Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts
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Lecture 27
Polymerization strategy for industrial preparation of LLDPE

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Welcome to our course Metallocene and Metal-carbene based Organometallic Catalyst for Advanced Polyolefin Catalysts so, so far we have discussed the prospect of metallocene based catalysts for olefin polymerization, we have learned that how this emerging catalysts have really revolutionized the polyolefin industries and then we have tried to compare with the Ziegler–Natta catalyst, the advantage over the Ziegler–Natta catalyst and we have seen that the stereo selectivity is much better for the metallocene based catalyst and also the activities especially to get the high molecular weight polymers you have learned that CGC based like titanium-based catalysts are much more superior.

And it is very easy to understand the stereo selectivity associated with the prochiral monomers and you can basically control to make a particular stereo selective polymers, we can make the stereo block polymers by selecting your catalyst, so you can use the catalysts as a toolbox and according to your desired you can select your the catalysts and then we have also discussed the recent advancement in non-metallocene or called post metallocene based catalysts and we have seen that catalysts like Brookhart catalyst which are palladium based catalysts are very much efficient for like non polar molecules not only the non polar also for the polar olefinic monomers.

So we can have a very diverse library of the catalysts in this scenario and you can basically make a whatever you want you can make the different type of homopolymers block copolymers or a specially designed polyolefin based homopolymers like that, today we will discuss mostly the synthesis of the LLDP as we have we have already learned that LLDP that is the linear low density polyethylene is a category of the polyethylene and you know that polyethylenes are one of the heavily used plastics in our daily life and for bulk and for various sophisticated purpose as example like medicines or various domains like cosmetics like packaging industries and etc. So today we will discuss the polymerization strategy for industrial preparation of the LLDP so let us try to learn today.

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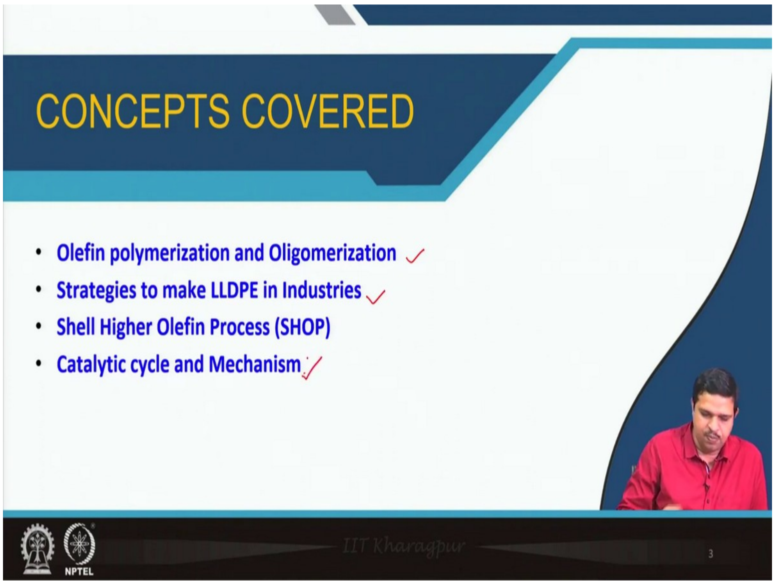

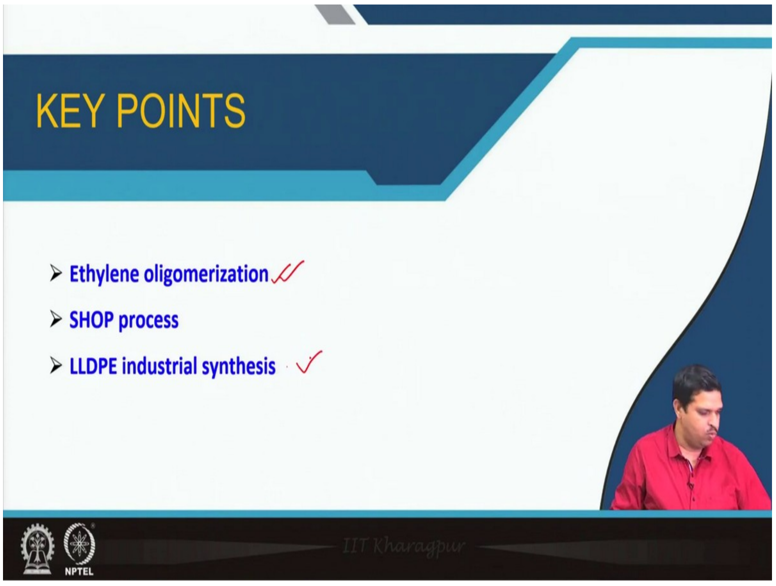

So the what are the concepts, the concepts we learned the olefin polymerizations and we will learn here that oligomerization is also important and how we will take the advantage of the oligomerization of say ethylene and try to make try to use it in LDP preparation and then we will try see how what are the strategies followed by industries to make the LLDP P for polyethylene and we learn here what are the shell higher olefin process, so it is basically that this is called SHOP process s h o p, it is basically to make the oligomers of the ethylene so to make like a hexane butane pentane heptane like that so that it is used for alpha copolymerization and to make the LLDP in industries okay.

