and the catalyst is the wrappers hydro carbon will go into this action. And, the catalytic is taken into another unit which is known as spent catalytic after reaction. So, deactivate catalyst and that will be taken into to another unit like this your catalytic will come continuously.

And, where you pass the oxygen from the bottom and then your catalytic is regenerated you get the few gas that is CO, CO2, and water whatever like this. So, and oxygen or nitrogen and whatever you are using air. And, then the regenerated catalyst is taken back into the reactors system leg this, so this your Regenerated catalyst, so this one kind of simple design that how reactor and regenerated are place in the parallel. So, you have Reactor here which is a cracker and this is a regenerator. And, continuously the catalyst recycle is back regenerated in the cycle continue so, now this design of this kind of system will depend type of licenses or the different kind of design are available for utilizing feed stock. So, you need to control the temperature here this here the temperature may be around 550 degree centigrade.

So, that catalyst come 550 when you have heating here the temperature can go up to 750 degree centigrade where, its exothermic endothermic So endothermic reaction here and exothermic regenerated reaction here. So, you need to control the oxygen ration in the fuel gas or CO2, CO ratio here, so how much oxygen should be given to burn a given type of catalyst amount so CCR which is the catalyst circulation rate. And that decide your reactor inventory size of the reactor here. So, this very a complex system if you look at a design of reactor and regenerator with proper heat balances mars balances and included the kinetic here.

So, kinetic main reaction kinetic deactivate reaction and then control CO2 and CO ratio in the few gas there should not be any after buddy. The, catalyst temperature should not exceed more than 750 or 650 degree that depends on the type less stability on the catalyst and catalyst also need to be in here. So, but this is also you need to look when the carbon deposit on catalyst or catalyst deactivate. So, reactor regeneration combination or a novel kind of reactor system design is required. So, this but I mean to say here, you need to look at that how much carbon is depositing on the catalyst per gram of catalyst per hour per unit time.

And, how much carbon is being removed from the catalyst. So, you need to look at a control a carbon say if I if you are making a bench mark then coke and regenerated catalyst should be less than 0.1 percent and starting it may have around 5. So, from 5 to 2.1 percent how the carbon has to be removed from the catalyst and that need to be calculated accordingly this sizing should be done or kinetic is to be discussed. So, the coke formation can be reduce by running the reactor at higher pressure. And, you can hide the hydrogen by that is the partial pressure of hydro carbon that can be reduce less like an a reforming processes this is done, that operation is done in at high pressure to reduce in a coke at catalyst. Because, the coke formation is a function of temperature is a function of partial pressure is a function of concentration of the poison precursor. So, catalyst deactivated by coking can usually be regenerated by the burning of the carbon that is what I discuss about the carbon react with the oxygen and gives to carbon dioxide.

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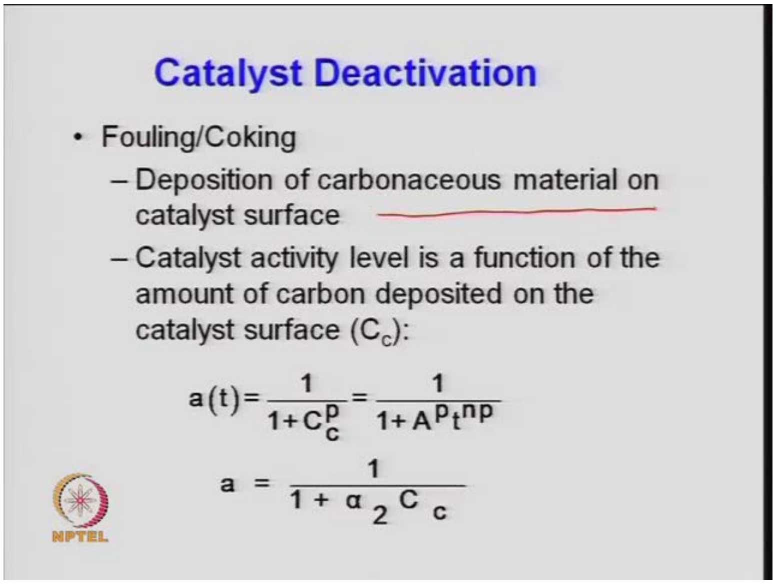

Catalyst Deactivation

- Fouling/Coking
  - Deposition of carbonaceous material on catalyst surface
  - Catalyst activity level is a function of the amount of carbon deposited on the catalyst surface (C_c):

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

$$a=\frac{1}{1+\alpha_2 C_c}$$

So, the falling phenomena, that is the deactivation phenomena by coke formation or fouling is define. Basically, the deposition of carbonaceous material surface of the catalyst and how much carbon is deposit that is what we has discussed. And, this activity level is the function of the amount of carbon deposited on the surface of a catalyst and that what a expression different kind of expression that can be used for this purpose.

