Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Polymerisation Strategy for Industrial Preparation of LLDPE (Contd.)

Welcome, so in the last class we started our discussion about the polymerisation strategy for LLDPE preparation and today we will continue, in the last class we discussed the what are the strategy for the LLDPE and we learned that we need to do the alpha co-polymerisation. So there are two co-polymerisation means, there are two monomers, one is here the ethylene, and one is the another alpha olefin but with the shorter carbon atoms not like a very large number of carbon atoms of alpha olefin.

So today we will continue, the mainly the chemical structure, the design of the catalyst, and we will discuss that what are the very popular and famous catalysts which are used in industries and the laboratory, and we will try to discuss or understand the reaction mechanism involved in the oligomerisations.

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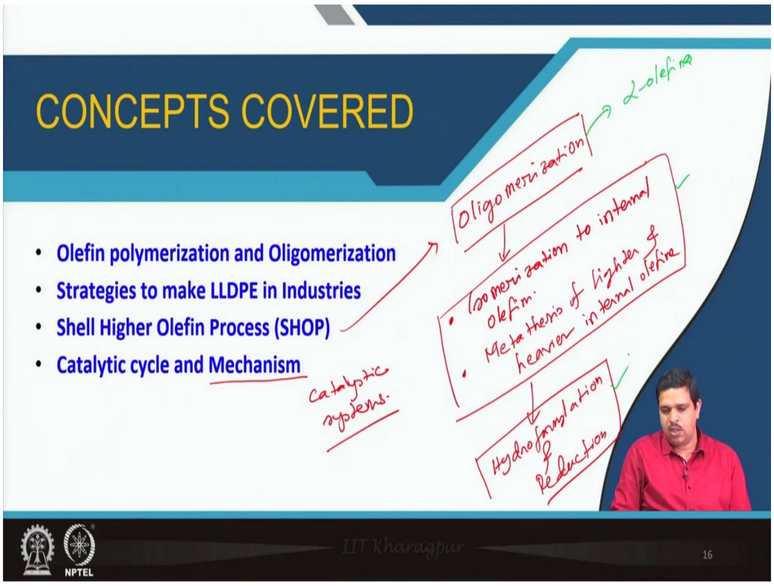

CONCEPTS COVERED

- Olefin polymerization and Oligomerization
- Strategies to make LLDPE in Industries
- Shell Higher Olefin Process (SHOP)
- Catalytic cycle and Mechanism

Catalytic systems.

Oligomerization → α-olefins

- Isomerization to internal olefin.
- Metathesis of lighter & heavier internal olefine

Hydroformulation & Reduction

So in concepts you will see that it will continue. So we will try to understand mainly the, here that is the catalytic cycle and mechanism and the catalytic systems. So that we will concentrate in today's class. So, so far what we have understood that, there is a process in the SHOP process, that is the SHOP the Shell Higher Olefin Process. So what are the steps? So first step is the oligomerisations that is basically the homogeneous catalytic system and then is the isomerisation to internal olefins. And the metathesis of lighter and heavier internal olefin. And then eventually the last one is the hydro formulation and reduction.

So it is basically you will see that, we will be getting the our desired alpha olefin from here we needed there is some purification steps are involved here and here these steps is basically to use the byproducts to a useful materials that we discussed in our last classes.

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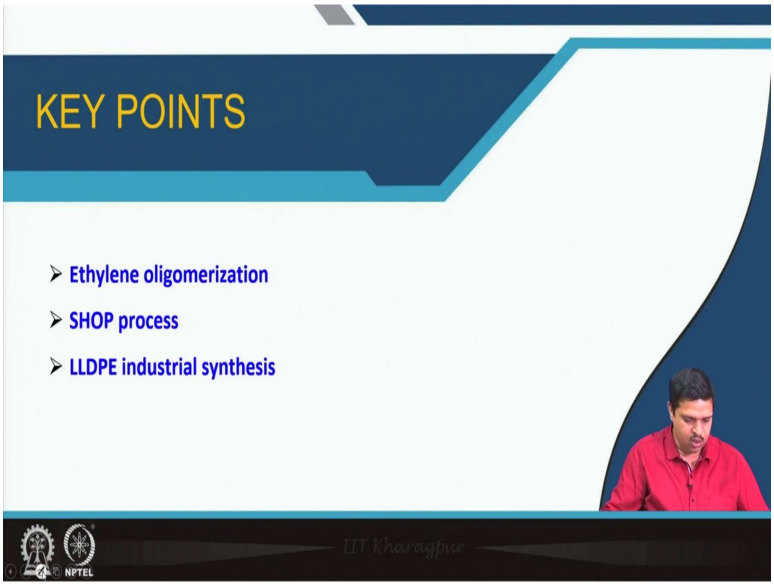
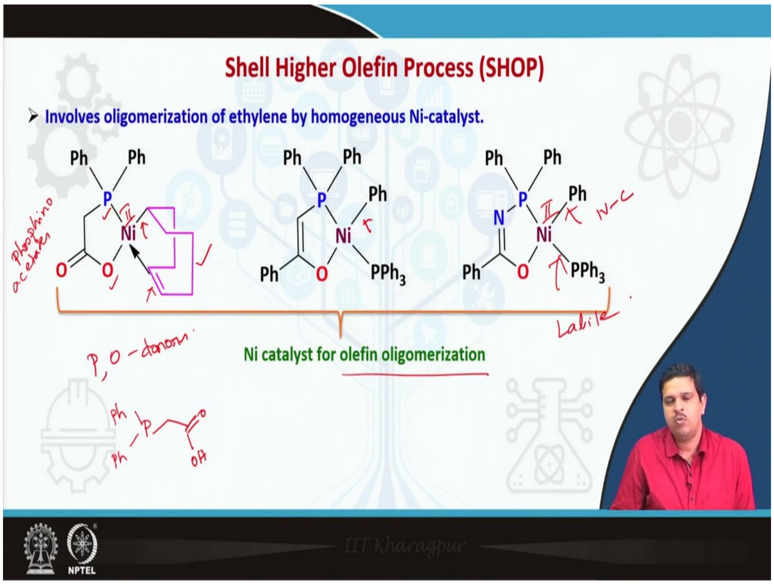