And obviously we will learn how this catalyst operates so we have to have a deep knowledge of the mechanism and the hold the catalytic process so that we can understand the process associated with this one and how this bond baking and bond making are happening in the polymerization reactor, so the key points you will learn here the ethylene oligomerization that is very very important because unless it unless we do it we cannot really make the LLDP and we will see how we can do the LLDP synthesis with the combination of the ethylene oligomerization and the polymerizations both, both are important here.

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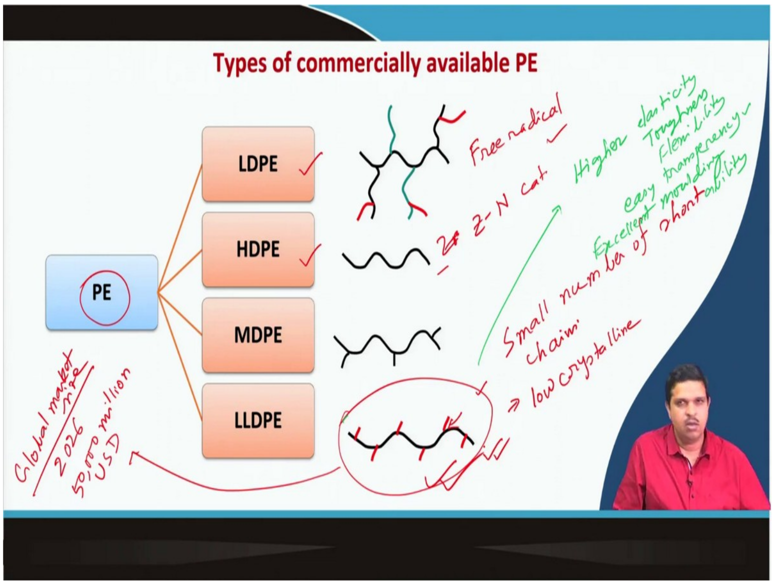

So this we have already learned in previous classes that polyethylene we know that one of the heavily used polymers in various domains we will not, I am not going to repeat again, various type of polyethylenes are possible like low density polyethylene, the high density polyethylene we know that the low density polyethylene synthesized by free radical polymerations free radical pathway and the high density polyethylene generally we do Ziegler–Natta catalyst I am just write ZN, ZN catalyst system medium density polyethylene also Ziegler–Natta catalyst and this is the one of the very interesting and very useful materials that is the low density polyethylene that is the linear low density polyethylene.

So you can here you see that this is basically in between the LDP and the MDP so the branching associated you see there is a smaller branching, shorter branching and less number of branching so and here you will see the LDP that is a low density polyethylene is a more number of branching longer branching there is no control in the branching of the from the main polyethylene moiety.

And why it is important this is very special and due to the small number of small number short chain here you will see this is the small number of short chains this is the short and numbers are smaller than the LDP and so this is actually that is why the it is low crystalline polymers and this is again basically the more number of shorter and smaller branches than the high density polyethylene if you compare with this one and that is why it is a low crystalline polyethylene and due to that, that is that, there are several interesting properties.

As example like here, higher elasticity, the higher toughness, higher flexibility because this is low crystalline and easy transparency because it is a low density polyethylene, excellent molding ability this is important so that is why we can, excellent molding ability and that is why we can make a different type of materials by the LDP, we can shape it according to our need and as it is you see that it is a flexible and easy transparency so this actually the LLDP polyethylene are heavily used in packaging industries and to make the flexible materials even for the medical industries and pharmaceutical industries.

And this we discussed in our previous class that this LLDP is a global market is used you will be very surprised that by 2026 the global market size is almost like 50,000 million dollars US dollars, million US dollar, that is the global market size so you can understand that how this LLDP apart from the other polyethylene polymers how the these are important in industries because it has a very high global market. So now it is we are very much familiar that why LLDP is very special for various applications in many domains.