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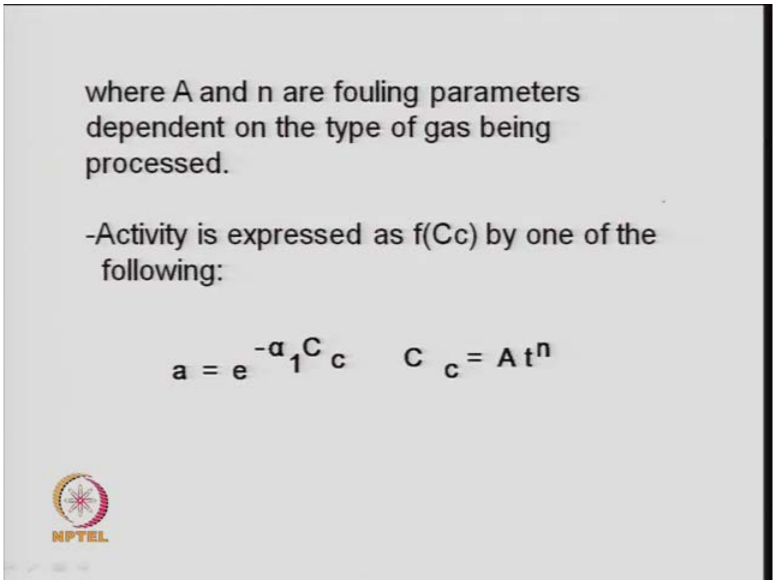

where A and n are fouling parameters dependent on the type of gas being processed.

-Activity is expressed as f(Cc) by one of the following:

$$a = e^{-\alpha_1 C_c} \qquad C_c = A t^n$$

So, different kind of rate expression has been used here so activity expressed as a function of coke formation and that is given by it e to the minus alpha times coke formation, so that what I discuss earlier and CC to the A to the A t to the power n. So, one can used it either expression or one can design the kinetic of coke formation or find out the expression for coke formation.

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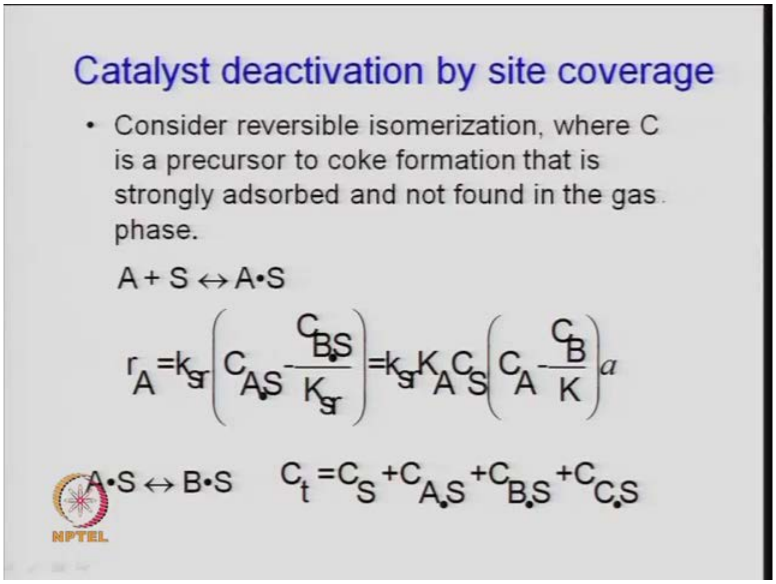

Catalyst deactivation by site coverage

- Consider reversible isomerization, where C is a precursor to coke formation that is strongly adsorbed and not found in the gas phase.

$A + S \leftrightarrow A\bullet S$

$$r_A = k_{Sr}\left(C_{A\bullet S} - \frac{C_{B\bullet S}}{K_{Sr}}\right) = k_{Sr}K_A C_S\left(C_A - \frac{C_B}{K}\right)a$$

$A\bullet S \leftrightarrow B\bullet S$ $\quad C_t = C_S + C_{A\bullet S} + C_{B\bullet S} + C_{C\bullet S}$

So, sometimes they said the same coke formation which is CC I have written as a function of the time on a stream that is t is a time on a stream t to the power n or the concentration of the precursor which is ending to form coke, which is to the power n which can be written sometime as a function of feed stock concentration itself so, one can very easily do that and can find out. So, here if you look at n just an isomerization reaction which is reversible isomerization reaction and C is the precursor, which tend to form coke. So, this is present in the coke itself it coke precursor. So, and A is your main reactant so strongly adsorbed on the surface and not found in the gas phase so this C a coke precursor. So, A plus S gives you AS that is your main reaction rA for this we have already discuss this very quickly I will go through that.

