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

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Lecture 25

Metallocene to Post-metallocene catalysts for olefin polymerization

Welcome to our class, so in the last classes we have discussed about the metallocene based catalyst for olefin polymerization and we have discussed very thoroughly about the mechanism and most interestingly that how the symmetry dictates the stereoregularity in polymers where you will be using is a prochiral monomer as example propylene and we saw that several advantages factors upon the Ziegler–Natta catalyst and we have now very good knowledge about the metallocene based catalyst.

So today we will try to discuss that how the metallocene catalysts from the metallocene catalyst how the recent development of the post-metallocene based categories have been done by various groups and not only for academic interest and also for the industrial importance so we will discuss what is the need? We had already very good catalyst Ziegler–Natta catalyst then metallocene the Kaminsky type catalyst then what is the need of developing the post-metallocene based catalyst so that we will try to discuss and also we will try to discuss with the emphasizing its chemical structure, design and the mechanism and what is the advantages output.

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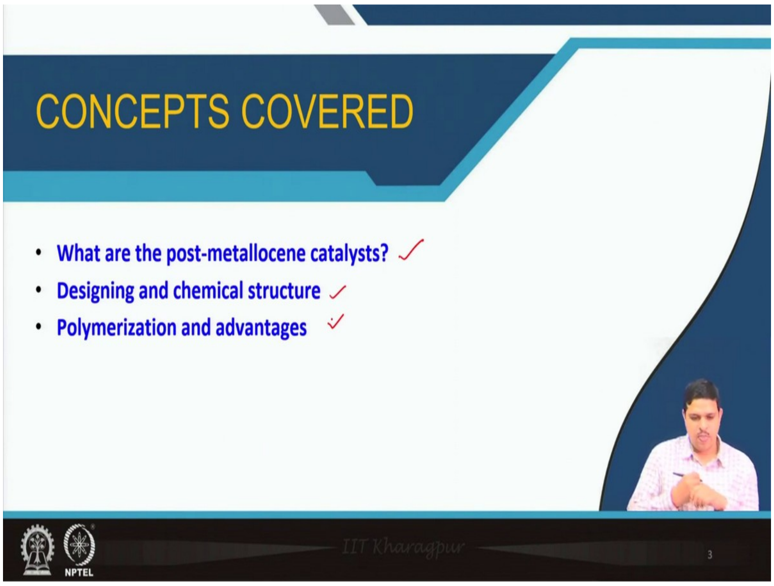
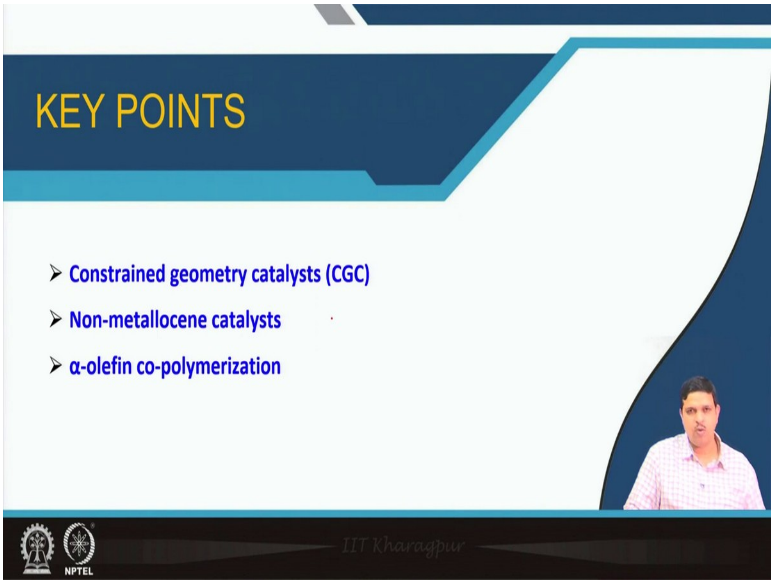