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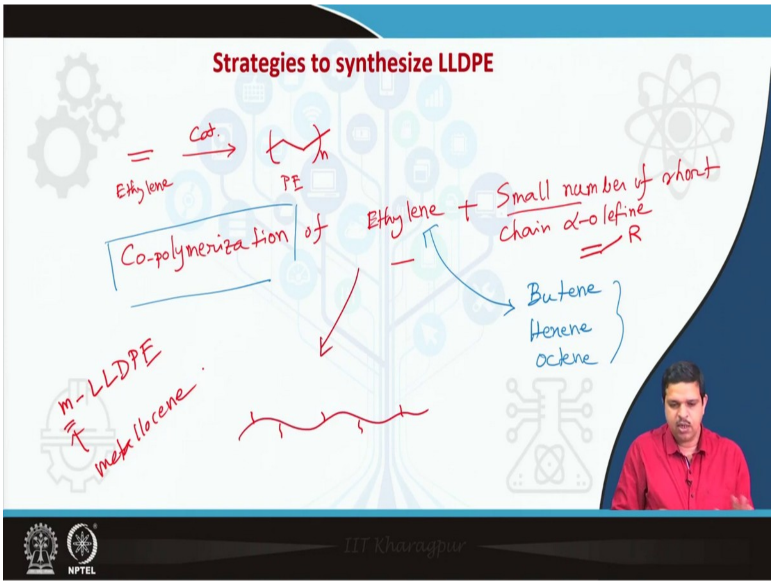

Now how to synthesize the LLDP that is our aim that how we synthesize LLDP how we can control to have a short chain but limited short chain not like a free radical polymers the polymers obtained from the free radical polymerizations of the alkene or ethene so what we have to do, I just first I try I will write down the strategy and then we will discuss that how we can do in real life so what we have to do we have to so this ethylene we know that this is if you do the polymerizations we will get like.

So this is polyethylene and this is the ethylene monomer, so this is the you can use the catalyst or you can use the any other free radical initiator so now how I will make the LLDP, so what we have to do basically we have to do through the co-polymerization so LDP is not really the homopolymerization product it is a copolymerization of what, of ethylene plus the small number of short chain alpha olefins so small number of short chain alpha olefin so something like that, so R should be here the smaller alkyl group and this is the ethylene.

Now you see here it is written the small number that means ethylene will be, ethylene will be the major component and we will introduce in the polymerization chamber a small amount of the alpha olefin monomers, mostly used like butane or hexane or octane, the even number of the alkenes of the even number of carbons are much cheaper and why it is cheaper because it is easy to synthesize and so here we have to do that we have to take the ethylene plus the another monomer that is butane or hexane or octane, the small amount and the process it is called the copolymerization.

Now due to small number of now what you will get you will get the polymerization and like that and here you will get this is actually the coming from like that, so this is actually coming from the butane, hexane or octane the other monomer other than the ethylene so that is the strategy to synthesize the LLDP and you might have seen that in some book or some journal it is written m-LLDPE this m actually stands for the metallocene or in some journals or reviews or book you might have seen the term metallocene grade LLDP that means the this m-LLDPE or metallocene grade LLDP have been synthesized by the metallocene based catalysts like Kaminsky catalyst. So now it is very clear that what are the strategies.

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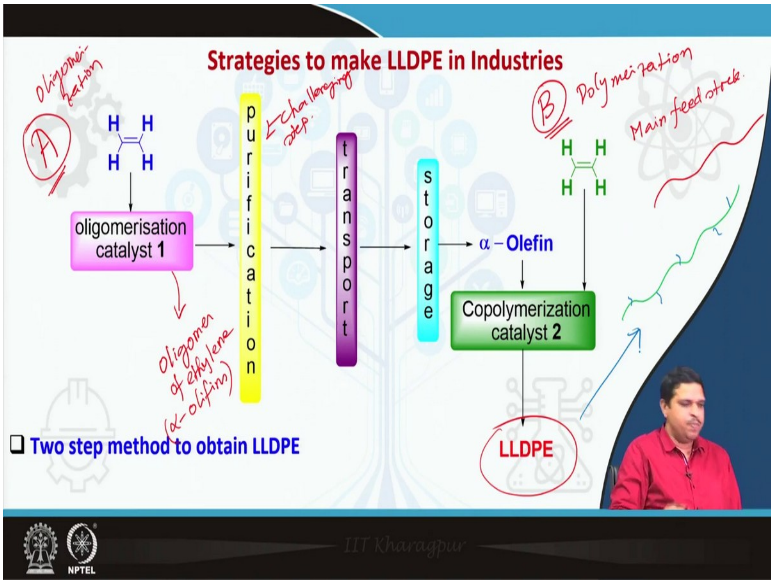

Now let us see how we can do it in our in industry or in lab what would be the protocols, now you will see here what I have to do from my, from the last slide so we need the ethylene definitely because that is the main feedstock that is the main component to get this polymer that is the polyethylene, now I need the another monomer for the co-polymerization, how will get it, either we have to make it or you have to get it but how will get it somebody has to make, how we can make, so let us try.

