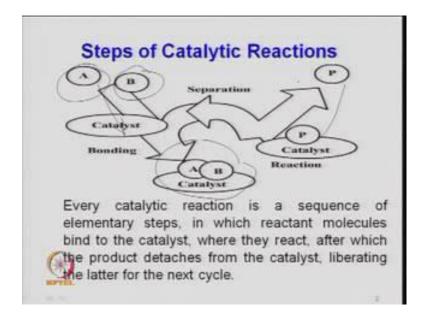
Heterogeneous Catalysis and Catalytic Processes Prof. K. K. Pant Department of Chemical Engineering Indian Institute of Technology, Delhi

Lecture – 02

In the last lecture, we were discussing about introduction about the catalyst and we were just discussing fundamentals of the catalyst. So, in continuation of that today I will just talk about some more fundamentals of catalyst their applications in industry and type of catalyst.

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The basic fundamental of a catalyst what we were discussed last time also is some metals and support and the species; gaseous species which adsorbs on the surface. So, if you look at here this the 2 reactant species A and B; they adsorb on the surface of the solid which is a catalyst.

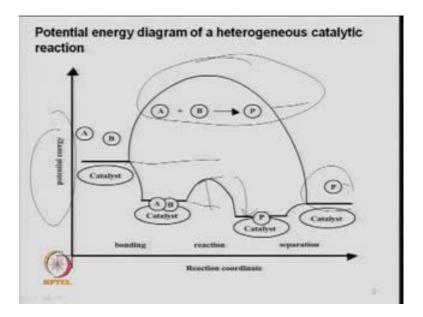
So, it can be a solid, it can be a liquid also. Here, we are talking heterogeneous catalysis so throughout I will talk about only the solid surfaces. So, basically solid surface as a kind of orientation the metals are oriented on the surface. And, how these metals are attached to the surface whether they are very strongly binded or weakly binded; depending upon that you will get a definite catalytic activity or the molecules which collides and strike on the surface will have some time to interact with the surface. Now,

it may retain on the surface or it may be repelled also; that depends on the material or electronic configuration of the molecule. So, lots of material science, lots of electronic configuration studies are also required when you look at a metal configuration; and selection and design of these metal and support.

So, here if you look at A and B 2 species they collide on the surface of a solid; and then they make some adsorbed species which is a kind of A, B right. So, it can be just like A is adsorbing on the surface and B is adsorbing on the surface. And, then they are transforming into some complex which may be A, B right. The same and this is happening because of the collision between the gas molecules the molecules are colliding. So, there is some kind of collision frequency. So, based on the kinetic theory the number of molecules which are striking on the surface and out of some molecules are adsorbing. And, that is what is defined sticking coefficient.

So, fraction of the molecule which are colliding and adsorbing on the surface out of that only a certain fraction will be effective for transformation into product. So, this is what the A, B a complex which is transforming into a product p; which is adsorbed on the surface again so p adsorbed. And, then this desorbs from the surface and separates. So, this is what we saw last time also; that when you look at a catalytic reaction it has lot of elementary steps. And, overall catalytic reaction it is non-elementary.

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The potential energy diagram what I discuss is the activation energy last time; and thermodynamics where you look at the delta g the gilts free energy minimization fundamental. So, when the gibbs free energy is 0 the reaction is not possible and you call that the reaction is at equilibrium. And, which is related to your equilibrium constants, equilibrium composition; and maximum conversion during a reaction in the presence of catalyst.

So that is why the catalysts are very specific in their action. We call it specific of the catalyst. So, specific activities of the catalyst are that. So, potential energy versus reaction coordination if you look at so the molecules are adsorbing. So, adsorption is generally the exothermic reaction right. So, they will have some kind of energy of surface and exothermic.

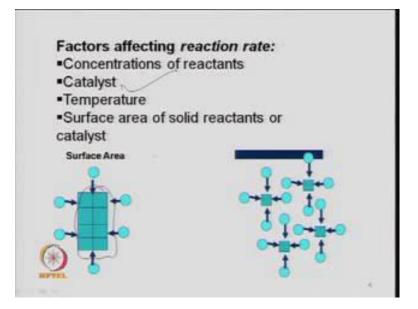
So, heat will release; so energy of the molecule will decreasing right. And, then the kind of energy which is required for the transformations. So, this is just for saying non-cat reaction here that a without a catalyst. So, A plus B and the kind of transition complex which forms here and that transforms into a final product p. So, this will be some kind of activation energy required for the reaction. In this case if you look at the reactant and the gas molecules that A and B and finally p. So, whatever the enthalpy of the product minus enthalpy of the reactant you call that heat of reaction or if you define the gibbs free energy.

So, accordingly you can calculate the activation energy for the non-catalytic reaction. And, when the catalyst is available on the surface; so it is adsorbing so some kind of heat of adsorption; and the it is transforming into some transition state. So, it different transition state or different product which is intermediate now is forming in the presence of the catalyst. And, then this catalyst this intermediate because it is highly energized molecule; and what you call it transition complex unstable type of molecule. So, this will remain in the reaction only for a small period of time. And, finally it transforms into a product species; it may be on the surface of the solid itself or it may be on the gas phase also.

So, it they lot of complex mechanism may be available for depending upon the solid, depending upon the gas. And, finally this comes to the surface. So, overall energy if you look at the delta g for the system is not changing whether it is a catalytic reaction or non-

catalytic reaction. And, in most of the cases generally we assume that the heat of adsorption and heat of desorption is almost similar. So, ultimately it becomes whatever the overall heat is nothing but the delta g of the product minus whatever delta g of product minus reactant; we call it in terms of the energy of the reaction.

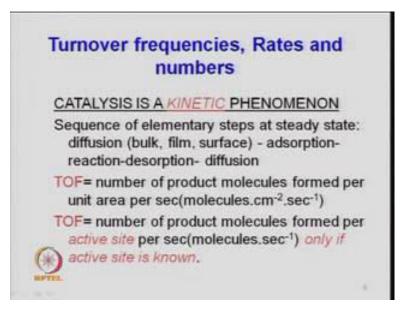
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If you look at the design; the catalyst design selection of catalyst and the finally the for a given reaction it is a very complex system. So, depends on the concentration the how faster reaction takes place in a reactor will depend on the concentration of the reactant species. So, high or low concentration or what you say in terms of the partial pressure of the gaseous species. Then, catalyst of course but we are looking here temperature; reaction temperature is very crucial, surface area of solid reactants or the catalyst is also equally important in the case of heterogeneous reaction.

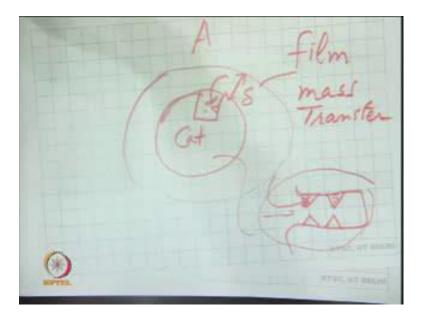
Because the reaction is actually what you look at here these are the molecules which are coming to the surface. So, how much is the surface which is active actually for the reaction or what is the total surface area of the solid that depends? And, then the molecules are colliding on the surface and then are transforming into the product. So, the surface area of the catalyst is 1 of the important factor; which gives the high amount of metal dispersion on to the surface or sometimes the support itself takes part during the reaction. So, the metal surface area is again a very important during the chemical reaction factor.

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We have already discussed this last time that the catalysis is a kinetic phenomena right. So, it means the sequence of elementary steps which are taking place during the reaction there are diffusion basically what we say the molecules there is a gas, there is a solid surface. So, on the surface so details I will talk later.

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But quickly of I just look at suppose there is a solid; so a gas is coming to this. So, there will be a transport limitation because the gas this is the film of the gas. So, this is a gas

film. So, which may have a certain thickness of delta? So, the gaseous species has to cross this barrier and come to the external surface of the solid.