CONCEPTS COVERED

- What are the post-metallocene catalysts? ✓
- Designing and chemical structure ✓
- Polymerization and advantages ✓



KEY POINTS

- Constrained geometry catalysts (CGC)
- Non-metallocene catalysts
- α-olefin co-polymerization

So in this class we will try to learn what are the post-metallocene catalyst and what the design and chemical structure associated with it so what are the basic criteria of the ligands and also the metals the then we will discuss the its polymerization and reactivity and obviously the advantages factors upon the oil developed and industrially accepted metallocene based catalyst which are Kaminsky type catalyst, so these are the key points constrained we learned, constrained geometry non-metallocene.

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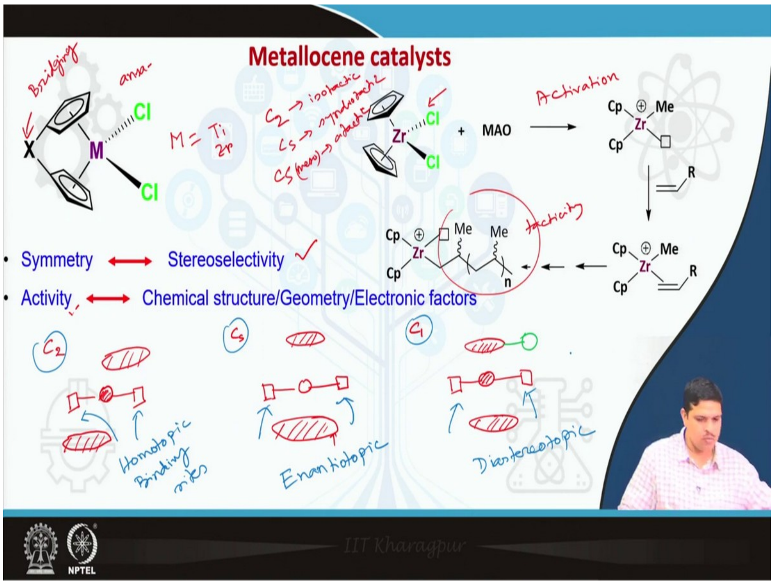

Metallocene catalysts

- Symmetry ⟷ Stereoselectivity ✓
- Activity ⟷ Chemical structure/Geometry/Electronic factors

So let us start so, so far as I told just a few minutes back that now we are very familiar with this kind of metallocene catalyst where you have metal is basically the titanium or zirconium and these are 4 oxidation, plus 4 oxidation state and you see here different bridging units will be there, this is basically the category of ansa cyclopentadienyl metallocene complexes and this X is a bridging and this bridging you know that we have now a good, very good idea that how the bridging units affects its reactivity the chemical structure and also the stereoregularity and activity.

So we now have a very good concept about the metallocene catalysts and we have now learned that how that symmetry is related with the stereoselectivity and which is the main beauty of this kind of metallocene catalyst so depending upon the symmetry of the metallocene initiator you will be getting the respective tacticity in the polymers and not only that one the activity also you can change by changing the bridging unit, by changing the substituents on the cyclopentadienyl and obviously using the co catalyst because here you will see that this catalyst is not active catalyst we learned, this is not active you have to do the activation so this is the activation of the catalyst which we use MAO or the Boron based that we have discussed in the last classes.

And then it undergoes the insertion reactions alkene coordination followed by insertion and then we get the respective the polymer unit here you see and also we have learned that depending on the polymer symmetry we will get the different tacticity so as example if you have, if you remember if you have C2 symmetry then we will get the isotactic then if you have a CS symmetry then we are, we will get the syndiotactic and if we get the CS meso we will be getting the atactic so that we have now learned so and very pictorially I will show you that that if you have a C2 symmetry then why you will get the isotacticity so that is.