So we need another catalyst which can do the oligomerization of the ethylene and give the so it will be a provider of the another monomer that is the alpha olefin monomer other than ethylene and then we can mix it to get the resulted LLDP polymer, so what will be the step is very easy to understand but in reality we have to much more complex but in reality you will see it is very easy to understand so here you will see that what you have to do this is the system A, so first is that I need a oligomerization catalyst which will give the alpha olefin other than the ethylene.

So something like hexene, butane and then you will get the oligomers so where you will get the oligomer of ethylene, so is basically you will get the alpha olefin, now you will have a mixture of the higher or shorter olefins so you have we need a purification definitely and after purification we have to introduce this to the main polymerization chamber that is the here, so this is the basically the main polymerization chamber that is the B.

So in the A we are doing the oligomerization and oligomerization and in the B we are doing the polymerizations, so here you will see 2 steps are parallelly happening oligomerization and polymerizations and in between there other steps like see once you make it the alpha olefins then you have to do purification that is a challenging, that is the challenging step and then you have to transport it then you have to store it the alkene monomer and whenever required you inject, introduce to the polyphene polymerization chamber.

So here is basically 2 step method, first, why 2 step because this is the step A and this is the step B 2 chambers, so this is one way and one strategy you can say strategy one to make the your desired LLDP, so like from here if I take this one as a green that is by the main polyethylene and if I take this one is a blue that is the monomer other than ethylene then you will get like this one and this is basically the LLDPE very simple.

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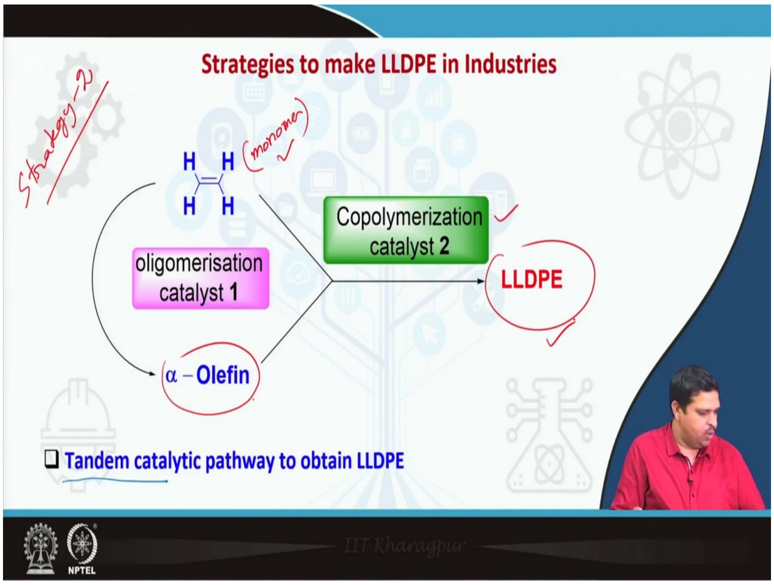