So, rate of adsorption of A which is a reactor of spices and here we are writing that KSr surface reaction rate cost for this minus the concentration CAS that is already is being done. So, I m quickly writing minus CBS divide by KSr. So, generally this is surface reaction rate constant which is control based on this type of expression here. So, that is rate controlling where as gives you BS product expression. So, rate will be propositional to k1 time the concentration of this precursor minus k2 time the concentration of this precursor and k1 and k2 has been taken out. So, that it will become a rate constant KSr that is a surface reaction as a rate controlling step so, you will have CAS that is a concentration of the adsorbed is spices which is like this minus the concentration adsorbed spices B dived by the equilibrium constant for the surface reaction rate constant.

So, this part we have already discussed when we were discussing about the, linger type of mechanical so that one can easily look at that. So, one can write these expression CAS CBS in terms of the total concentration of the known this spices. So, side balance as I told you so total concentration of the side will be CAS plus CBS. And, part of the activity is decreases, because of the concentration is decreasing because the poison is depositing. So, we introduce the factor here A to incorporate that. So, one can that in the denominator at the adsorbed Spices or one can write in the terms of the activity function this is the same expression KSr times the you have just calculated CAS and CBS in terms of the know concentration like this for CAS. At, equilibrium rate of forward reaction is equal to rate of backward reaction.

So, one can very easily find out CAS that is substituted here in terms of the equilibrium constant which has been taken out and same thing for CBS so CBS also because CBS will BS adsorbed and gives you B plus S. So, one can very easily write down the expression. And, over all equilibrium constant can be calculated from this reaction A equal to B so, this your over all equilibrium constant. So, basically this your rate when the catalyst fixed one can write like this rA and t is equal to 0. And, that is determine from the longer type of mechanism simple. So, and I multiplied this with the activity of the catalyst and activity determination function is started. So, one can write this activity which is written here in terms of the concentration of the vacant site plus concentration of site covered by A plus concentration of site covered by B plus the concentration covered by poison precursor. So, this is the number will come in the denominator of Languor Hinselwood expression that is.

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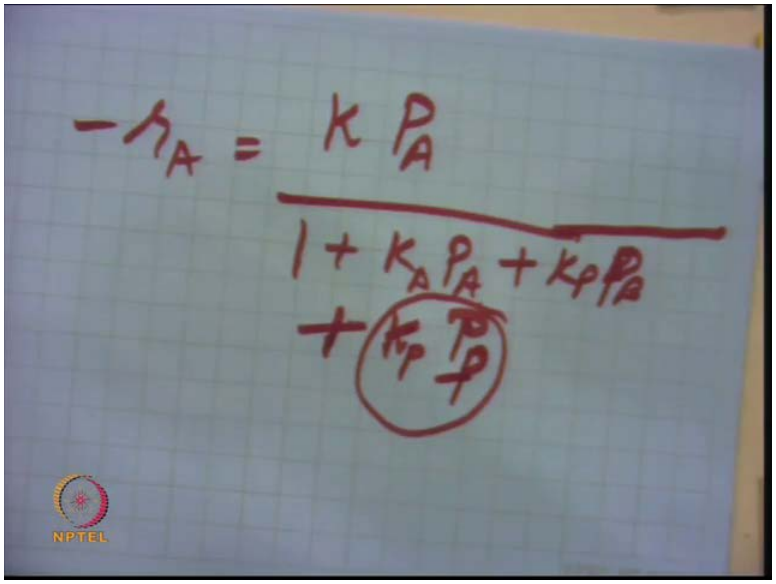

$$-r_A = \frac{k P_A}{1 + K_A P_A + K_P P_B + \boxed{K_P P_P}}$$

So, when you write this minus rA is something K and PA dived by 1 plus KA PA because it is adsorbed plus Kp Pb because this is also adsorbed plus addition terms which we got now because poison is here. So, K times some poison precursor times the concentration of the poison or the parcel pressure of that poison precursor Pp. So, this the unwanted term which has arise in the denominator this the term which is because of the chemical reaction you cannot aluminates these terms. Because, they are strongly semi adsorb but they transform in the product due to the course of time because of the surface migration or surface reaction. But, this poison precision not taking part in this and this is a kind of irreversible can be adsorption of the poison precursor or something like C plus S is converted into CS.

So, C plus S this use CCS and this term is raising because of this and irreversible poison precursor. So, that is also taken part in terms of total side balance that will come in the denominator. So, rather you write or either you write it in the denominator and determine the concentration of this because this not very easy to determine to this the concentration of CCS. So, you can write in the terms of the concentration of the feed stock the partial pressure of the feed stock and some fraction of that. Or, one can write the activity term and then calculated rate because of this concentration of the poison precursor. So, and how is decrease? So, minus dA by dt can be calculated and then activity function can be substituted.