So, this is the catalyst here right. And, this catalyst will be a porous material; so on this the diffusion will take place. So, this is known as the mass transfer stop basically here and external mass transfer. So, this gas depending upon the resistance offered by the gas film the transport resistance may be high for the gas site right. So, this may be one of the resistance which is offered.

So, here and then it is diffusing inside the pallet for chemical reaction. So, chemical reaction is inside a pore of a catalyst because if you look at the surface of a solid there a lot of cracks here basically. And, what we call them pore; if you look at the structure or a macroscopic view of a catalyst. So, this is 1 pore of a catalyst. So, there may be millions of pore inside a catalyst; where you are depositing your active metal.

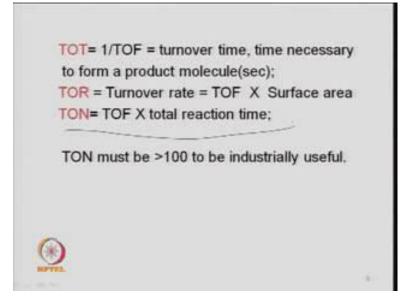
So, this is our active metal which will take part during the reaction. So, this gaseous species are adsorbing here something. So, your chemical reaction term if you look at that is basically on this surface which is a micro pore or macro pore inside a large pore pallet geometry right. And, the similar reaction or regular reaction is happening in all channels which are millions in the number.

So, that is the crucial factor in terms of catalyst design. So that how do you generate these kind of pore structures or porous structures and allow the metal to deposit on these structures, right. So, this we will discuss in detail later; but right now, what I am talking here that this sequence of elementary steps which I am talking here in this, it can be a mass transfer step, it can be a chemical reaction step right.

So, this bulk film surface what you are talking is diffusion or external mass transfer step right. And, when it reach to the surface; when the gas species is able to reach this point then we are talking about the chemical reaction; then we are talking all the steps which is something like adsorption on the surface right. So, this is the adsorption, then you have a chemical reaction and then the transformation into the products species which is adsorbed product species. And, then that product species is transformed into product. So, it is a series of steps which takes place during in the reaction and we have to just eliminate the resistances during the chemical reaction. So, there may be a large number steps which may takes place during the chemical reaction. So, turnover frequency we are defining because I said a large number of metal concentrations may be available on the surface of a catalyst. But the effective when I say the rate of reaction is effective only on these active centers. So, these are very crucial; that the number of these active centers which are effective for chemical reaction actually. So, that is we define in terms of turnover frequency which we are already defined last time also; that the number of product molecules formed per unit area per second right.

So, this is a kind of rate of reaction but only on the active surface. Because the catalyst surface may be a large surface as I said just like a football ground that where we have a large surface area. But the if you are just cultivating a kind of grass on that then; that specific points where these are locality they are a specific in terms of the production right. So, it is something like a large surface area 220 meter square per gram or even larger say 1000 meter square per gram which is a support surface area. And, all do support you are depositing the metal and that is where you are getting the kinetics of rate of reaction.

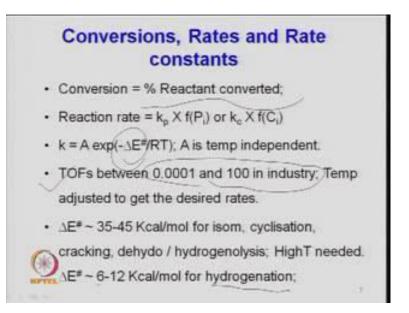
So, turnover frequency is basically number of product molecules formed per active site per second right. And, this is only when the active site is known; if active site is not known then you can just define in terms of per unit area of the sometime metal surface is alike right, some time you define total surface area of that catalyst. So, there can be different definition for turnover frequency. (Refer Slide Time: 12:17)



And, sometime we define turnover time also. So, again it is the time necessary to form a product molecule. Basically in that how much time it takes to convert a reactant species into product species? So, basically this will be a used for the design of the reactor right. So, how much what should be the size of the reactor in order to get into the given the productivity.

So, you can just correlate with the catalytic activity. And, then another definition turnover rate we have already defined last time is nothing but the turnover frequency which multiplied by the total surface area of the catalyst or in other words what we have defined last time that, how much or the cycles that catalyst can be used again and again; and we define that in terms of the turnover number. So, catalyst life can be or stability of the catalyst can be defined based on this factor turnover number. So, it must be greater than 100 for a good catalyst.

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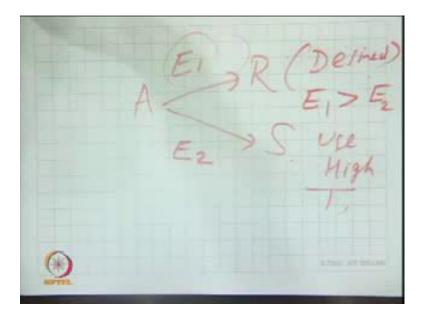
Some simple general definitions which are generally used in catalytic reactions, the conversion. So, all of you must be knowing before also it is nothing but the fraction of the reactants which is converted into the product. So, the that is known as fractional conversion and if you define in terms of percentage. So, that is known as percent conversion right reactant which is converted into a product right. And, the reaction rate all of you know that also; that is number of molecules reacted per unit time per gram of catalyst.

So, generally when you talk a heterogeneous catalytic reaction; we define it in terms of moles reacted per unit time per gram of the catalyst. So that, that is something you are looking at catalyst activity we defined it in terms of turnover number or turn over frequency. But otherwise it is generally per gram of catalyst because most of the time you do not know the number of active centers present in the catalyst.

So, basically this will be a function of your rate constant; the pressure partial pressure of the reactant species or concentration likewise right. So, the rate is generally a function of temperature, concentration right or in terms of partial pressure or temperature. So, in a equation which is related to the rate of reaction k is equal to A e to the power minus e upon RT; where e is the activation energy of the reaction right. So that is just indicating that activation energy if it is high for a reaction. So, it may you need a high temperature

for that reaction right. So, and suppose if you have a multiple reaction where the reactant goes to A goes to R.

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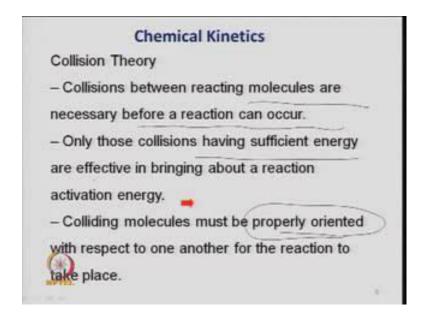
And, A goes to suppose I have reactions something like this; A goes to R, A goes to S and this reaction has activation energy E 1, this reaction has activation energy E 2. And, suppose if I say R is the desired product. So, you can have some idea that if you have higher temperature; the higher temperature favors the reaction of higher activation energy. So, it means if you E 1 is greater than E 2 then use high temperature right.

So that equal to this. This is related to the selectivity of a product that it desired product divide by undesired product. And, that can be calculated based on simply ratio of the this moles of this produced divided by moles of this produce and that can be related in terms of rate. So, you can very easily calculate this number; so and generally pre-exponential factor a is temperature independent right.

So, turnover frequency between 0.01 and100 industry; 100 is used in the industry. And, the you can get now set the temperature because the increasing the temperature well increase the rate right. So, whether reaction endothermic or exothermic it does not matter. So, rate is always increasing with temperature right. So, you can have that depending upon temperature you can adjust this. So, the activation energy actually as I said here; that if you have a reactions something like mass transfer controlled reactions or diffusion controlled reaction the activation energy value is low.