So you can assume that this one, I am just doing in a very cartoon using a cartoon diagram so that you can easily understand so this is say is a metal center and this is my backend side that is the active sites actually where the polymination growth will be happening and the alkene coordination will happen that is a monomer coordination and these are my the CP rings so I will let us say this is the 1 CP ring and this is the 1 CP ring, now you see here in this case, this is the 1 C2 symmetry.

Now if it is CS then what will happen although in the last class we have discussed with the with all the symmetry axis so here again these are the active side and these are the one CP ligands and in cartoon diagram and this is the another CP ligands, this is definitely is a fused CP regions it may be the let us say indenyl another may be CP ring and this case this is this one and then another one like let us say C1 so what will be the scenario so again let us say this is my metal and this is my backend site that is actually the active sites for the polymerization.

And let us say this is one ligand and this is the another ligand what but this is not symmetric so like put like another substrates or another aryl or alkyl so now you try to understand that what is here so you see here this is obviously the homotopic that is this binding site and this binding site if you see the symmetry that is the homotopic binding site, homo topic binding sites and for the next one, this one and this one is enantiotopic binding sites and this one and this one is diastereotopic and in the last classes we have discussed in depth using the symmetry axis and symmetry operation and we know now that that how the active sites differs by changing the symmetry of the metallocene units and what are the output so output will be the different tacticity in the polymers if you take as one prochiral monomer as example propylene.

So that we have learned and these are the most advantageous factors of the metallocene based catalysts so we can very nicely control the stereoregularity in the polymers so that is the most beautiful factor in the metallocene based catalysts.

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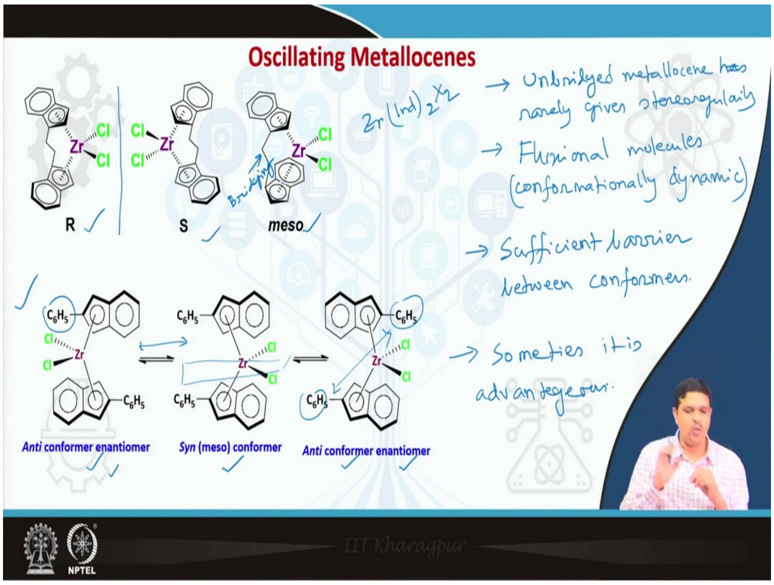

Oscillating Metallocenes

$Zr(Ind)_2X_2$

→ Unbridged metallocene has rarely gives stereoregularity

→ Fluxional molecules (conformationally dynamic)

→ Sufficient barrier between conformers.

→ Sometimes it is advantageous.

So however one thing we have to understand that in if you, if your CP ligands are not breached then due to the first rotation of the CP ligands CP rings we do not get any kind of tacticity means very difficult to get the a particular tacticity in the polymer, so as example like this one so here see you see that this one, this one, this one and this one so with the same composition of this Zr, indenyl 2 and X2 this one you will see that it can exist in the 3 conformance, one is the enantiomeric R and S that is the racemic and another one is the meso so R and S that is the racemic mixture will give the isotactic polymers and the other one will give the attractive polymers that we know now and we now can explain why we get it.

However it is very difficult to control the tacticity using this kind of ligands if you do not have the bridging unit in this case it is easy because it is you see this is the bridging that means there is some restriction in the rotation, so unbridged metallocene has rarely gives stereoregularity however we can do it by designing the ligands in a very judicious way, what we have to do, we have to basically increase the barrier energy.