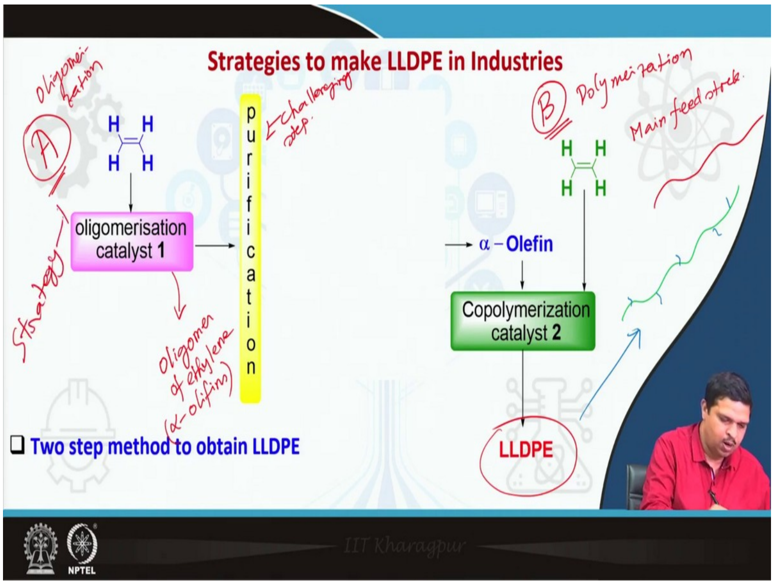

Now what will be the other strategy, that strategy is the not using 2 steps, single step and the concept of the tandem catalyzes, tandem means the in situ, the same catalyst will do the 2 process together, so using the concept of the tandem catalyst we can make this is more challenging but it is a more economic and more easiest method, so what we are doing we are basically taking the ethylene that is the monomer, main monomer and we have to take a catalysis system in situ not the separate then it will make the alpha olefin one catalyst that catalyst may be 2 different molecules or maybe one molecules, homo metallic or bi metallic whatever so then after getting the alpha olefin and you have the monomer in the system that is the ethylene and in presence of copolymerization catalyst 2 you will get the LLDP.

So the first strategy that is here, there are 2 step, one is the A and the B that is the oligomerization and the polymerization but that is 2 separate chamber and in this one strategy 2 we can write here strategy 2 and this one is basically strategy 1, so here you will see that it will be in situ and there will be 2 catalysts and one catalyst will do the oligomerization and one catalyst we do the polymerizations and you will get your LLDP so that is very advanced concept and however it is more simpler if it is implicated in industries in some cases it is successful I will give the real examples.

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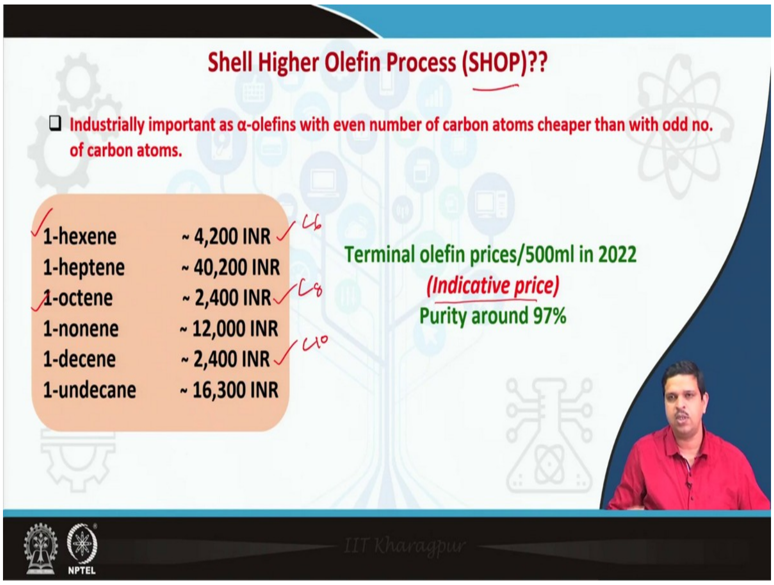

So now why you, we now we understand that we need 2 monomers, one is the ethylene that is the main monomer for polyethylene and one we need the other alpha olefin monomers like butane hexane or like octane or pentene whatever but we will be interested which will be more cheaper, industry will be more interested to make the economic polyethylene with the same properties so that it is easily accessible to the common people.

So here you will see that hexane cause this is the indicative price do not take it with the absolute price you know it is just indicative to have a comparison so here you will see that this is hexane is like for per 500 mL it is almost 4200, octane is 2400, decene is almost similar that is with you will see that is the C6 C8 so C10 like that and here you will see that it is an odd number the price is quite high so that is why normally in alpha copolymerization to make the LLDP we normally use the hexane or butane or octane the even number of carbon atoms.

So this is now we will try to understand how this hexane octane can be made by the very very effective and very famous and very well known process that is called the SHOP process, so what is the SHOP that is the shell higher olefin process, so we basically we will be increasing the number of carbons to make the olefin from the ethylene so it is nothing but a oligomerizations.