But when your reaction is kinetic controlled the activation energy will be higher. Higher means something of the order of say what is mentild here that 35 to 45 kilo calorie per mole. So, generally if the activation energy is more than 20 kilo calorie per mole it means the reactions are towards the kinetic control; what diffusion control reaction the activation energy will be low. So, most of the reactions something like isomerizations, cyclisation, cracking, dehydrogenation hydrogenolysis. So, a high temperature is required right in order to activate the reaction whereas for this hydrogenation reaction generally the activation energy of the lower of ((Refer Time: 17:03)). So, that we will discuss later.

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Now, what we have discussed is that the a surface metal surface or supported on some surface the type of metal. And, which is interacting with some support and the gas species which is adsorbed or adsorbing or what you call a reactant species. So, basically the there are different theories are available for kinetics. So, the collision theory is again one because this is what I told earlier is that the molecules are colliding based on the kinetic theory of the gas right. And, this is nothing but the number of collisions between the molecules; and then transforming into a product when you have a simple gas phase reaction right the homogeneous type of reaction.

So, collision between reactive molecules right are necessary before the reaction can occur. So that is the first thing that; there should be a some kind of kinetic energy and translation energy, vibrational energy which is available in a molecule. So, depending upon the energy they are just colliding among themselves. So, only those collisions having sufficient energy are effective in bringing about reaction activation energy. So, all the molecule may not be active right. So, only some molecules which are able to adsorb on the surface. And, they have the sufficient amount of energy to transform that adsorb species into a product that is or intermediate that only can transfer into a product species.

So, that is why this is a very crucial factor that the all molecules; which are the concentration when you are increasing the gas phase does not mean that your rate is high or does not mean your conversion is high. Because it will depend on the active molecules which are adsorbed on the surface and then they have transferred. So, it will depend on the orientation of that metal and also the electronic configuration or the molecular property of that gas molecule which is reacting. So, colliding molecule must be properly oriented. So, this is very important now when you look at a selection of a metal or a given reaction. So, the now lot of softwares are available you can use the tools or you just study the chemical bonding of these molecules and the support electronic configuration. And, then you can choose a kind of reaction.

So, density ((Refer Time: 19:19)). Suppose based on that you can identify if you have these kind of reactant or molecules and if you have this kind of metal. Then, what kind of product you can get right. So, based on which will be related to thermodynamics. So, thermodynamic check the possibility and then all this configuration; and then wherever the energy reaches to a minimum level right. And, accordingly you can have the series of the product distribution from a reactant gas molecule.

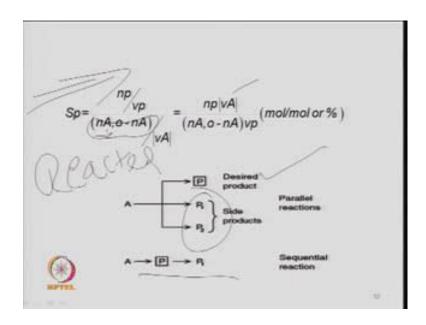
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Selectivity The selectivity (*Sp*) of a reaction is the fraction of the starting material that is converted to the desired product P. It is expressed by the ratio of the amount of desired product to the reacted quantity of a reaction A. In addition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

So, selectivity is very important when you look at a catalytic reaction especially for the multiple reactions. And, where there is a probability of transforming A or getting a different kind of product from 1 reactant species. So, basically it is defined as a fraction of the starting material that is converted to a desired product. So, basically what fraction of the material is converted? So, sometime we define the moles of the product formed divide by the moles of the limiting reactant reactor right. So, which is controlling the rate of the reaction? So, expressed by the ratio of amount of desired product to the reacted quantity of reactant A right. In addition to the desired reaction parallel and sequential reaction can also occur.

So, mainly for the multiple reaction when you are doing then the selectivity becomes a very important parameter. So, there may be different definitions for defining the selectivity. But general definition is that moles of the product formed divide by the moles of limiting comp1nt. But other as I said in the multiple reaction you can have the moles of desired product divide by moles of undesired product also. So, there you try to maximize the product compare to the undesired. So, especially when you look at the atom efficiency.

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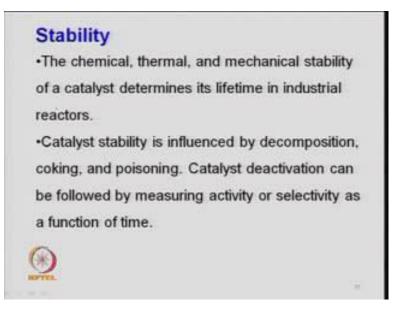
So, this is what the definition of selectivity that is n p is the number of moles of the desired product; mu p is its stoichiometric coefficient right divide by n A 0 is the moles in which is at t is equal to 0; initial number of moles of reactant a right. And, n A is the final moles of a which is left after reaction. So, basically n A 0 minus n A is the number of moles of a reactant right.

So, this is the reacted moles; moles reacted and divide by what we are writing here because we are defining it in terms of their stoichiometric coefficient right. Because your n number of a moles of a can give you n number of moles of the R or product right. So, we are just talking per mole of A if reactant then how many of moles? So, we just divide by their stoichiometric coefficient. So that in 1 way the definition of selectivity is nothing but moles of the comp1nt i formed or product i formed divide by its stoichiometric coefficient divide by moles of the reactant reacted divide by a stoichiometric coefficient right. So that can be a very general definition.

So, most of the when you write the multiple reaction or reforming reaction. So, we define it in terms of this as for the compression of the product right because per mole of the reactant how many reacted; so you can very easily calculate from this. So, this is mole or mole percent either basis it can be given. So, this is the where the stoichiometric coefficient can be negative or positive. So, we always take it a mod of that is a stoichiometric coefficient right.

So, this is what the reactions on so A goes to p and which is a desired product here; and then it go to p 1 p 2 undesired; and it can be like this also a series reaction right. So, selectivity can be defined here in terms of desired product divide by undesired product also; it can be define desired product divide by total moles of the product form also right. But in most of the cases the selectivity definition which is generally for usage purpose also is that right.

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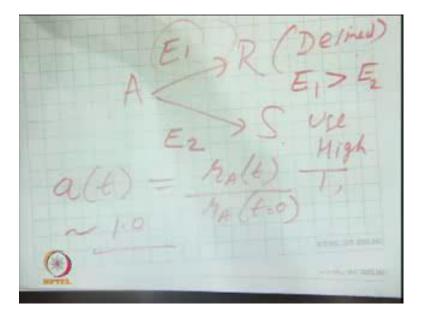
So, we will look at a catalyst then will talk in terms of the activity right that is towards how fast is the rate of reaction; that is 1 thing. Then, selectivity that is how much is the desired product you are getting? But again the more important factor is stability right deactivation property of that catalyst; because we do not want the catalyst for a shorter period. So, we want that the activity should be prolong for a larger time without decreasing the product concentration or product productivity of for the given reaction.

So, the stability of the catalyst is again important for checking or short listing the catalyst. So, the chemical thermal and mechanical stability all it can be the poisoning because of poison precursor, because of high temperature right, prolong high temperature and environment. And, it can be the mechanical stability like an fluid catalytic cracking or moving by reactor where the particles are colliding among themselves right attrition. So, it should have sufficient attrition resistant and enough mechanical strength right. Because they are striking among themselves and that time they may crumble. And, when

the particles get a smaller in size it may leave the reactor right because you are improvises by reactor condensations.

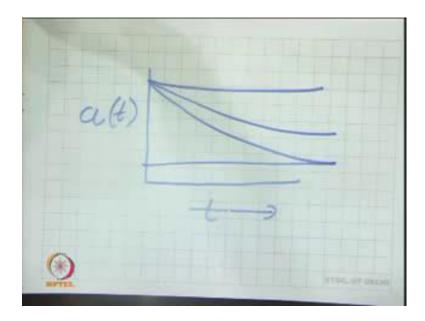
So, this is very important. So, catalysis stability it can influenced by decomposition by coking by poisoning. So, we will talk on that later. And, deactivation can be followed by measuring activity or selectivity as a function of time. So, last I was last time I was defining the rate at any time t divide by initial rate right. So, generally that is defined in terms of the catalyst activity if I just look at briefly I will talk right now.