So suppose in this case if you see this one what is there, there is a phenyl group, now in this scenario what will happen there will is a sufficient barrier, energy barrier between this one and this one and due to this one what will happen there is the lifetime of the anti, so this is you see this is the anti-conformer, this is also anti-conformant because this phenyl group and phenyl group is in anti, here, now this is basically enantiomer of this is the pair of enantiomer these are because these are the it is a relation of mirror image relation is there and this is a meso type of conformal, you will see that this is the plane of symmetry is there so this is a meso type of conformer.

Now if the barrier is energy is sufficient or more than the alkene insertion so that means if lifetime is more then the alkene insertion then what will happen we can have a sufficient time to get the particular conformer or to react of with the prochiral monomer and then what will be the effect, effect will be that you can get a stereoblock copolymers and that is important I discuss in the last slide what is the stereoblock copolymers and what is the importance.

So this kind of molecules call the fluxional molecules, fluxional molecules that means that conformationally dynamic so it can exist in different conformers but with sufficient lifetime. So in this case what is the barrier, sufficient barrier between conformers so that and what will be the result, the result will be that it can provide the different stereo polymers with the same metallocene catalyst and sometimes it is advantageous I will discuss I will give one example and you will understand then why it is advantageous.

So it can play the role of 2 catalysts, so single catalyst dual role we no need to use the 2 catalysts.

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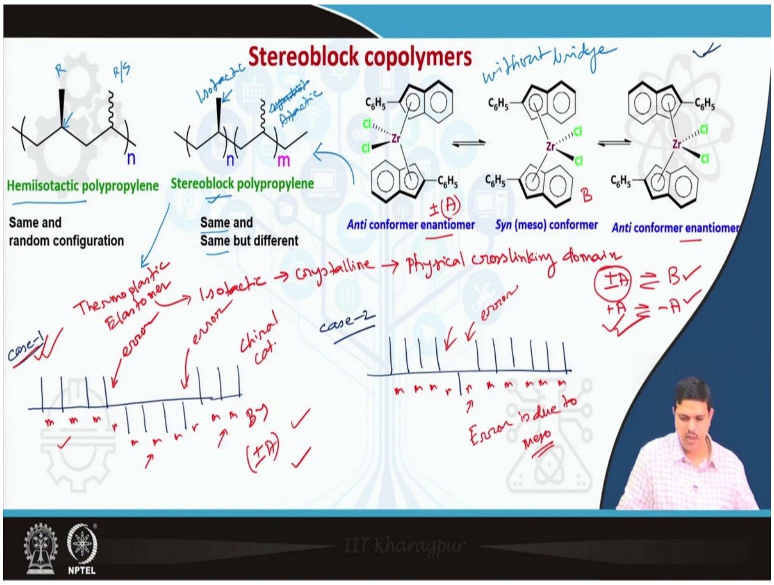