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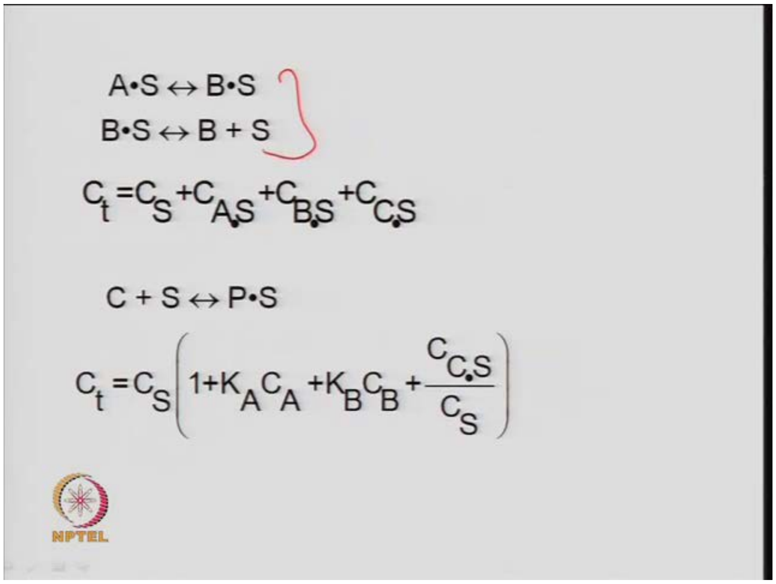

$$\left.\begin{array}{l} A\bullet S \leftrightarrow B\bullet S \\ B\bullet S \leftrightarrow B + S \end{array}\right\}$$

$$C_t = C_S + C_{A\bullet S} + C_{B\bullet S} + C_{C\bullet S}$$

$$C + S \leftrightarrow P\bullet S$$

$$C_t = C_S\left(1 + K_A C_A + K_B C_B + \frac{C_{C\bullet S}}{C_S}\right)$$

So this, details have been given here further A S gives you BS and then finally BS comes to B plus B which we have already done here. And, Ct is CS plus CBS plus CCS so, poison precursor and this CCS comes from this C plus S ratio PS or CS. So, one can very easily write a side balance in terms of Ct so CAS CBS and CCS can be determine from the constant equilibrium constant so this is what written here Ct so CS is the total concentration times 1 plus. So, CS is a vacant site concentration so CB or CS plus 1 plus KA CA that is the adsorbed spices of a KA CB adsorbed spices of B and time plus additional term which is CC over CS. So, this not known basically you cannot find the experimentally also very difficult. But over, all activity or drop in conversion can be estimated which is because of it this stuff.

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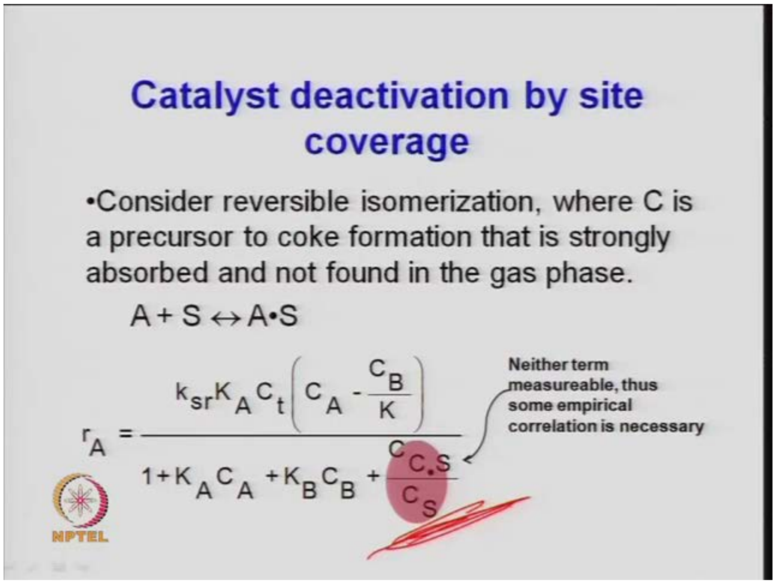

Catalyst deactivation by site coverage

- Consider reversible isomerization, where C is a precursor to coke formation that is strongly absorbed and not found in the gas phase.

$$A + S \leftrightarrow A \bullet S$$

$$r_A = \frac{k_{sr} K_A C_t \left(C_A - \frac{C_B}{K} \right)}{1 + K_A C_A + K_B C_B + \frac{C_{C.S}}{C_S}}$$

Neither term measureable, thus some empirical correlation is necessary

So, that is what shown here that one can find out these concentration and then look at the deactivation because of surface coverage this number. So, your rate of reaction which I have wrote the can be written instead of activity term which is I have here shown that one can write this term instead of writing the terms of denominator and related to the activity of the catalyst. So, here now this is the term which is come in the denominator because this is if there is no deactivation then this term is 0.