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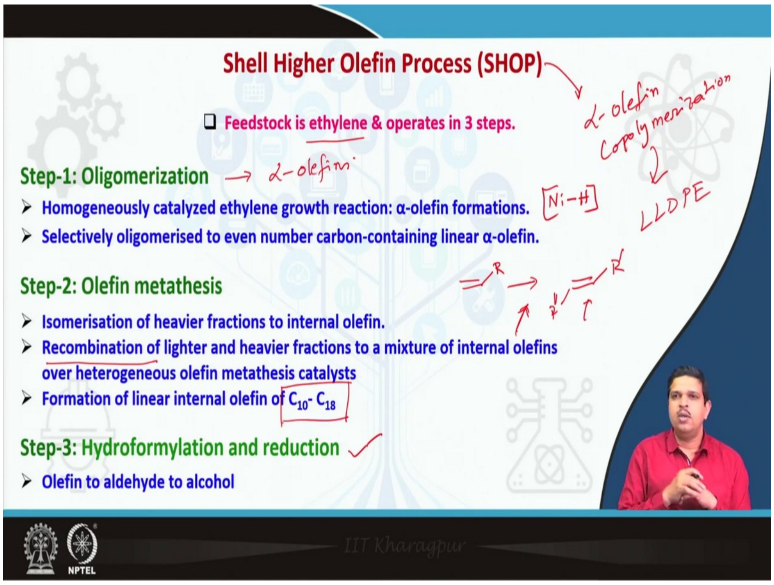

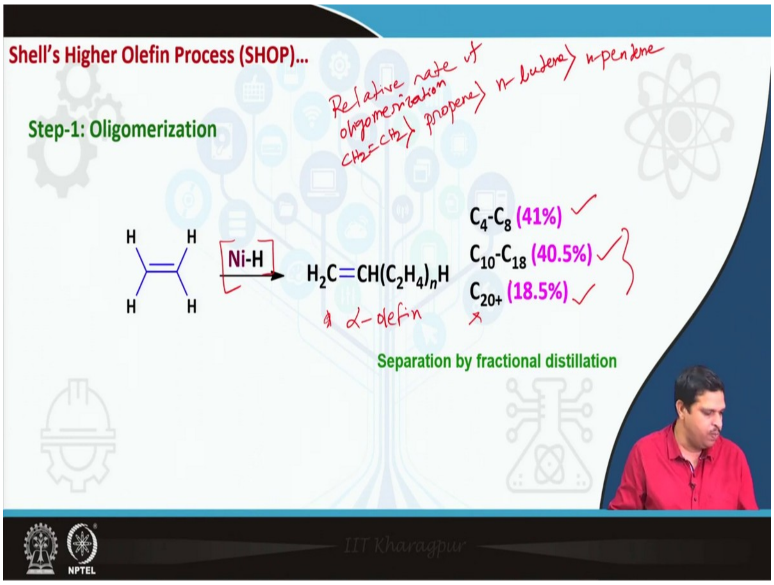

So we will now try to understand what is the shell higher olefin process what are the steps associated with this one, these are not actually a single step process industry follows 3 steps and this is not a single catalyst or single step, multiple steps very complex, quite complex but it is very effective, you will not you will at the end of our discussion you will understand that how effective it is, how economic it is and why industries love this process you will get the byproduct but that byproduct is also useful for other purpose.

So let us try to understand very carefully because this one is very important, so here again the feedstock is ethylene, so ethylene is the main monomer and more main component for the shell higher olefin process and why we are required because this SHOP process actually will give the monomers other than the ethylene for alpha so it will give the alpha olefin and why it is needed because we have to do alpha olefin co-polymerization and to make the final product LLDP.

So let us try to understand the steps, so first step definitely is the oligomerization, so for ethylene you will get a number of the alpha olefins so you will get number of alpha olefins, so it is a homogeneously catalyzed ethylene growth reaction so you will get number of alpha olefin polymers, generally the nickel hydrogen catalyst we will discuss the catalytic system first you let us try to understand the strategy, so is basically the nickel hydride catalyst which are homogeneous in nature and then what happens it undergoes the selective oligomerizations to even number of carbons to have the alpha olefin different type of alpha olefins like say let us say butane you will get, hexane you will get, octane you will get, different mixtures.

And we have to separate I will discuss that what how we have to do it then second step is a olefin metathesis reactions we have to do what why the isomerization of the higher or heavier fractions, you will see that in here you will get this like different type of alkenes varying the number of carbon atoms like here you will see that quite C20 C10 to 18 which will be much longer for our LLDP which are not required we have to remove from the system otherwise we will get a good number of branching and then we will not get the good LLDP if we target for only LLDP so this one we have to remove, fine.

Now there will be second step is a isomerization of heavier fraction to internal olefins so what we will get you our desired is this one now you have to isomerize and you will get basically like this one, that is for the and so heavier fractions will undergo the isomerization to have a internal olefins, internal olefins means that the alkene bond is not at the terminal then the recombination the second step, recombination of lighter and heavier fraction to a mixture of internal olefins.