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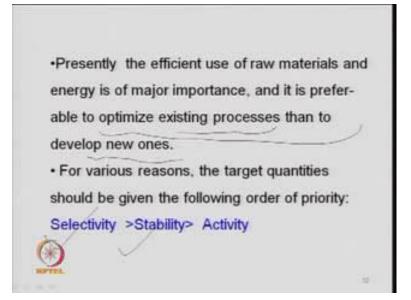
So, a is a function of time is nothing but r A at any time t divide by r A at t is equal to 0. So, here we are just defining the rate for transformation into a desired product. So, this if this is activity theoretically we want 1. Because all the time that the same rates should be achieved but it does not happen because in most of the chemical reaction either because of the dispersion problem; that is molecules are coming together they are reacting. So, dispersion is decreasing right they are colliding; so the they become larger in size. So, surface area decrease.

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So, because of these problems your activity graph which is a as a function of time now at here if you time on a stream. So, it can go like this right, it can go like this also. This is because of what we are talking the activity of the catalyst is decreasing. And, it can go like this also when there is severe coking like we have to look at a fluid catalytic cracking unit like the they may have this kind of deactivation problem. So, you have to look at continuous regeneration of the catalyst if possible right; otherwise discard the catalyst and look at for a new first catalyst. So, this is another challenge when you select a noble catalyst for a system.

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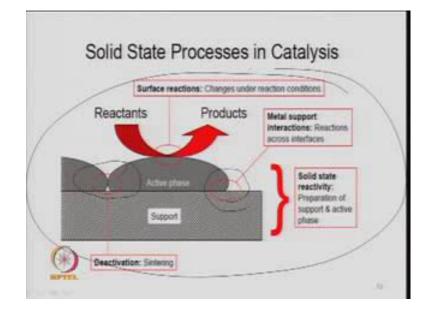


So, if you look at presently we currency in the efficient diffusion of raw material and energy is of major importance. So, this is what the application of catalyst in the current scenario. So, that is the new energy sources we need. We need alternative energy alternatives we need existing catalogy where the conversion maybe a problem, catalyst deactivation maybe a problem, the productivity maybe a problem the desired product what you want it may have lot of undesired product also; and that is the concept of rain catalyst now a days. So that is what we are looking the optimize the existing process and rather than developing new one. So, there are still lot of challenges as I say again and again that fisher top process it is a 80 year old process right; where the sin gas and hydrogen is converted and you get methanol, you can get gasoline, you can get diesel right a series of or alcohols.

So, series of hydrocarbon can be obtained from this fisher top process. And, developed during 80 years before by a shore technology right in South Africa they have a plant on that. But the new trained what says that you need a narrower down product distribution right. You are looking for some different kind of poles right and you are gasifying coal converting into sin gas and then neutralizing. So, your trends are something that the traditional catalyst which maybe iron based or cobalt based they may not be sufficient for this kind of reaction right. You need to change the activity, you need to look at that texture property of the catalyst mass transfer limitation, diffusion, pore structure and stability of the catalyst. So, this is the meaning here that it is preferable to optimize the existing processes and then develop the new one.

So, there are still lot of challenges where the technology which have already been developed they need the revamped right; they need to be upgraded. So, we need to look at new catalyst new process for these kind of process. So that is a challenge. So, for various regions the target quantities should be given of the following order of priority. First preference we give to selectivity that is the desired product; then we look at in terms of stability; and finally in terms of activity. All these terms are equally important in 1 way but when you look at the compression then we just see that the it should be selective in reaction. Then, it should be stable also simultaneously and activity for the reaction should be high right. So, these are that is the property of a catalyst should be compared in all way.

But when you look at you have to look at a pure balance or optimize these process and then select the best catalyst for those process.

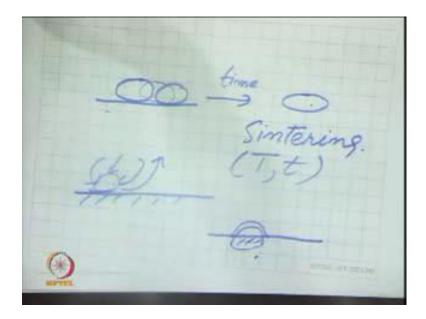


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Before going for details again just I want to say the same thing; but here earlier also I discussed that the reactants they come on to the surface of this is a kind. How does a catalyst look on a surface? So, this is a support, right. The support objective is to provide you a high surface area or something like a base on which the metals can be placed or adsorbed or maybe just a placed on that in terms of physically. But generally we look at a kind of metal support interaction.

So, a basically it is a platform for the metal. So, active phase is this one, this is your metal part here and these metals may club like this. So, there may be different metal. So, when the sintering takes place so this is the problem this is a high temperature reaction here. So, these 2 particles may enumerate and you can get a bigger particle. So, why sintering happens?

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It is because of the time course temperature. So, initially the metals are well dispersed like this right. So, these are nothing but in terms of crystal size if you look at it if you look at their structure. So, they are well dispersed but what happens due to time course when the catalyst has been used continuously. So, these 2 make plug together and make like this a bigger particle.

So, they are joining here like this, right. And, this is nothing but because of solid-solid reaction. Metals they are interacting and they may give you and this is the problem when you have a nano particle. Because they are unstable and these stable particle for a long period of time is a challenge here. So, this is what called sintering of this; which is because of temperature and time. So, high temperature reaction and for continuously long period of time. So, you may have the growth of the crystal. So, crystal size is increasing and because of the increase in crystal size surface area reduces. So, activity will reduce. So, that is a another challenge or problem in the case of catalyst surface.

So, the actually if you look at here the metal support interaction; another important property here that we will discuss again in details later that the reaction across the interfaces here. So, the sebatiate principle says that the metal and support should be interacted. But if the binding is too strong then metal will have the more chemisorption activity towards the support rather than a gas molecule right; and if the binding is too strong weak. So, what will happen? The metal will leave the surface right. So, we need to tune

this thing. So, neither the metal has a very strong interaction with the support nor it should have a very weak. So, this is the in one way that if you look at I want to dispersion like this just attach to the surface like this.

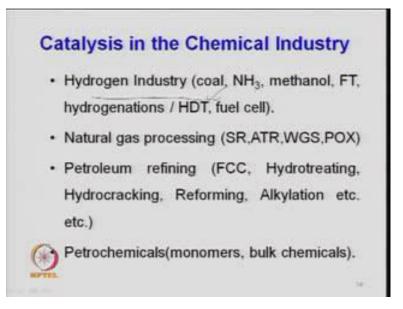
So, what is advantage here? Every surface is expose for chemical reaction here the molecule can come and strike on the metal throughout right. So, but the problem is that in this case it is a weaker kind of adsorption. So, what will happen the metal itself because of high temperature when you heat it; the metal itself may leave the surface.

So, this is known as a weak metal support material. And, the second scene may be like this you have a metal which is binded to the support like this. So, more oriented towards the support side and less expose to the gas molecule which is coming to that. So, this is the strong metal support interaction here right. So, this is also not good because you have wasted part of the surface area of the metal.

So, this is again a part of design or catalyst selection or catalyst design. So, you need to look at that we should have so this is shown here metal support interactions are it strongly binded. And, we need to tune these metal support interaction while designing a catalyst. And, if you look at solid state reactivity though preparation and support the active phase. So, this you have to design during your catalyst preparation. So, what temperature you are doing the heat treatment or aging? Then, how those your catalyst is prepared from which solution, what was the p h right, what was the heating rate, what was the agitation speed? And, then finally you are doing calcinations and reducing it.