Then, A is 1 all the time. So, you have 1 plus KACA plus KBCB your usual languor Hinselwood type mechanical or surface reaction rate control and spices A is adsorbing or if B adsorbing on the surface. So, one can very easily write this expression. So, the meaning here is that for the reversible isomerization reaction where C is the precursor co precursor for the formation of the carbon. And, spices are strongly adsorbed on the surface this is adsorbed and not found in the gas phase. So, A plus S gives you AS and your rate of reaction which can be written in terms of rA 0 times A or you can write in terms of surface reaction constant rate or equilibrium site concentration which is at t is equal to 0 times whatever the driving force concentration driving force. So, CAC minus Cb by K because over all reaction is this. So, this over all equilibrium constant reaction for reaction which we have already discuss about this. And, divided by the terms which absorbs on the surface so, 1 plus KACA plus KBCB and this is what the CCS divided by the CS. So, nether term by this is measurable thus some empirical correlation is necessary.

So, these two are unknown but you know that the rate is decreasing so because of this. So, the time on a stream how is dropped so one can correlated and that is what the activity of a catalyst as a function of time or stream. So, basically this a mechanism actual mechanism that the rate is decreasing because of the poison precursor are covered or poison precursor are covering the active sites of the catalyst.

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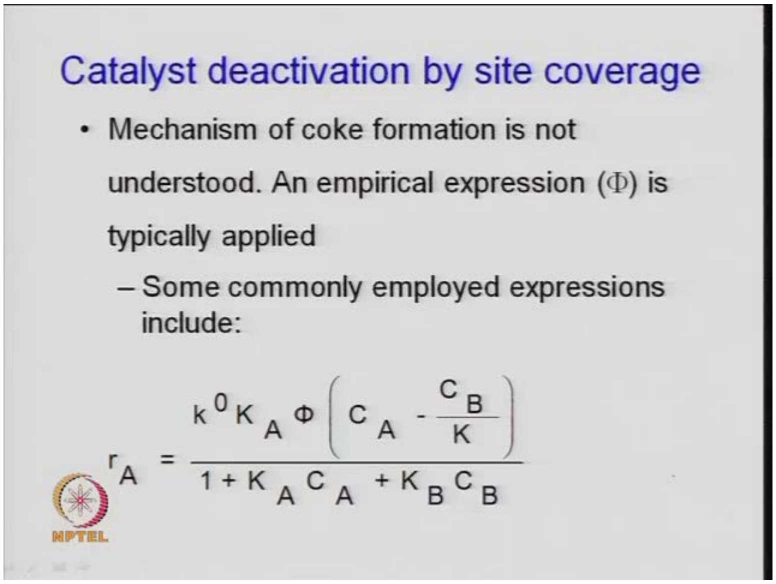

Catalyst deactivation by site coverage

- Mechanism of coke formation is not understood. An empirical expression (Φ) is typically applied
  - Some commonly employed expressions include:

$$r_A = \frac{k^0 K_A \Phi \left(C_A - \frac{C_B}{K} \right)}{1 + K_A C_A + K_B C_B}$$

So, deactivation by side coverage which I have shown that the coke formation mechanism is very difficult to understand. So, this not well know so we write the in the form of empirical correlation. So, I said minus dA by dt that is my phi deactivate function so some commonly employed expression if you look at. So, this is has been defined A kind of deactivation function which is related to the coke formation. So, this phi is related to A t to the power n something like that related to the carbon formation. So, K0 KA time phi CA minus CB divided K but you have seen before divide by 1 plus KACA plus KBCB. So, now we have removed that term from the expression. So, from this expression we have removed this third term which was CCS dived by CS because this is not known or experimentally also one cannot determent them. So, but one can write down the expression in the form of some deactivation function and that is what done here.

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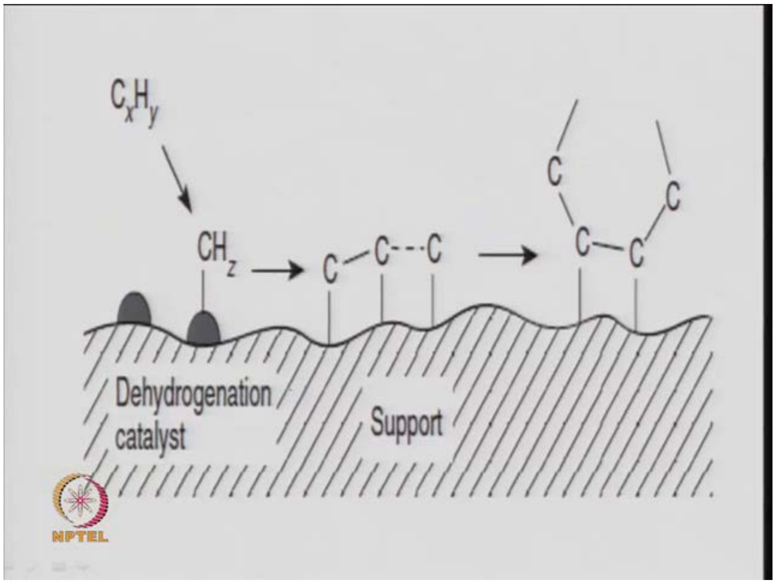

In this, case if you just look at the hydrogenous or dehydrogenation catalyst which is just a mechanism of coke formation shown here a surface a Dehydrogenation catalyst. And, you have a precursor a feed stock it can be the dehydrogenation a in terms of when you look at the formation of the aromatic hydrocarbon and they tend to form coke.