KEY POINTS

- Ethylene oligomerization
- SHOP process
- LLDPE industrial synthesis



Shell Higher Olefin Process (SHOP)

- Involves oligomerization of ethylene by homogeneous Ni-catalyst.

Ni catalyst for olefin oligomerization

So we will continue our discussion and we will see that what are the basic steps in oligomerisations of the alkenes? Let us say Ethylene. So here you will see that these are the catalysts developed all are like he is a nickel based catalyst which are the most effective catalyst here. So here you will see that in most of the cases you will see that here the phosphorus and oxygen donors and you will see this in most of the cases in the phosphino acetate. So like here this is basically the phosphino acetate.

So if you, so this is Ph, these are the ligand and so this you will see that this kind of, mostly these kind of ligands like a phosphino acetates or its derivative and nickels is here you will see that oxidation state is plus 2 here. And this is the basically the coming from the COD after the oxidative addition I will show how to, what are the general synthetic protocols, but you try to understand that what are the chemical structure of this catalyst very simple complex, very simple way to synthesize, but it is very effective as a first step of the SHOP process.

So this is for the olefin oligomerisations. So here you see the oxidation state here also this is a plus 2 oxidation state, nickel plus 2 and how to synthesize it. So this is all you will see that mostly the phosphorus oxygen donors and there will be one nickel carbon bond here. So this is basically nickel carbon bond, this one, and this one, and this is the phosphorus, this is oxygen donor, and here there will be one more labile. So this is either this one or either this one. So this is quite labile in nature, it may be the alkene or it may be the phosphine which can come out from the vicinity of the metal centers to get the space of the alkene for the reaction.

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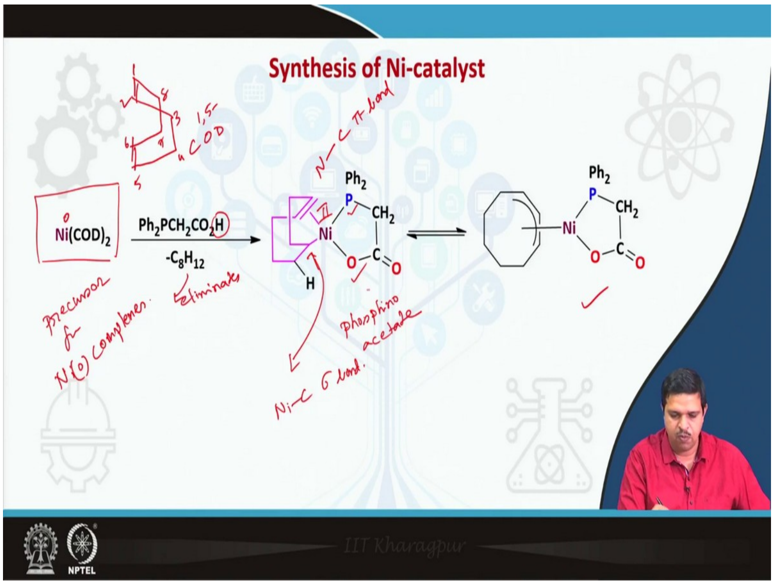
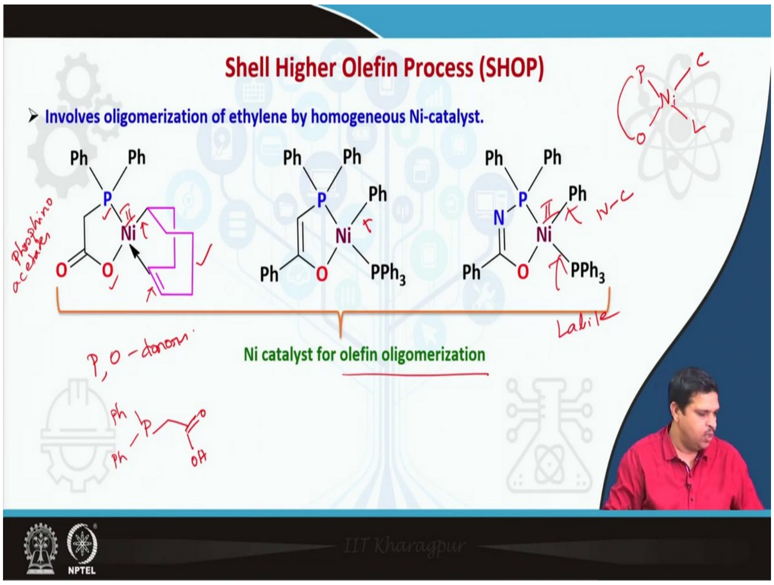