Stereoblock copolymers

Hemiisotactic polypropylene

Same and
random configuration

Stereoblock polypropylene

Same and
Same but different

Anti conformer enantiomer

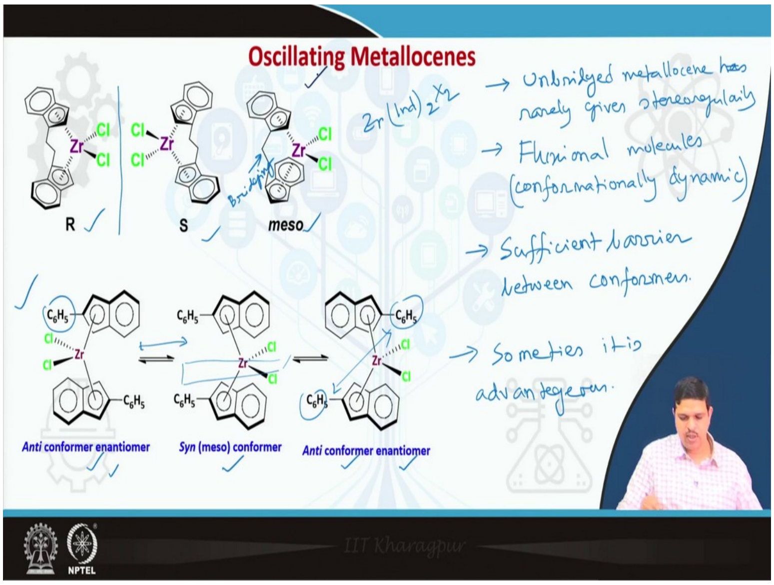
Syn (meso) conformer

Anti conformer enantiomer

Thermoplastic Elastomer → Isotactic → crystalline → Physical crosslinking domain

(±A) ⇌ B

+A ⇌ −A



Oscillating Metallocenes

Anti conformer enantiomer

Syn (meso) conformer

Anti conformer enantiomer

→ Unbridged metallocene has rarely given stereoregularity

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→ Sufficient barrier between conformers.

→ Sometimes it is advantageous.

So here you try to understand this two type of so we now know that isotactic polymers syndiotactic polymers propylene or atactic propylene so that we know what is this, here I have used one term hemiisotactic polymers, hemiisotactic polymer means that here in all the polymer chain in the polymer throughout the polymer chain there will be that methyl group the particular configuration and the adjacent methyl group all you have is the random as example one let us say one is the R that will be adjacent R or S like that randomly there will be no order.

But in the stereoblock propylene you know that block copolymers we have discussed in the beginning so this is you see that this is a block so here it will what will happen here will be the same a particular configure that methyl will be and the other block will have a same but different that means if it is isotactic then this will be syndiotactic sorry, this will be atactic or syndiotactic so one block fully contain the isotactic and the other block is either atactic or the syndiotactic then in this scenario we will got the stereoblock polypropylene so that is why I have written here in one block same a particular and other one same but different configuration so this is called the stereoblock copolymers.

Now here you see that this is very interesting so if you use this catalyst this is you see without bridge, without bridge and as the barrier between the 2 conformer is quite good that is why it can exist and the lifetime is sufficient enough to react with the alkene prochiral monomer so now what will happen you can get the stereo block propylene using this catalyst so you no need to use 2 catalysts you single catalyst is enough and stereoblock polymers is interesting in some for some applications because this one is actually is can be used as a thermoplastic elastomer.

Because you know that that isotactic block, it has isotactic block this block is actually crystalline and this crystalline block actually acts as a physical cross linking domain so that is why sometimes we have, we also are interested for the stereoblock propylene where one block will be a particular stereoregulatory and other block will have a different but the different stereoregulatory so and you can make using this kind of catalyst with a properly designed metallocene catalyst so this is one beautiful example of for such applications.

So I will just discuss in little depth about this stereoblock copolymers using the oscillating metallocene based catalyst so this is also called the oscillating metallocene because it oscillates between the anticonformer then meso conformer and the other anti-conformer, so suppose I am doing the polymerization of with this catalyst, this catalyst and it exists in the solution in 3 conformers and I am using the monomer that is the propylene let us see what kind of stereoregulatory we will get.

So let us take a small chain of the polymer and we will try to understand that how, what are the tacticity we can get it, so let us say take a small chain and let us try to understand by using this line diagram, so this is the case 1, I am writing I will explain what I am doing and this is the case 2 so 1 2 3 4 now you label it, so we have learned this in our previous classes so this is m this is r so this will be again m m m r m m so here also m m m this will be r this will be r then again m m m m m, now you will see that there is basically this is the enantiomer this is the enantiomer.

So if we consider that this is the A form and this is the B form and this is basically you can say plus minus A so basically actually it contains the 2 species one is the equilibrium between plus minus A and the B, B is the meso so we discussed in the last classes that whether it is a 2 enantiomer but eventually it will give the isotactic polymers whether it is the plus isomers enantiomer or minus enantiomer.