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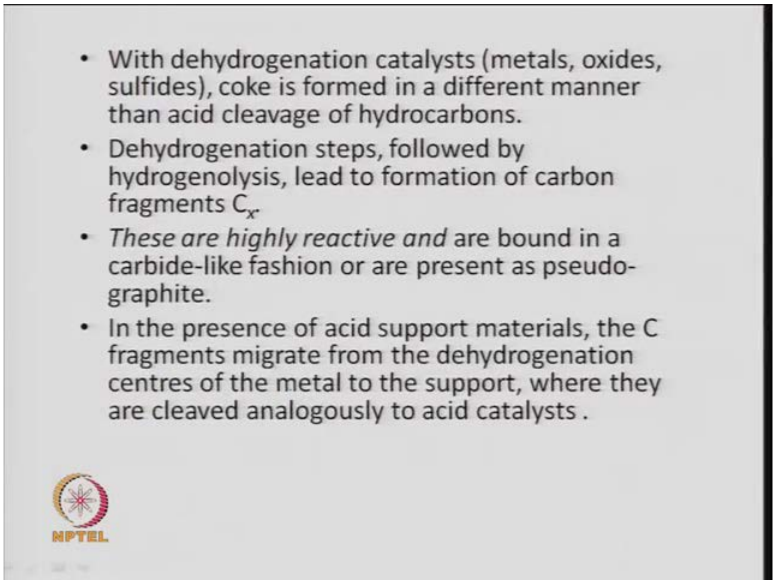

- With dehydrogenation catalysts (metals, oxides, sulfides), coke is formed in a different manner than acid cleavage of hydrocarbons.
- Dehydrogenation steps, followed by hydrogenolysis, lead to formation of carbon fragments C_x.
- *These are highly reactive and* are bound in a carbide-like fashion or are present as pseudo-graphite.
- In the presence of acid support materials, the C fragments migrate from the dehydrogenation centres of the metal to the support, where they are cleaved analogously to acid catalysts .

So, basically the dehydrogenation reaction is nothing but removal of hydrogen from the feed. S, it can be something like ethane the hydrogen and you get ethylene which is kind of cracking basically. So, for this case dehydrogenation catalyst where metals or oxides sulfides are used as catalyst the coke is formed in a different mechanism. So, mechanism of the coke formation is very complex and this, vary from the type of the metal and the type of feed stock. So, the coke is formed in a different matter compare to the acid cleavage of hydrocarbon. Generally it is, assume that during cracking reaction the hydrocarbon adsorb on the surface and then it dehydrogenises basically. Basically, it is cleavage of carbon bond not the so it is a kind of season beta season is the bond breaks into points and form. How, does the bond breaks that and that depend on the type of metal and also the bond energy.

So, bond story is to be understood in terms of carbon hydrogen carbon, carbon double bond and triple bond and the surface of the straight which has the kind of protons available acidity of the catalyst. So, that is one thing if you look at in one form the cleavage of with hydrocarbon a large molecular weight something like a normal obtain that something that has been cracked. So, haplite radical forms or methyl radical excel radical form and so, on change progresses. So that, is the different kind of mechanism but in the dehydrogenation and hydrogen is removed from the catalyst. So, in that case hydrogenolysis will also happen and that leads to the formation of carbon molecule that is coke formation. So, these are highly reactive but about the dehydrogenation if you look at the product the hydrogenous only says the formation of the carbon fragments that is Cx type.

So, they are highly reactive and a bond in a carbide like fashion or present in a pseudo graphite form. So, the carbon may be different form of carbon graphitic form of carbon. So, in the presence of acid support material the carbon fragment fragments migrate from the dehydrogenation center of the metal to the support. So, this is the kind of migration from the metal to the support site where they are cleaved analogously to acid catalyst. So this, what the mechanism shown here that this is a kind of support, so this is a dehydrogenation active site so the spices come here and adsorb from the surface and that it keep like this a kind of coke formation you can see here.