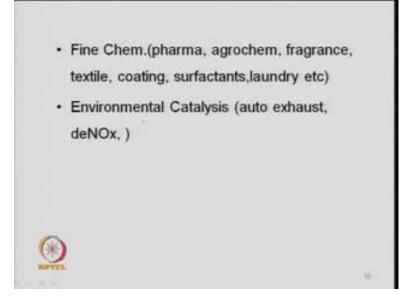
So, many factors are involved when you look at this complete geometry or a complete catalyst preparation. So, we need to look at a science here we need to look at art here; and simultaneously we have to look at electronic configuration of the metal and support. So, it involves the chemical engineering, chemistry physical science, nano science, nano catalysis and electronic theory also right. So, many things are associated when you look at a better catalyst design or select a good metal and support for the reaction. So, large number of catalyst are being practiced in the process industry right different process industry.

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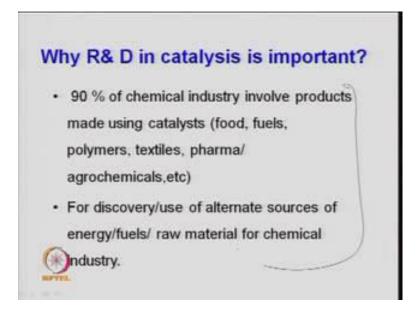
So, I told that it is a billion dollar business and different process industry is different kind of catalyst. So which may be patented or licensed right? So, if you look at hydrogen industry the generally they for coal, ammonia, methanol, fisher crops, hydrogenation, hydro treatment, fuel cell. So, lot of catalyst are being used here natural gas processing again esteemed forming, auto thermal reforming, water gas saved, partial oxidation. So, these all process need catalyst for the reaction petroleum refining, abscissa, food catalytic, cracking, hydro treating, hydro cracking, reforming, alkylation; they need a catalyst petro chemicals, no more bulk chemicals, pharmaceutical industry right.

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Fine chemicals, agro chemical, fragrance, textile coating affected where ever you see the process you find a catalyst for the process right. Because you need to develop a selective product right. So, you need to have the high efficiency, high productivity. So, you need something which is a foreign element but it increase the activity for that reaction. So, something now the environmental catalysts you must attain automatic exhaust catalyst known only converter right. So, they are again the or socks, knocks right volatile organic carbon. So, 3 way type of catalyst are used nowadays in your automotive vacuole side for the treatment of these types of pollutants. So, we will talk on that later.

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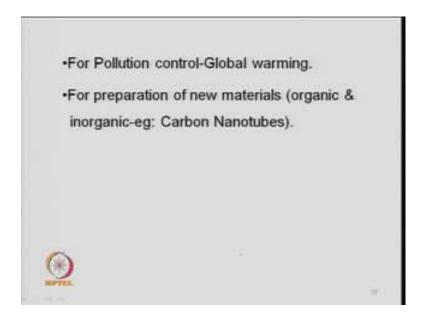


Why R and D's catalysis is important because lot of R and D's being done in terms of catalyst design, catalyst development, new process development, novel process development, new technology. So, for all these you need a catalyst right. The reason is that the 90 percent of chemical industry involve products made using the catalyst; whether you look at food industry, you look at a fuel industry, polymer, textile, pharmaceutical, agrochemical in every area the catalyst plays major role.

So, even the bio-catalysis nowadays; enzymes which are nothing but the proteins. So, a different kind of catalyst system but again you be or again are being used for the process industry. And, need to be developed for the novel process for their technology also. So, for discovery use of alternative sources of energy fuels, raw materials, for chemical

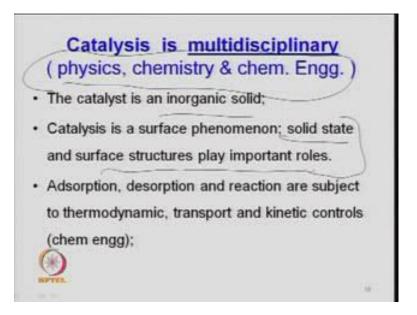
industry again you need a catalyst right. So, lot of R and D is being done in these areas. And, new technology have come up also and more yet to come.

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Same thing for pollution control global warming. Nowadays carbon sequestration, carbon taxing you know right So, you to sequestration is to be done for the removal of carbon dioxide from the environment or minimize the elimination of carbon dioxide from the environment right or just control it from the source itself. So, in all cases you need a catalyst. So, catalysis basically is a multi disciplinary if you look at here; that is whatever we have read so far that it requires physical science, it require chemical science right and nano catalysis material science.

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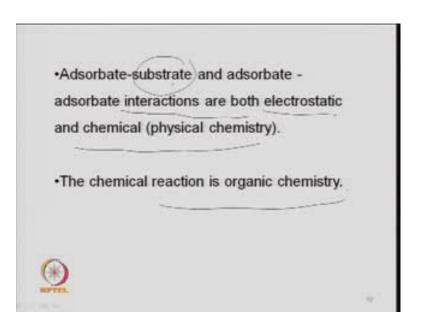
So, basically all these fundamental things are involved when you look at the phenomenon of catalysis right or development of a new catalyst, development catalytic process you should learn all these things right. So, the catalyst basically in organic solids. So, it can be other also polymer based catalysts are also being used now a days ligand based right, organo metallic complexes. So, different kinds of catalysts are general being used. So, basic mainly it is inorganic solid say alumina, silica right all these kind of materials support. And, then metals right the catalyst is a surface phenomenon I have already said this solid state and surface structures play important role. So, this is what crucial in terms of the preparation of the catalyst right.

So, what is the structure? How these molecules or metals are oriented right where as they are face centered, body centered, cubic centered. So, accordingly they are orientation of the molecules right which you identify from x ray fraction patterns that how these metals are oriented or what is the configuration? So, the depending upon these orientation f c c; you have to say 1 0 0 or 0 1 1 something like that there can be different orientation or an x y z plane if you look at right. So, depending upon that the gas molecule comes and strikes on that and adsorbs there. So, rate of adsorption is strongly depends on these and that is your what you call electronic theory of that right.

So, the catalysis involves that electronic theory. And, so during preparation you get these kind of structures and adsorption, desorption and surface reactions are again subject to

the thermodynamics, transport and kinetic control. So, they are you need a chemical engineering right. So, this is involving your physics, this involves your chemistry and then finally a chemical engineering. And, when you select a metal you look at their s, p, d structures right because d orbital's they have unpaired d orbital's all these metals. So, they are more active as a catalyst right. So, to have a kind of activity you need a kind of exchange of the electrons right. So, how fast they can do that that is the exchange the electron that will give you a different kind of catalytic property right. So, this is very crucial in terms of catalytic design or selection.

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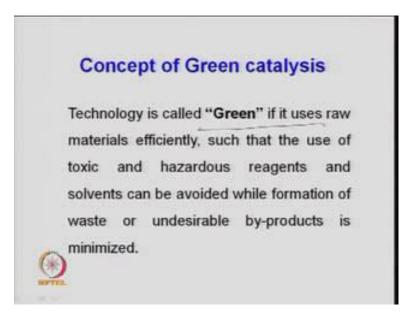


So, adsorbate substrate again or adsorb it adsorbate interaction. Adsorbate means the gas specie right which comes at the adsorb on the surface right. So, and this solid is an adsorbent. So, adsorbate adsorbent interaction. So, substrate I can call as an adsorbent this 1 right. So, this is adsorbate, adsorbent, substrate where which is your catalyst basically right or adsorbate among them also the molecules are colliding right to gas a gas b. So, they are colliding in the gas phase right or the single molecule they the hydrogen say this colliding among itself right. So, there also there is a collision between different kind of molecule or same kind of molecule that is similar to what you are kinetic theory of the gases right.