Synthesis of Ni-catalyst



Shell Higher Olefin Process (SHOP)

- Involves oligomerization of ethylene by homogeneous Ni-catalyst.

Ni catalyst for olefin oligomerization

So here you will see that it is very easy to prepare. So this is the nickel COD, so this is 0 oxidation state you know, and COD you know is very easy to synthesize. So we generally write the COD like this one. So this is the cyclooctadiene. So this is, 1, 2, 3, 4, 5, 6, 7, 8. So you can write 1, 5 cyclooctadiene and if you take the phosphino acidic acid. So one COD is eliminated here. So this actually illuminates because these are alkene is weakly bound however it acts as a creating ligands. So that is why it is very easy to prepare, it is actually very good precursor for many precursor for nickel zero complex and which can be very easily prepared in a lab.

So then what you will see here. So you will this ligands that is the PPh2 and Ch2 Coo that that is the phosphino acetate and this h plus that is the, that that OH this one, this one is basically the protonated here and you will get the, it basically you can you can see that here it is nickel 2 oxidation state. So this is 2, this is the anonic ligand, and this is the C minus here. So this is the nickel carbon sigma bond and here nickel carbon pi bond and here the nickel carbon sigma bond. And this is an equilibrium with see the allene type of bond. So this is C3 allene and you will get this kind of a, so it is in equilibrium.

So the nickel catalyst is very easy to synthesize you start from the nickel COD add phosphino acetate or any other phosphino acetate derivatives, you can make your desired catalyst and that is why it is so popular, synthetically is easy and also very effective.

So now you will see here. So this is the catalyst, this is my phosphorus donor, this is oxygen donor, this is alkene, and this my nickel carbon bond as I told that they are you will be if you see very carefully that in where case 1 phosphorus, 1 oxygen donor, 1 carbon donor, and 1 ligand is the labile, that is the basic chemical structure of the nickel to catalyst.

So this is also preserved here. Here in instead of the phosphine instead of the phosphine you will see you have one alkene here, the this, in this case the alkene here fine.

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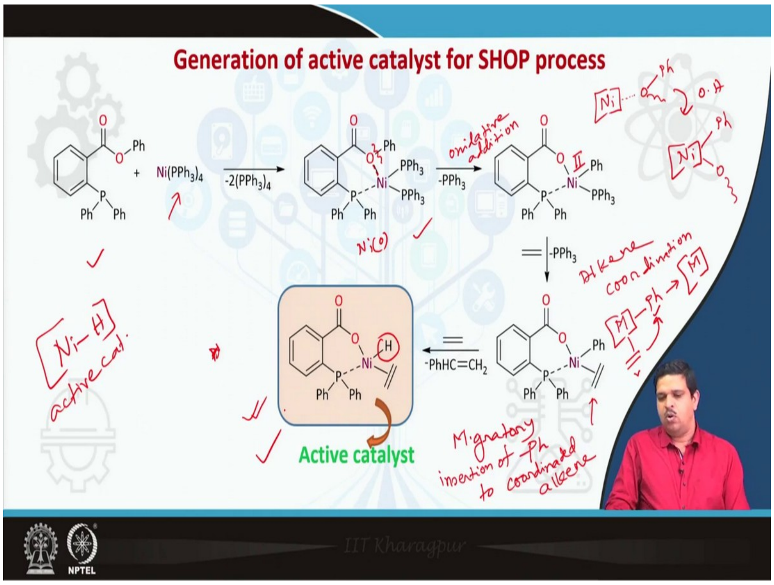

Generation of active catalyst for SHOP process

So let us take one example that this is the another way of another way of synthesizing nickel catalysts here the precursor is NiPPh3l4. So this is also quite popular precursors. So I showed 2 example one is the nickel COD 2 and one is a nickel tetra triphenyl phosphino, tetrakis triphenophosphino derivative of the nickel both are 0 oxidation state here. So how you see here, you have, so after treating this phosphino acetates, what you are getting, getting, you are getting this complex where it is nickel you will see that this is my zero catalyst, actually this is not real bond this is just a weak interaction. So this is nickel 0 catalyst.