So, hydrogen is being removed and then the precise the magnetic support which has acidic site on a support. So, more coke formation on this kind of acidic support so you need to control that or at some kind of promoter to reduce this. And, finally if you look at here that makes a, dehydro aromatization type reaction. So, further hydrogen is removed and it start to form a ring compound cyclic compound. So, then more and more hydrogen is removed and then finally it gets a ploy cyclic aromatic hydro carbon so, that is your coke carbon precursor. Finally this, will result a coke formation it is complete nothing but a ploy cyclic aromatic hydro carbon condense ploy aromatic hydro carbon.

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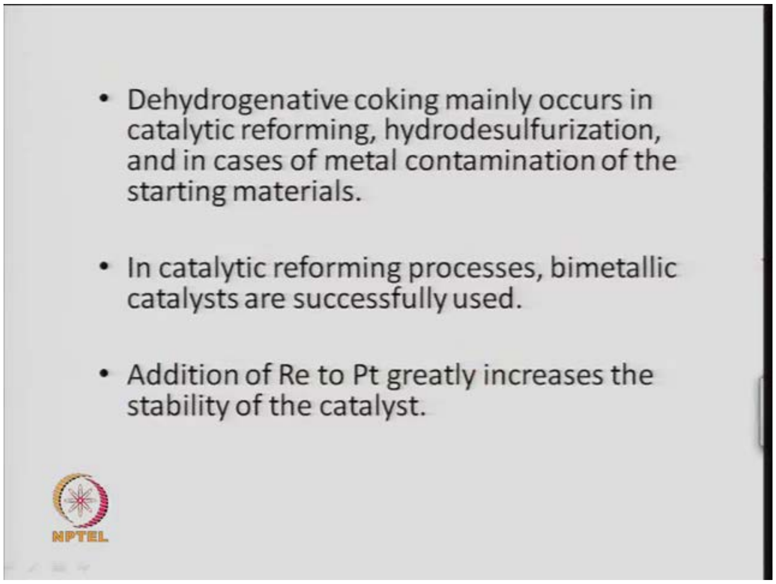

- Dehydrogenative coking mainly occurs in catalytic reforming, hydrodesulfurization, and in cases of metal contamination of the starting materials.
- In catalytic reforming processes, bimetallic catalysts are successfully used.
- Addition of Re to Pt greatly increases the stability of the catalyst.

So, here the Dehydrogenative coking mainly occurs in the catalytic reforming. So, forming catalyst are very much found to form coke formation large amount of coke form so the catalyst life draw more faster same to the hydrodesulfurization also, because feed stocking itself contain a lot of coke precursor and in the cases of metal contamination of the starting material because as I said continuously deposit on the surface of the catalyst that is again a forming. In, the catalytic reforming process generally to avoid coke formation the bimetallic catalysts are preferred if your bimetallic catalysts. So, these type of catalyst have shown the reduction in the coke formation so the catalyst life have been improved by using the platinum rhenium type of catalyst which is a bimetallic catalyst the details mechanism I am not disturbing at this point. But, one can very easily use this kind of bimetallic catalyst that is rhenium to platinum. And, it greatly increase the stability of the catalyst which is shown here.

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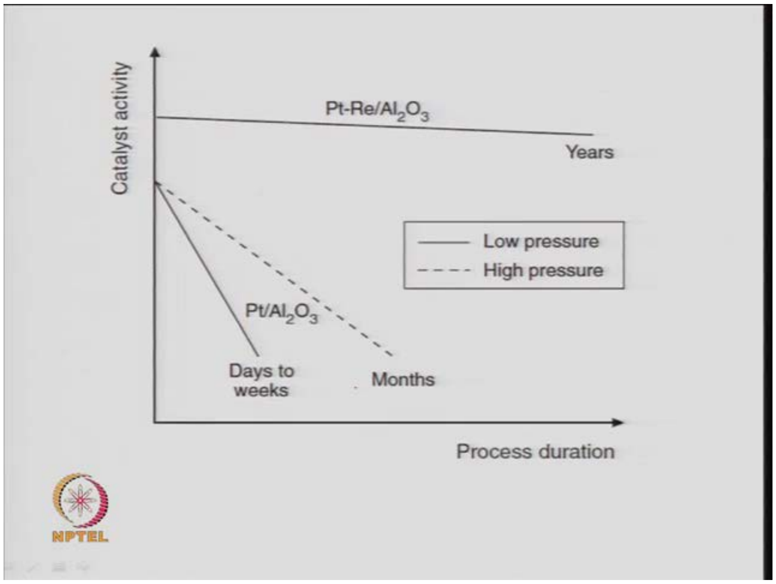

You can see here platinum rhenium on alumina catalytic the activity is almost constant and the catalyst can in last year’s. So, this can have 3 year life 1 and a ½, 2 year 3 year life but if you look at here. In, this case the catalyst life is just day a week which is a platinum alumina type. So, platinum alumina type catalyst has a kind of life which is of week order. But, if you do the operation of high pressure the life can be in 2 months that means you have two option one thing you optimize the process condition so, you need optimization.