So, depending upon that so the molecules may dissociate they may associate right and then they adsorb on the surface also. So that depends on your temperature condition, your reactant condition right. So, based on that or collision theory. So, there may be a different kind of interactions and that is associated so are both electrostatic and chemical. So, this is part of physical chemistry right. So, kinetic theory of the gas and then chemical reaction basically organic chemistry but that can be the other kind of theories also involved in that right. We are talking now a days green chemistry and catalysis right.

So, what is a new thing green catalysis the concept is same right. Now, the only thing that as I said that R and D is being done in order to develop new product. R and D is being done in order to utilize the catalyst properly or efficiently right; C o 2 should be removed from the environment or should be minimized in the environment right. And, similarly for other gases methane all these global warming gases or green house gases right which may cause that the disturb the psychological system right.

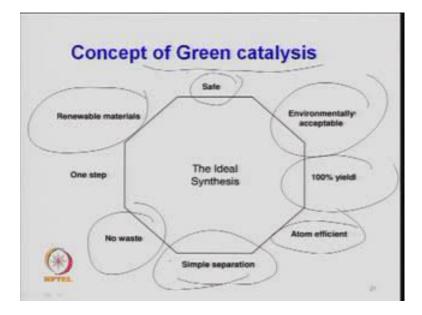
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So, the technology is called green if it use raw materials efficiently right; that is the first basic thing that all the materials or all the raw materials which are being used in the process should be utilized properly right. So, 0 waste basically, discharge of this 0 waste discharge right. So, efficiently such that it use; the use of toxic and hazardous reactants and solvents can be avoided while formation of waste or undesirable by product is minimized. So, this is the new concept of green catalysis. And, Sheldon has just defined this a scientist who has just talked on concept of green catalysis. And, they just the group

research group wide this research being done now a days. In order to develop new technology, new process and that which use these reactants and converts everything into a product or a byproduct; which can be used for some other process right rather than wasting. So, this is known as a green catalysis. So, what you look at here the structure right.

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So, this the green catalysis concept is that we need to develop a safe technology right. So, it should not harm the society right that is one thing and catalysis the role here. So, a safe technology; environmentally acceptable right free from pollutants; yield everything what you are looking that should be in terms of desired product right or the byproduct even if it is being generated that should be reused in the process or should be used by some other process; efficiency every atom is counted now. Earlier we were talking overall efficiency but now we are talking atom efficiency. That is, how many moles of the product or instead of talking that we are saying atoms produced divide by other total what are the other atoms or byproducts form right.

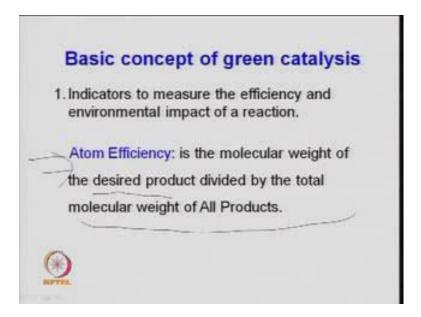
So, atom to atom you are looking now right. So, atom efficiency I will just define this term again. Simple separation is easy that is problem with the homogeneous catalysis right; when you have a same phase system. Then, the separation of this catalyst and the product is a problem right. So, that is why the all though the homogeneous catalysis is better it is high conversion right but the problem is separation and purification. So,

simple separation is required no waste. So, this is the 0 based discharge right. So, then the steps number of step should be limited right in a shorter step you should get. So, what will be the advantage? Your size of the system will reduce right because if you look at just a if you are something a coal can be converted to liquid fuel in single step rather converting to a sin gas. And, then you are converting using the fissiotropy is there any technology by which coal can directly be converted to liquid right.

So, your numbers of steps are reduced right. And, then you have to look at the exergy analysis or energy whether the process should not be energy intensive at the same time right; same thing for bio mass conversion to liquid fuel. So, you need to look at the technology, you need to look at the process which is environmentally friendly 0 waste discharges right. And, all kind of renewable materials that can used in the process right.

So, because the energy sources are limited right. So, we are looking alternative sources of energy. So, if you have these kind of technology where these renewable biomass or all these kind of waste materials; and they can be converted into energy that is again a good thing. So, the this is the concept of green catalysis that you develop a process; and the catalyst in such a way that it should fulfill all these requirements right.

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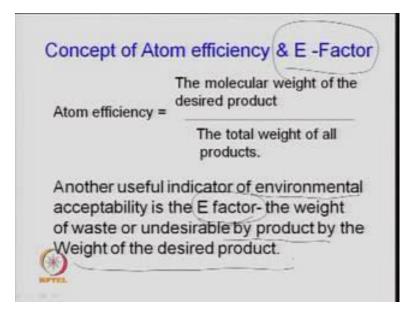


So that is what I was talking in terms of the green catalysis concept; the important thing is now atom efficiency right. So, atom efficiency is basically nothing but the molecular weight of the desired product divide by the total molecular weight of all the products right. So, if you are saying that you are a goes to p plus q in a single reaction even right. So, we are counting the molecular weight of p divide by the total weight of p plus q right. So, especially when you look at the pharmaceutical industry or specialty chemical this number is very small. Because you look a small suppose if you have a extraction process that simple extraction process.

You are taking a seed cloud say right and from that you are extracting its oil. So, oil percentage is very low just 8 percent or 10 percent oil in a seed right cold seed, linseed oil when you are taking. So, the percentage wise when you are developing the process the maximum yield is say 8 percent. So, what will do what will you do with a residue? So, try to convert into some other useful processes right or other useful product converted into energy because residue may be able to convert right.

So, these are just concept in terms of the new technology or new process which is nothing but a green technology or green process. So, you need to develop a technology such a way that molecular weight of the desired product should be that is divide by the total molecular weight of all the products should be high right; atom efficiency that is everything is converted to the desired product right that is the idea.

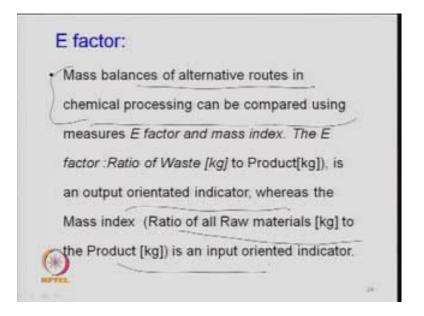
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So, concept of atom efficiency the bio and the E factor; another important term is that how much waste is been produced from that right? So, if you are just discharging that the by byproduct not utilizing that property right. So, atom efficiency generally as I defined the molecular weight of the desired product divide by the total weight of all the products. So, the second one which is your important environmental acceptable factor is E factor. So, this is this word is used in more and more commonly; the weight of the waste or undesired product divide by the weight of the desired product. So, how much is I am saying that a goes to p plus q. So, I am defining or p is the desired product, q is the undesired product. So, I am talking q by p how much is that?

So, that is what I said that in pharmaceutical industry the waste product is very high. Because they need a only they are getting a small concentration of the desired product right purity 99.99 percent in terms of that chemical specialty chemical and rest is discharged. So, the E factor if you look at for these kind of industry it will be large number right. So, this should be a small number basically right. So, E factor is basically the weight of the waste or undesired product divide by the weight of the desired product right. So, this should be controlled in 1 way because you cannot make it minimum but you try to make it minimum right you have to make a 0; you cannot make it 0. But you can minimize this number.

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So, basically this related to mass balance for alternative routes right. So, E factor mass index what we are talking that they are related to the amount of waste generated during the process right. So, ratio of the waste to the product that is the output oriented indicator

here right. So, whereas mass index is ratio of all raw materials divide by the product to an input oriented factor. So, these can be used intermittently.

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For example the conventional oxidation of a secondary alcohol 3C6H5-CHOH-CH3 + 2Cr2O3 + 3H2SO $3C_{a}H_{a}-CO-CH_{a}+Cr_{2}(SO_{4})$ Atom efficiency of 360/860 = 42%. ₆H₅-CHOH-CH₃ + 1/20₂ $C_6H_5 - CO - CH_3 + H_2O$ tom efficiency of 120/138 = 87%, with ater as the only by product.