So 2 PPh3 is coming out. So coordination number is 4 here and then one PPh3 is coming out and what is happening here is basically happening the oxidative addition, oxidative addition here we are very familiar with the 4 unique reactions in organometallic chemistry that is oxidative addition, reductive elimination, and the insertion reactions, elimination reactions. So here you will see that oxygen addition between this one. So this one.

So here you will see that o, o is a now o minus and phenyl. So now it is plus 2 oxidation state. So what is happening here. So this is a nickel and so it is actually coordinated like that one. Now it is happening oxidative addition. So here is basically Ph and they are o like that I hope it is clear now. Now another PPh3 is coming out. So you are getting the back end position here. So it is become coordinately unsaturated and then the alkene is coordinated here. So a say basically the PPh3 coming out and alkene coordination, very simple to understand.

Now the second, the last step it is very very very important because you are actually making the active catalyst here because as I told that nickel hydrogen species is the active catalyst. So this one is basically you can tell it is a pre-catalyst but this one is the actual catalyst. So what is happening here you will see here, this is now the phenyl is here and the alkene is here. So what is undergoing, it is migratory insertion, migratory insertion of phenyl to coordinated alkene.

So it is basically in alkene insertion of alkene in metal carbon bond, here metal carbon means metal phenyl bond. So is basically what is happening, if you, so in a simple way, so this is my phenyl and here is a alkene. So it is okay. Now this one. So this is basically now, this is the phenyl and this is my alkene. So this is now (hap) due to the migratory insertion of the coordinated alkene to here that styrene will form and after the styrene you will get the metal hydrogen species. And the vacant side will be again saturated by the alkene, because here ethylene is in the reactions ethylene is available and wherever there is a vacant position ethylene will coordinate.

So this is the last step is very important. This is, that is the migratory insertion of the phenyl and the coordinates is alkene to make the styrene that is the byproduct and here you will see that styrene will be useful this is also a good monomer, you know that this is the monomer for the polystyrene and here, here you will get that the nickel hydrogen species, that is the active catalyst for the SHOP process. So these are step is very important, because this steps from these steps you will understand that how we can make the active catalyst from a pre-catalyst, where there is no nickel hydrogen bond because in this fire we need a nickel hydrogen bond for oligomerisations.

Now in the next slide you will understand, why we need nickel, we need nickel hydrogen bond.

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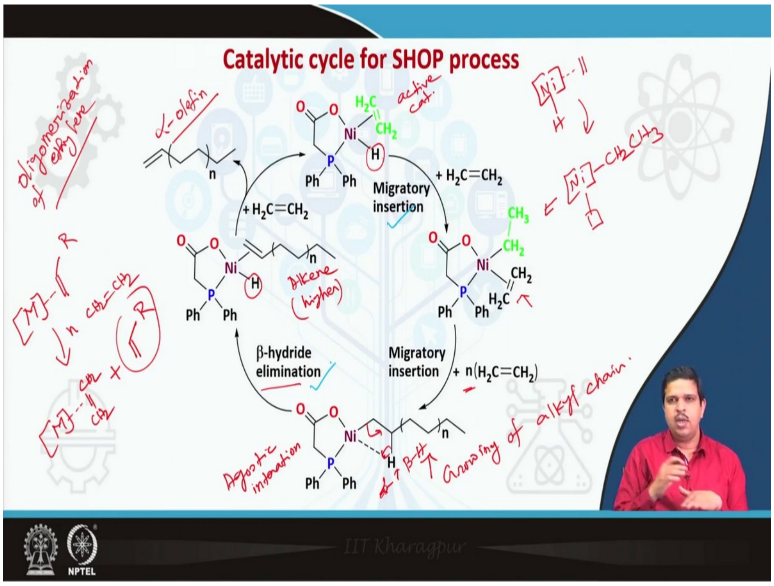

Catalytic cycle for SHOP process

Here you will see that, how this SHOP process that is the first step of the SHOP that is the alpha oligomerisations takes place the oligomerisations of ethylene. Now you see that is the active catalyst. Now you have the phosphino acetate here that P o, that coming from the phosphino acetate and here we have a nickel hydrogen that is the nickel hydrogen and that vacant position is coordinated by the alkene.

Now what will happen, you there will be a migratory insertion between the alkene and the hydrogen and you will get the CH2 CH3 that is the ethyl. So you will basically getting the nickel CH2 CH3 from here and again there will be another vacant position, because what is happening here, you will get have a hydrogen and you will have a the alkene. So there and then there will be vacant position and this vacant end position is coordinated by another molecule of alkene. And throughout this what will happen, the migratory insertion will be repeated there will be repetition, let us say n number of the alkene, then this will grow.