So, in order to reduce coke from catalyst you do not operate reaction at very high temperature high temperature will be not good. But, high pressure may be effective so one need to do the reaction at high pressure. And, simultaneously one needs to look at a novel catalyst system just like a bimetallic system where the activity of the catalyst or ((Refer Time: 53:43)) of the catalyst in here because of the presence of the rhenium in the catalyst. So, this is a kind of reforming the catalyst which is used for the reforming of the lepta. So, reforming of lepta is finally is done to produce more and more aromatic hydro carbon an idea is that reformatted gasoline when the desire the high optimum gasoline. So, reformatted gasoline is produce by the reforming of this lepta compound but now a days you known that the high aromatic may not be desire so, this can be used for blending purposes.

And, to produce the aromatic which can be which can be used for petro chemical industry or ((Refer Time: 54:28)) chemical. So, once you have kind of deactivation you need to design a complete reaction. So, you need to find a out kinetic of main reaction you need to find out the kinetic of the deactivation of main reaction. And, then correlate this two together main reaction deactivation reaction and combine and use it for a reactive design. So, I just said that feed catalyst carking is one. But, moving by reactor straight through transport reactor these are other kind of reactor where continuously feed is being passed. You, find out what is the resident time in a reactor and then take the catalyst to the other regenerator unit and regenerate and send it back.

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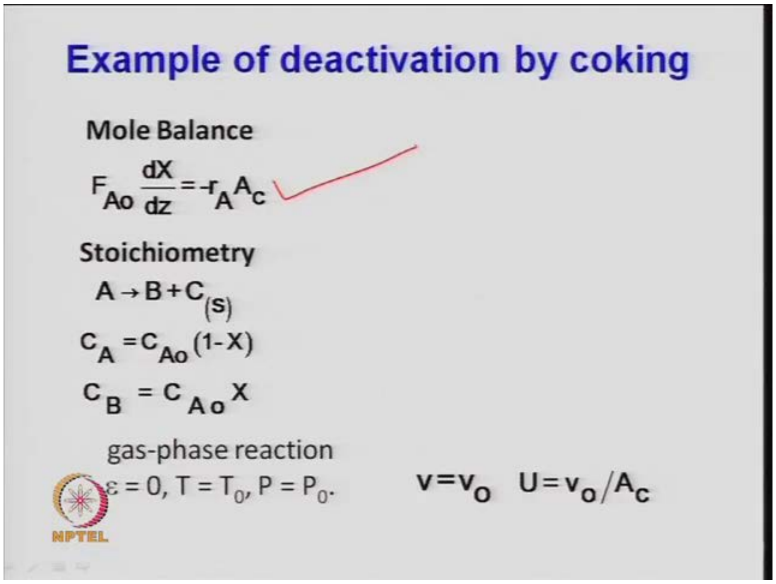

Example of deactivation by coking

Mole Balance

$$F_{Ao}\frac{dX}{dz} = -r_A A_c$$

Stoichiometry

$$A \rightarrow B + C_{(S)}$$

$$C_A = C_{Ao}(1-X)$$

$$C_B = C_{Ao}X$$

gas-phase reaction

$\varepsilon = 0, T = T_0, P = P_0.$ $v = v_o$ $U = v_o/A_c$

So, in all cases you need to write a mole balance equation which is you have already have done or we have discuss this FA naught dx by dz is equal to rA dash rA in terms of mole volume. So, rA time area for question whatever rA triple dash time AC. So, this your area for section of that reactor. So, one can very easily write the rate of reactor in terms of moles for volume or volume of mass of the catalyst and can be there and can write that question. So, FA naught dx by dz is simply mole balance equation, which is simply your minus rA times the areas process stoichiometry may be different depending on the type of the reaction.

So, A gives you b plus C. So, C is a kind of coke precursor coke is deposit in the surface of the catalyst the concentration of the A and B will be define beside on this CA is equal to CA naught 1 minus x. Which, has already has been discuss same thing CB, because one mole may react one mole of B will form surface naught x all can be written in the terms of the concentration so CA naught x times. If, it is a gas phase reaction so all of you known the homogeneous reaction kinetics so, that has been used here. So, the change in volume because this a solid coke which deposit in the catalyst and this your b which is your gas phase where there is no change in the volume of reaction.

So, functional change in the volume is 0 so, you are epsilon is 0. So, this a no change in the volume in the reaction temperature T is T0 and P is P0 volume florid V is V0. And, superficial gas velocity which is define as volume florid device by the area of cross, so that generally basically very important factor when you look at straight through transport reactor or a moving by reactor. So, how much time a catalytic spices or a catalyst spend inside the reactor that will depend on the superficial gas velocity. So, T time required in a reactor will depend on the length of the reactor dived by the velocity of the gas. So, that is height of the reactor basically or one can design height of the reactor or size a reactor if these two things are fake and the conversion is fake.