So, this is an example if you look at here for this green process concepts or green technology concept that any molecule right convention oxidation of any secondary alcohol this in presence of chromium oxides, sulfuric oxides right. And, this is your desired product here right. So, if you look at here the other products are chromium sulfate and water. So, atom efficiency the if you calculate here the atom efficiency is nothing but this is just 396 basically; this is 396 divide by 860 total of this right total molecular weight this water plus chromium sulfate plus this right. So, this take the division of this.

So, this divide by this; this comes out of 42 percent right. So, basically what I am saying that molecular weight of this total molecular weight of this that is total mass in terms of this now. So, 3 moles are formed. So, total molecular weight into 3 right and this 120 is this just and then this water. So, total mass of the desired product divide by all the product formed mass right. So, this is form this you are getting; using this 3 molecules of this right.

Secondary alcohol you are getting this is as the desired product. So, the basic idea here in this is that this should be maximized rather than these two. So, similarly if you look at other reaction here for the oxygen you just oxidize it and get again this product. So, this

is just a comparison of two process the whether you use this chromium oxide and sulfuric acid. And, then get this the second is direct oxidation partial oxidation and then you get this. So, if you in this case if you just calculate this atom efficiency 120 divided by 138; because this is not there right the one byproduct you have minimized. So, 120 divided by 138 it comes roughly 87 percent. So, here the atom efficiency is 87 percent.

So, this process is more efficient compared to this see right. Now, we are just comparing in terms of the process or reaction you are not talking in terms of feasibility right. We have not said in terms of temperature, pressure, catalyst which is used for these two process. So, you have to look at those also but as a look thermodynamically these this process is better compared to this right. And, this is the concept of your atom efficiency or green catalog.

So, we if you are able to get this process then you can very easily increase the yield output with less amount right input processor. But need to check; same thing just like the methane you convert into sin gas or you get hydrogen by reforming process. So, reforming consumption are large amount energy highly endothermic right. But if you are able to generate a process just by methane plus oxygen right; partial oxidation of methane which is exothermic reaction.

So, you are generating energy from that right but the only problem is that high where the reactions are highly exothermic; the control becomes a problem right. So, run away a problem comes unsteady or tragent conditions arise. So, in that case if you are able to develop a technology or catalyst or process for partial oxidation of methane to hydrogen it will be good process right. Because there if you calculate your atom efficiency is high right. So, these are the different challenges or challenges for the process.

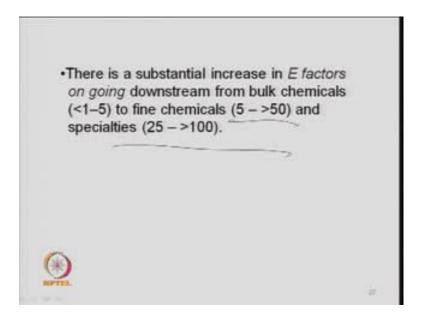
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Industry segment	Product tonnage	E factor kg waste/kg product
Oil refining	104-108	(dl)
Bulk chemicals	10*-10*	4-5
Fine chemicals	102-104	5-50
Pharmaceuticals	10-101	25->100

So, this is just the flexibility process if you look at I have taken it in the reference Sheldon. So, the most of the environmental acceptability product if you look at in different segments of chemical industry. So, E factor which is very important in terms of k g waste divided by k g product. So, oil refining has E factor less than 0.1 right. So that is the waste generated in this oil industry is relatively less. But if you look at here pharmaceutical industry the E factor is even 25 more than 25 or 100. So, very high right same thing for the fine chemical also it is between 5 and 50. So, it means these for the there are lot of challenges in developing new processes for this right. Because the every product has to be used as a useful product rather that is right. So that is the challenge especially for the pharmaceutical industry.

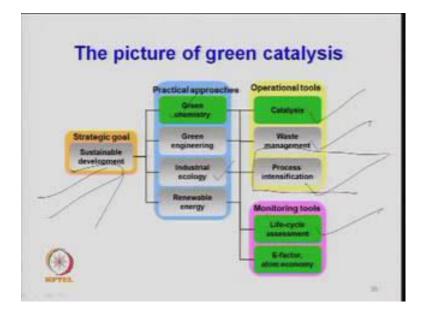
So, you need to develop the technology, you need to develop the process or catalyst for these processes which where these can be minimized. So, there are still lot of opportunity in reducing this number from 0.1 to 0.01 something like that right for the oil refining itself bulk and chemical itself right. So, this is what the concept of green catalysis.

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So, as I said these is substantial increase in E factors ongoing downstream from bulk chemicals to fine chemicals and then specialtic chemical. So, E factor is increasing right as you just look at your specialty or purity of the product. So, your waste generation is more and more right.

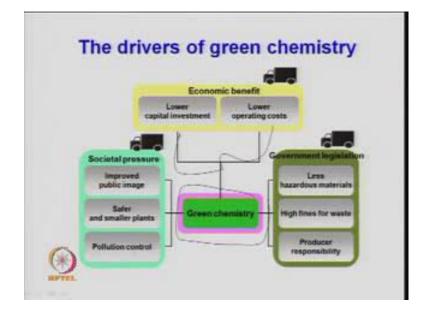
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So, this is the just typical picture of a green catalysis which you as talking in terms of concept of green catalysis. So, strategic goal; so goal is sustainable development. So, what about technology? You develop right that should be sustainable right that is 1 of the

most important thing sustainable development right. So, approaches can be you look at the green chemistry but I was saying develop the process right in terms of atom efficiency, in terms of E factors and then in engineering apply the engineering. Because when you look at the scale up of the process you need to look at engineering and then industrial importance. So, industrial ecology and then renewable energy sources; all these practical approaches these can be done right these can be our approach.

And, then your operational tool can be catalysis just look at the waste management process intensification very important; when you look at the commercialization of the process right. And, then monitoring tools like life-cycle assessment E factor atom economy. So, this is the complete picture of green catalysis which I said.

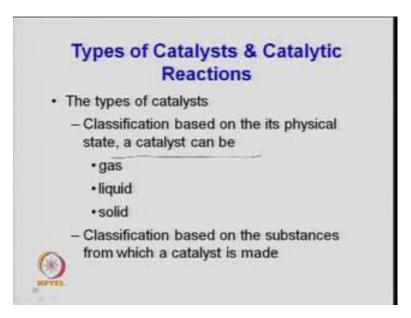


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And, drivers for green catalysis this you have look at economic benefit; that is the first thing when you look at the commercialization of the process right. So, the different aspects when you look at that correlate this green chemistry in terms of low operating cost, low capital investment. So that will be the economically benefit right. So, to what extent we can move to this point right that is important. That will depend on the selection of suitable process, selection of suitable catalyst and then finally technology right through process intensification.

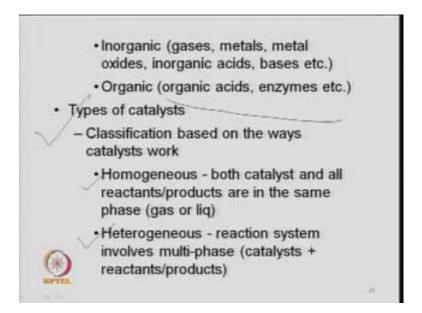
So, you need lot of say government legislation the you look at the social environmental and governments rights legislations, And, then you have to just produce less hazardous material as per the requirement right environmental protectionists high fines for waste. So, you have to just look at the producer responsibility. So, all these things look to be controlled and same thing for the societal responsibility in terms of improved public image right safer; and smaller plants pollution curfew right. So, all these things need to be looked into when you look at the green catalysis concept.