So this is basically this side is the growing of alkene, alkyl chains, alkyl chain. Now these are the alkyl group. Now I have to come get back my olefin alpha olefin. How it will happen, we know that if there is a beta hydrogen beta hydride elimination is very favorable for transition metals. Now this is my, this is my beta hydrogen and we know that how this beta hydrogen is eliminated because these are through agostic interaction. So those we have already discussed in our previous classes, so I am not going depth and then it will undergo the beta hydride elimination that is very important. So here you will see that this will be like that one.

So beta hydro elimination. So you will get the corresponding alkene that is the alkene again, that is the higher alkene, not the ethylene and you will get back your hydrogen again and then you have lot of ethylene molecules. So this delegation that the D L alkene alkene steps will be favored because we have lot of alkene molecules. So this is basically what I am mean to tell, that if you have a like this one and if we have, they are a n number of ethylene, then this will drive to the right side due to the last interior principle and you will get the, and this will be coming out this one. So this is you will see the alpha olefin and then again this cycle will be repeated.

So here you understand that, the important steps and the reactions if you understood that 4 unique reactions in organometallic chemistry, you will be able to understand without any confusion, that one is the migratory insertion and then you see beta hydride elimination. And from this repeated step of the migratory insertion you will get the higher number of alkyl groups. And then beat eventually at the last step, due to the b for beta hydrated elimination you will get our desired alpha olefin and then again this will be repeated the steps will be repeated.

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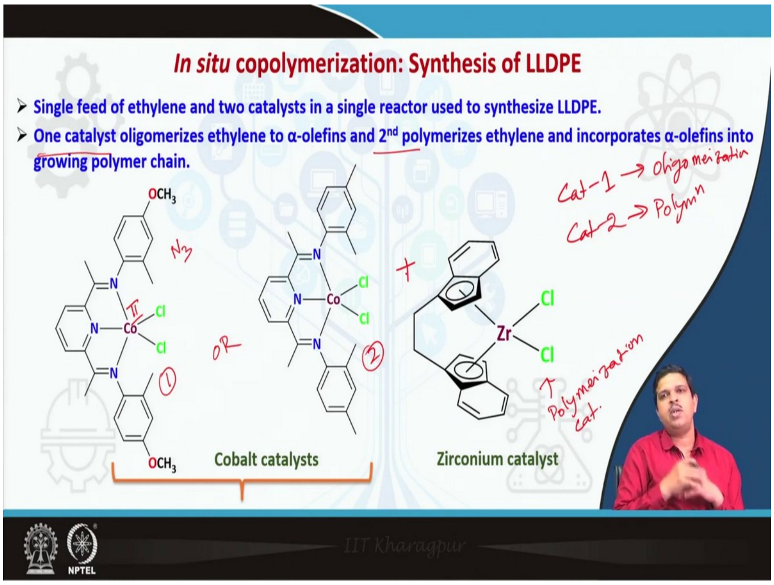
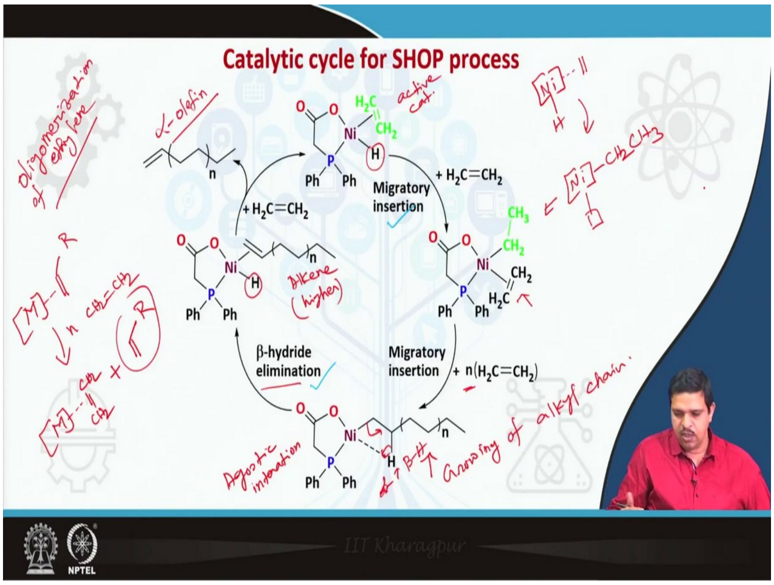


In situ copolymerization: Synthesis of LLDPE

- Single feed of ethylene and two catalysts in a single reactor used to synthesize LLDPE.
- One catalyst oligomerizes ethylene to α-olefins and 2nd polymerizes ethylene and incorporates α-olefins into growing polymer chain.