So this is the step over heterogeneous olefin metathesis catalyst, so we will be using a heterogeneous cyst catalyst system which actually gives this step that is the recombination of lighter and heavier fractions to have a, to get the internal olefins and then you will get the basically eventually you will get the linear, formation of linear internal olefins that with C2 C10 to C18 carbon atoms fine.

So C 10 to C 18 carbon atoms you will get so basically you will get a mixture of the internal olefins fine, now third step because we have to remove this one or we have to we should not waste this one because if we waste this then it will be the process will not be economic, so what we have to do converting to a useful material useful compound and how we do it the through hydroformylation and the reduction and you will get the olefin to aldehyde to alcohol we will discuss in the next slide that why these are so important.

So let us see now these are the step that first step is the oligomerization, second step the olefin metathesis and third step is the hydroformylation and reduction, let us try to understand now in more depth, so this is the oligomerization here you will see this is ethylene and as I told that this nickel hydride catalyst we will use I will try, I will come later where you will be what exactly what catalyst what is the chemical structure of the catalyst generally used by industries and which are more common and famous.

So what you will get, you will get basically this kind of alkenes, so that is the alpha olefins you will get, now like now you have to separate by fractional distillation if there is, if the difference between the carbon number of carbon atoms the boiling point difference will be quite good so you can separate by fractional distillation to some extent like C20 you can separate but in some cases where the number of carbon atoms are very close it is very difficult so these are the statistical distribution of the products.

So like here you see that lower number of carbon atoms or olefins you will get like 41 percent the C10 to 18 you will get around 40 percent and C20 will get around 18 percent and it is important to understand that relative rate of the oligomerization is the ethylene is much higher than the propane and then the n butene and n pentene and that is actually good otherwise we will have will have a very more amount of higher alkenes.

So this is the relative rate of oligomerization, so this is important and actually this is more advantageous fine, now so you are now we have we got this different alpha olefins.

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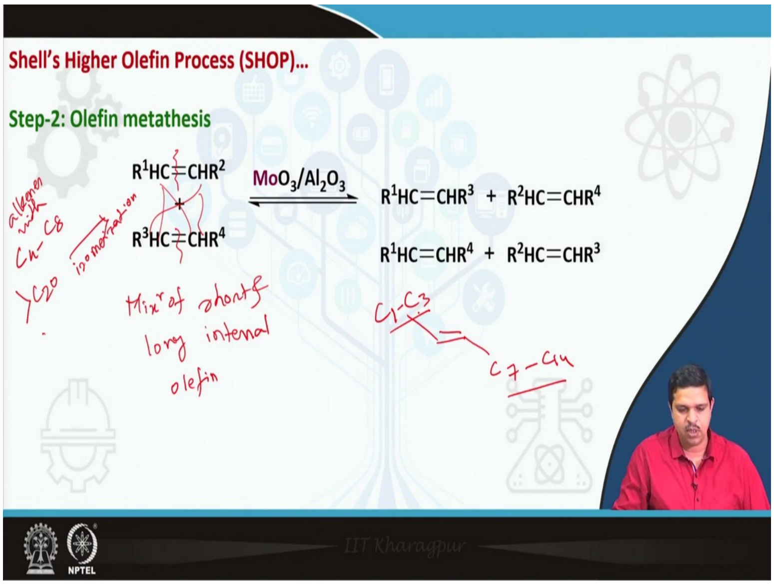