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So, this is just a basic introduction about the catalyst and the green chemistry and the catalysis concept. So, when you look at a catalytic reactor design or catalytic process; we need to understand first avoid the type of catalyst right that is for a given process. So, catalyst can be defined in a different way also depending upon the their applications for the reaction depending upon the phases involved, depending upon their itself the chemical composition right.

So it can be solid, it can be liquid, it can be gas also; so, all type of catalyst can be used. So, basically when you say the catalyst for it based depending upon a physical state they are gas liquid and solid right. So, this is very general but most of the time when we talk heterogeneous catalysis, we will talk a solid catalyst. So, classification of the catalyst which is based on substance from which the catalyst is made. (Refer Slide Time: 57:06)



So, it can be inorganic solid right so gases, metal, metal oxides, inorganic acids, bases. So, different kind of catalyst can be available see in the environment also you know that depletion of the ozone layer through u v light right. That is again a kind of h the ultraviolet lights and that cause the depletion of the ozone layers right. So that is a kind of catalytic reaction same thing the poly acrylonitriles or the these other environmental polytines they get converted during in the environment itself. So, they are gas kind of reaction the presence of some of the gases species may activate the reaction for the other right.

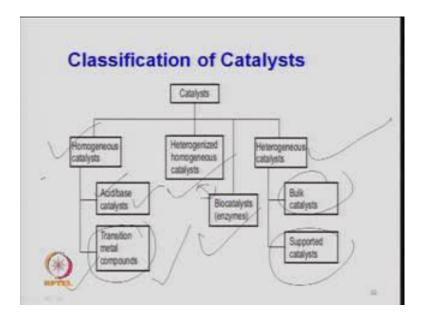
So, they can act as a catalyst. So, same thing here the organic catalyst they can be organic acids, enzymes etcetera. So, enzymes are again a kind of catalyst which is hetero-homogeneous catalyst right because partly it dissolves in the dissolve phase. And, partly in the solid phase because it is a nothing but a kind of emulsion proteins right. So, they remain in the emulsion form. So, bio-catalysis, enzymatic catalyst. So, basically this is just the depending upon whether they are in the solid phase, liquid phase and gases phase and then depending upon their inorganic type or organic type.

So, just very general definition or general classification of catalyst. But the more important if you look at in terms of the catalyst selection or characterization or type of catalyst that is the homogeneous catalysis and heterogeneous catalysis right. So, in broadly if you look at we divide our catalyst system just like in terms of phases they are

present right. So, homogeneous catalysis when both catalyst and all the reactant, products are in the same phase right to that is in homogeneous catalysis. So, it can be a gas phase, it can be a liquid phase. So, in fact if you look at your reaction rate because they are continuously directly in touch right a kind of micro-emulsion or nano particle when you what you say.

So, these kind of things can be obtained in the case of homogeneous catalysis, organometallic complexes are now a days being used right. Because they can be directly used in the liquid but the problem again as I said is the separation of the catalyst is a problem right. So that is why less used otherwise they have more activity right. Another category which is widely used in all refining petro a chemical is that your heterogeneous catalytic system.

So, here the reaction system and the catalyst so they are in a different phase right. So, it means the your reactant may be gas, catalyst may be solid; reactant maybe gas, reactant maybe liquid; it can be in liquid liquid. But two different layers right a kind of just like a aqua's phase and hydrophobic phase right where the organic layer and hydro water layer. So, they are separated by and the reaction is taking place from 1 phase to another phase right. So, this is also a case of a heterogeneous catalytic reaction. So, reaction system involves basically a multi-phase. So, whether it is catalyst, reactants, products.



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So, broadly if you look at your catalysis can be classified like homogeneous catalyst and heterogeneous catalyst right. But in between as I said for the enzyme type catalyst they are known as heterogenized homogeneous catalyst right. That means, they have the partly the homogeneous characteristic, partly they have the heterogeneous characteristic right. So, they are emulsion type catalyst basically. So, they are known as so they go and dissolve in there. So, there in the liquid they go into the liquid phase.

So, they remain in the liquid homogenous type reaction right and the part of that they remains in the solid phase; so there that is heterogeneous. So, the all these enzymes are basically amino poly-amino acids right. And, so they are categorized in this category hetero-homogeneous. And, same thing for the biocatalysts also there this category of similar where enzyme is kept on some substrate right.

So, again it is a heterogeneous catalytic part or a hetero-homogeneous. But since the enzymatic reactions are different then the your heterogeneous catalytic which is in terms of the inorganic or organic catalyst right. So, we keep them in a separate category. So, bio-catalysis right which is now a day a new type of catalytic system and use in the biomaterials right.

Say enzyme is one and they can separate different kind of this biocatalyst right. And, they can be used for the say the old process where you know the starch or the cellulose they can be converted to alcohol right the manufacture of the alcohol is true this enzymatic rule right. So, that is well-known process. Now, and in heterogeneous catalysis again we subdivide 1 thing in the bulk catalyst.

So, bulk catalyst means the entire material acts as a catalyst right. That is just like suppose if I am saying platinum only platinum is being added or mixed in a reactants. So, and itself the whole platinum will act as a catalyst right. So that is known as bulk chemical or sometimes say alumina just alumina is used as a catalyst, Zeolite is used as a catalyst right.

So, itself is acting as a catalyst not the purpose of the support or high surface area right. The second 1 the precious metal is deposited on this surface right because this metals have no surface area. So, in order to provide them a large surface area support or give provide a good kind of dispersion; we deposit them on a large surface area or on a substrate which has a large surface area. So, like alumina right; sometime alumina acts as a catalysis itself for dehydration reactions or Zeolite acts as a catalyst itself, sometimes they are used as a catalyst and the support also bi-functional catalyst right. So, that is known as bi-functional 2 functions right metal function and the support function. So, the that can be partly part of this metal can have the hydrogenation activity; whereas, the support have the cracking activity right acidic sites.

So that we will discuss later but the bulk catalyst means the entire material itself act as a catalyst. And, supported catalyst means where the precious metal or metal is deposited on some substrate and which is used for providing them in a large surface area or catalytic property where in the again in the homogeneous site. So, homogeneous like sulfuric acid alkylation right which is a homogeneous reaction right. So, you know that the sulfuric acid, phosphoric acid. So, they are used as a catalyst for alkylation or polymerization reaction generally used in the petro chemical industry right.

So, hydrofluoric acid alkylation h f alkylation is another 1 right. So, sulfuric acid polymerization right; so these are acidic strong acid which are generally used for the alkylation reaction right. So, you get alkylated gasoline from that; the similarity for bio diesel manufacture again when you look at trans rectification reaction that is sulfuric acid or potassium hydroxide in liquid form is used as a catalyst right. So, they are categorized as the homogeneous catalysis right. And, now if you are using acid catalyst so this acid catalyst like sulfuric acid I said, hydrofluoric acid, a base is used like ((Refer Time: 1:04:17)) then it is a base catalyst right. And, sometimes the same thing is done in the presence of transition metal compounds.

So, this is now a day's being used in a big way right that is what I said that they are providing even large surface area right and kind of metal complex. So, these are organometallic complexes based on ligand base theory right. So, metals are associated with some something like say EDTA and you have replaced the OH group and metal is collected there right. So, this metal now this organo-metallic complex will remain in the liquid phase or gel phase and it will act as a catalyst for the system right. So, the only thing that the separation of these catalysis from the bulk product after reaction is a difficulty right.

But this is coming up in a big way for the catalytic reaction because they have the they are acting like an narrow particle. There the what you get the sol gel; solution gel or

hydro gel it is the gel contains the metal particle inside it right. And, which is well dispersed right subtracted each metal particle is separated inside the gel. Because it can be a polymeric structure right; the polymer gel inside that you have metal complex right. So, ligand base theory which is used here for making. So, this is known as a transition metal compound and a category of homogeneous catalysis. So, I stop here I will continue it next time.