Catalytic cycle for SHOP process

So, far what we have tried to learn that you we need 2 monomers one is the alpha olefin and one is the ethylene. Now if you remember in the last class we discussed that there will be 2 strategies. One is the strategy one, that is the 2 separate chambers A and B, A is for the oligomerisations and B is for the polymerisation. Now the strategy 2, that is the tandem approach, they are in situ approach, that means the oligomerisations and polymerisation will be on the same vessel polymerisation vessel and 2 catalysts or 2 catalytic centers is better to call, 2 catalytic centers will be operating simultaneously to have the our alpha co-polymers, alpha olefin co-polymers that is the LLDPE.

So here, let us assume that one catalyst, that is the catalyst 1 which is and one is the catalyst 2. Catalyst 1 is the oligomerisations catalyst and catalyst 2 is the polymerisation catalyst. So now one thing you can imagine that we need 2 type, 2 catalyst one is very good for polymerisation and another one is basically the bad catalyst, bad polymerisation catalyst which will be using as a oligomerisation that means the that would stop, after say like a let us say 8 or 10 number of the insertion migratory insertion this one.

So let us say, it will stop or the reaction will be slower after 8 or 10 migrations, in migration in such a reactions. So here, here you will see that in this regard in the tandem process where one catalyst will be used for the alpha olefins synthesis the alpha olefins, and the other catalyst we will use, will be used for the polymerisation, the alpha olefin polymerisation catalyst. In this regard these 2 catalyst you will see that cobalt based see based catalysts here, here again you will see, this is at the plus 2 oxidation states and the similar structure, the COD structure you will see these 2 chlorides and 2 3 nitrogen.

So this is the nitrogen donor in 3 type of ligands and you can name the catalyst 1 or this is the catalyst 2 and another one is zirconium catalyst that is the well known systems Kaminsky type catalyst which is very good for the polymerisation very good polymerisation catalyst that is we already discussed in our previous classes.

So now if we can combine these 2 catalyst either this 1 or 1 or 2 or and the zirconium based or titanium based catalyst which is very good polymerisation catalyst. What will be what will happen?

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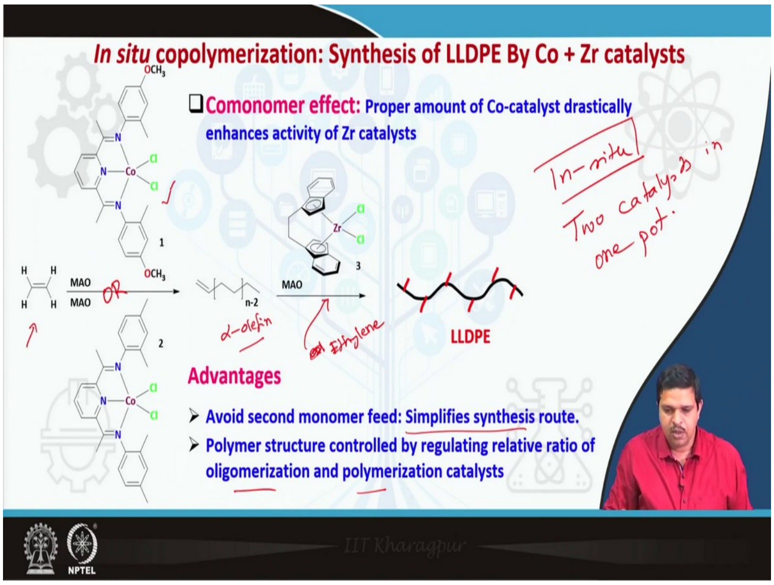

In situ copolymerization: Synthesis of LLDPE By Co + Zr catalysts

☐ Comonomer effect: Proper amount of Co-catalyst drastically enhances activity of Zr catalysts

Advantages

- Avoid second monomer feed: Simplifies synthesis route.
- Polymer structure controlled by regulating relative ratio of oligomerization and polymerization catalysts

In-situ

Two catalysts in one pot.

So in here you will see, try to understand, that if this is my the ethylene and if we use this one this is basically this one or that one anyone you can use it and you will get the alpha olefin and in the feedstock we have already alkene is the ethylene is there. So in the same reaction version, what will be, what we are getting? We are getting the alpha olefin and we are also adding our well known polymerisation catalyst zirconium or titanium waste whatever that is in your that is in our hand and you will get the LLDPE in same in situ, this one. No, there is no need of 2 separate chamber in situ co-polimerisation. So this is basically the 2 catalysts here the 2 catalysts in one pot.

So is basically simplifying the polymerisation steps and the removes the complication associated with the polymerisation reactors and the polymer structure can be controlled by regulating the relative ratio of oligomerisation and polymerisation catalyst. So is basically, if you, if I need a higher branching then we can use little bit more amount of this catalyst and if I need a short number of chains we can use the low amount of the oligomerisation characteristic. So by the way we can change the branching in the LLDPE. So this is a very advanced method and emerging to remove the complicacy of the strategy one.