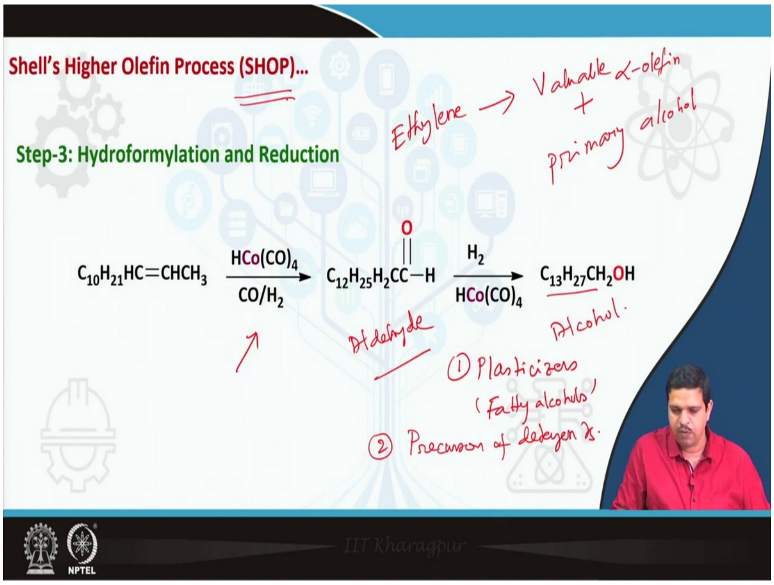

Now second step that is the olefin metathesis so what we are doing here, we there will be isomerization of 2 step here again the isomerization of alpha olefins to the internal olefins of different carbon atoms more like, so here you will get that C4 to C8 or C20 alkenes, alkenes with heavier, lighter and the heavier undergoes the isomerization so mixture of short and long internal, so this is you will get the isomerization and what you will get, you will get basically mixture of short and long internal olefin and you will then it will undergo the metathesis reactions, the alkene metathesis reaction so we have discussed briefly about the what is the alkene metathesis in the previous classes.

So is basically you can understand that you can if you can just break it here, break it here and then it is basically now threading so it is break it and then this will be combined with this one, this will be combined with this one so this will be combined with this one like that and then you will get a mixture of the alkenes you will get it and this are you will see that this is the if we take a general, so this is like a different combinations of C1 to C3 and C7 to like C14 like that so what we are doing we are basically making a medium, the internal alkenes with a medium number of the carbons from the lower number and the higher number of carbon atoms.

So this one then after so this is the range of and then the last steps are the so after that olefin metathesis by heterogeneous catalyst the last step is the hydroformylation and the reduction so what you will see we all know that process the cobalt catalyzed hydroformylation, we also discuss very briefly in our previous classes, so here you will see that you will get the aldehyde and aldehyde and if you reduce it you will get the alcohol, so here you will see that total C10 11 12 so C12 alkenes here see here so C13 alkenes here so this one representative example and from C13 alkenes you are getting the corresponding the alcohol.

So this alcohol actually with the long alkyl groups it can act as a plasticizers, so you can regard as fatty alcohols, you see that how the longer alkyl groups and also this is also percussion of detergent, so here you will see what basically we are getting from the whole process, the soft process we are from the ethylene, this is the final product of what we are getting, we are getting the valuable alpha olefin and what we are getting, we are getting the primary alcohol which also, which are also useful for different applications like as a plasticizers like a fatty alcohols or it can be used as a precursor of detergents.

So you see that there is no waste even the byproducts are also used for other purpose and the industry people love it if the whole process economic minimum waste so that is why this SHOP process is very much famous and very much effective to make the alpha olefins from the ethylene and where the byproducts are also useful.

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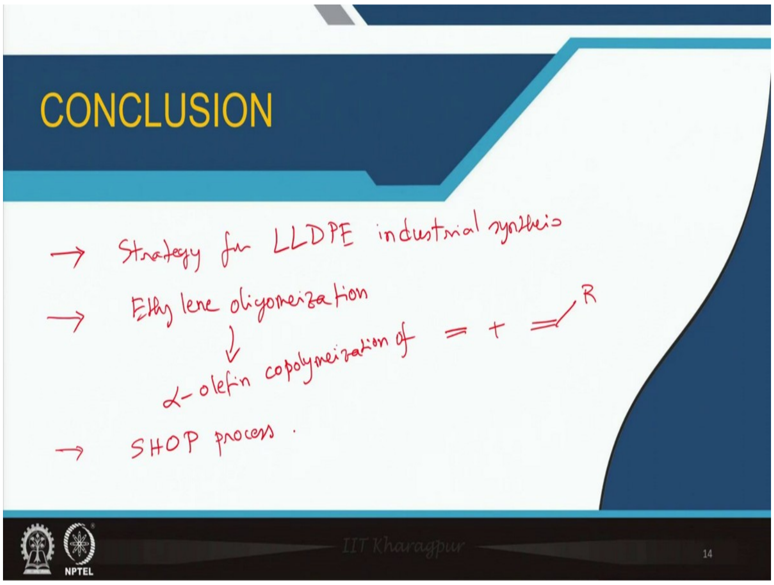

So in this class what we learned, we learned the strategy for LLDP industrial synthesis, how the industry follow the synthesis of LLDP, the strategy, we learned that the ethylene oligomerization is very important because from there we can we will get the alpha olefin like butane hexane octane and this is actually important for the alpha olefin oligomerization alpha olefin polymerization which is eventually will give your the LLDP alpha olefin copolymerization of ethylene plus another alpha olefin. And obviously we understand the SHOP process involving various steps.

So thank you and we will continue in the next class about the, we will try to understand that what are the design and the chemical structure of the catalysts used for SHOP process that is the first step the oligomerization process mainly nickel catalyst and will try to understand the mechanism the bond breaking bond making process in the next class, thank you, see you in the next class.