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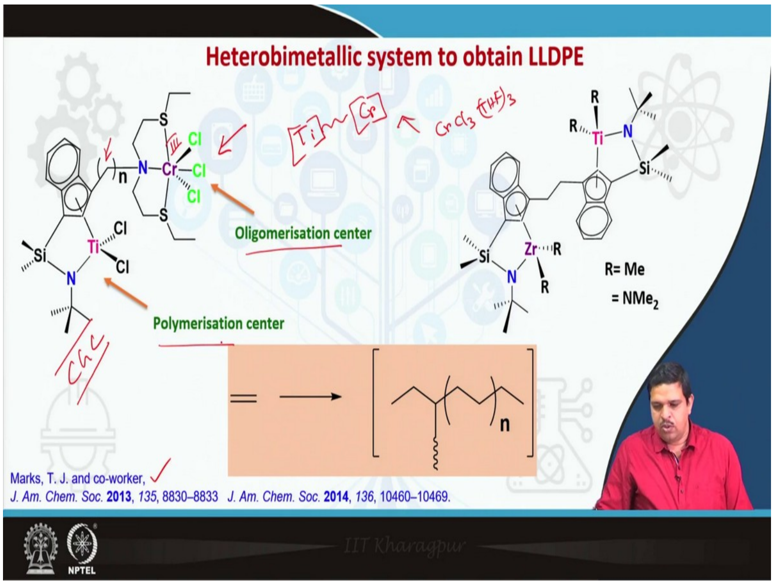


Heterobimetallic system to obtain LLDPE

Oligomerisation center

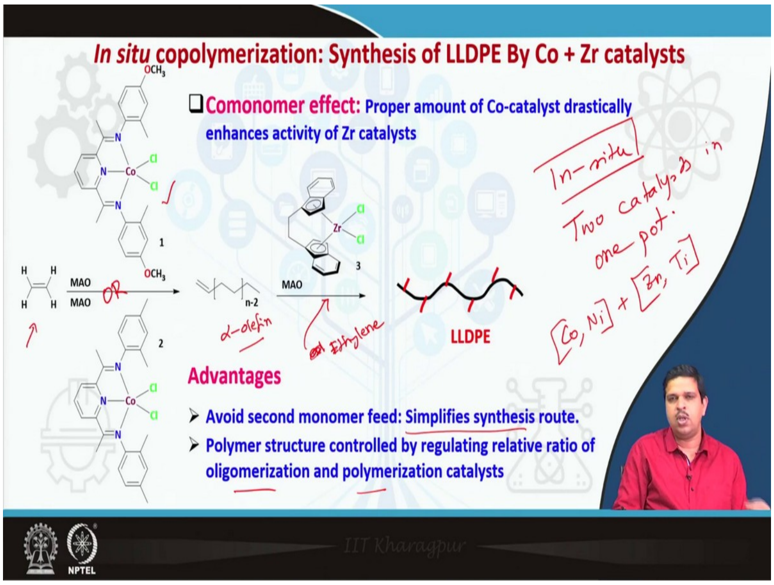
Polymerisation center

R= Me

= NMe$_2$

Marks, T. J. and co-worker, ✓

J. Am. Chem. Soc. **2013**, *135*, 8830–8833 *J. Am. Chem. Soc.* **2014**, *136*, 10460–10469.



In situ copolymerization: Synthesis of LLDPE By Co + Zr catalysts

☐ **Comonomer effect:** Proper amount of Co-catalyst drastically enhances activity of Zr catalysts

Advantages

- Avoid second monomer feed: Simplifies synthesis route.
- Polymer structure controlled by regulating relative ratio of oligomerization and polymerization catalysts

So another one that is very advanced method and advanced development in this area that is the same catalyst but heterobimetallic center and here you see that is the 2 catalysts, that is one is the cobalt based catalyst and one is the… Even you can use here the nickel based catalyst also and one is the zirconium or titanium based catalyst. So you can use for oligomerisation purpose you can use the cobalt or nickel separately or here zirconium based or titanium based catalyst for the polymerisation both combination in situ.

And here you will see, that we will be using again is in situ approach tandem approach but it will be using a single molecules but with heterobimetallic center and this the Tobin J Marks have developed this is quite recent, he develop this very noble catalyst, here you will see this we know, this is basically CGC type of catalyst here. We already discussed in our previous classes I will not go in more detail, I just want to show the design and the advanced advancement in this area.

So here you will see that this is a CGC based and this is the chromium based that is the plus 3 the oxidation state which is attached with a special, that actually end you can vary it, you can not only you can use the alkyl group or carbon group you can also use the other heteroatoms you can design. So mainly is basically the titanium and here the chromium. This catalyst attached together and it is a heterobimetallic system. This one, you can this mighty you can make it very easily from the CrCl3 THF whole 3 that is very well known researcher, you can make it in lab without any problem.

So here what is happening you see this is my oligomerisations center this one and this is the polymerisation center and this is also one of the very promising heterobimetallic catalyst for LLDPE synthesis following the strategy 2.

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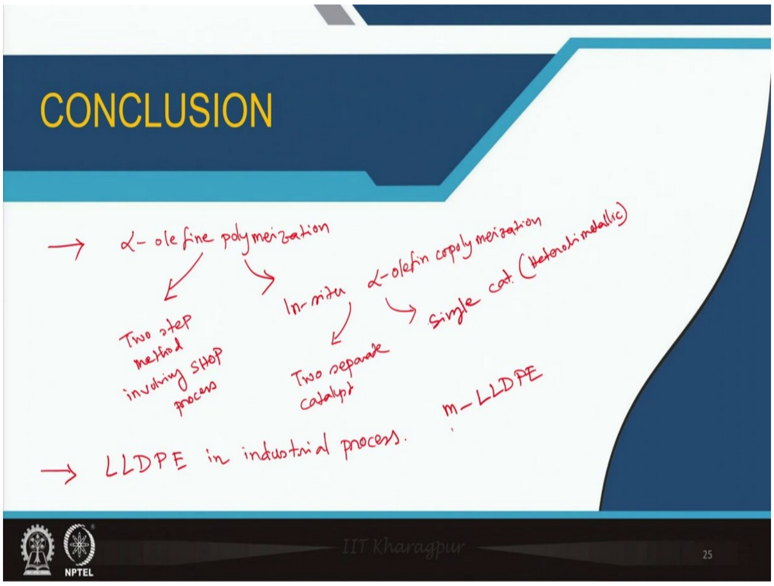

CONCLUSION

→ α- olefine polymeization

Two step method involving SHOP process

In-situ α-olefin copolymeization

Two separate catalyst

Single cat. (Heterobimetallic)

m-LLDPE

→ LLDPE in industrial process.

So this is, you will see that, this is, in a conclusion you can we can tell that alpha olefin polymerisation, you can approach in 2 ways, 1 is the 2 step method, one is the that is the involving SHOP process. So it is basically first you make the alpha olefins and then you separate and then you used as a separate feedstock to the ethylene polymerisation reactor. And this one you can do in situ alpha olefin co-polymerisation and again for this one you can do the 2 catalysts, 2 separate catalyst or you can use the single catalyst but it is a heterobimetallic, that means actually the 2 different catalytic centers.

Single catalyst but heterobimetallic and this way we learned how the LLDPE are synthesized in industrial process. So as I told that, if we use the metallocene based catalyst we can generally tell, it is LLDPE, if we, if it is through Ziegler-Natta catalyst or other way we simply tell it as a LLDPE.

So from today's class and the last class we understood that for industrial purpose for industrial LLDPE synthesis, we follow the alpha olefin co-polymerisation protocol. So we need to use 2 monomers one is the ethylene, that is the main for the main polyethylene skeletal and to make the linear short chain, we have to use the another monomer that is the alpha olefin like butane, hexane, octane, but in a lower amount and to get the alpha olefin, we have to do the oligomerisation. So both here oligomerisations and polymerisation both are important and for the oligomerisation we have to use the catalyst like nickel based catalysts, catalysts which involved in the SHOP process, the Shell Higher Olefin Process that is the SHOP and we can also in a use a tandem type of approach which are more advanced and very recent advancement.

So here you will be using either 2 catalysts or the single catalyst with 2 different metal centers, which are also effective and more advantageous because you can use, you can remove the complicacy associated with the two different chambers in the polymerisation.

So in the next class, we will be discussing, how we can, what are the another advantageous or how another strategy to make this metal lotion based catalyst to the industry. So we will discuss how you can convert a this metallocene based catalyst for laboratory to industrial process. So you can yes, you can get idea that what I mean to tell that, as I told that Ziegler-Natta catalyst is a heterogeneous catalyst system but our metallocene based catalyst are homogeneous based catalyst systems, the activity is much higher, you can very nicely control the stereo regulating, but for industrial process we have to make the homogeneous to convert homogeneous to heterogeneous system for to make it, to make the whole process as you more economic and obviously to reuse the catalyst.

Otherwise the cost will be very high, it will be not the process will be not economic. So we will try to understand, what are the basic steps or logic to make the industry viable catalysts or how to convert and also we will discuss very briefly about the, how the poly olefins can be degraded that is another very important area.

Because we have to use, we now all are promoting the governments and all the countries are promoting the recyclable and how we can make it, because you know that polyethylene is a very stable polymers, because it is a carbon carbon bonds, carbon hydrogen bonds, polar nonpolar bonds very difficult to break, but how to recycle, how to break, how to make the more you useful materials or useful molecules from the used plastics. So you will be very surprised to know that the same metallocene based catalyst can be used to bake the poly polyethylene by the concept of microscopic reversibility that is another very challenging and very emerging area that should be discussed in this class.

So thank you and see you again in the next class to discuss about the metallocene based catalyst. Thank you very much.