So now you see that there is a 3 equilibrium between this one so equilibrium may be 2 possibilities, this one or plus A minus A so we will try to understand that what are the dominating equilibrium whether the this one or whether the this one so that means what are the species actually present mostly and who are the responsible for the polymerization, now you see here if it is in this case 1 so you will see that m m m m and then m so that means that this one is this is the error, so here this is the error and here this is the error so what you are getting basically you see that you are getting the m m m m then there is a one error then again you are getting m m m then if there is another error then again you are getting m m m that means obviously that it will be this polymerization is by the plus minus A.

That means the enantiomer, not by the meso but because meso has no chiral environment so this one definitely by the chiral catalyst and this one so this is the error and this is the error so here you will see that this is r and again this is the r so that means you will see that this error is due to the meso isomers that is the achiral see this error is due to meso isomer but in the experiment it has been observed that case 1 is the dominating that means you will get the case 1 in major so it proves that mostly in solution the equilibrium the major species is basically the racemic the plus minus A so that is the…

So from this experiment and you can do it by simple proton nmr c 13 spectra, you can buy the concept of the dyads and triads, you can calculate that how much the toxicity is there and how much the and what are the errors are there and depending on that one you can tell that how whether this polymerization has been done by the catalyst side control or chain in control or whether by the chiral environment cap of the catalyst or the by the achiral catalyst and this way you can judge that who are the responsible or active species in this polymerization.

By this observation we can tell that most of the majority active species are this the racemic so this there is a equilibrium between plus minus A this one is the major equilibrium not the plus minus A and B between B so this is really a very good information and it is very helpful to make the stereoregular copolymers.

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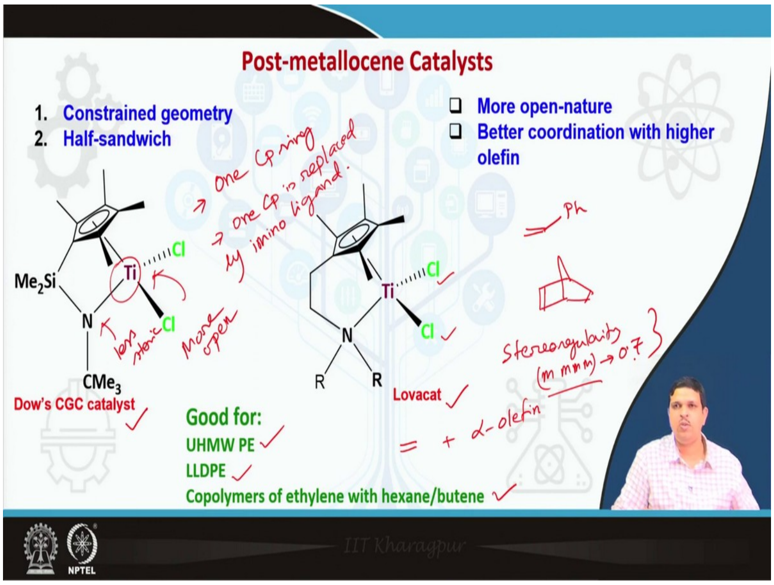

Post-metallocene Catalysts

1. Constrained geometry
2. Half-sandwich

- ☐ More open-nature
- ☐ Better coordination with higher olefin

→ one Cp ring

→ one Cp is replaced by imino ligand.

less steric

More open

Dow's CGC catalyst ✓

Lovacat ✓

Stereoregularity (m m m m) → 0.7

= + α-olefin

Good for:

- UHMW PE ✓
- LLDPE ✓
- Copolymers of ethylene with hexane/butene ✓

Now today we will introduce a different type of catalysts that is the post metallocene catalysts so the name suggests that post metallocene that means ahead of the metallocene so something will be definitely we are either modifying or replacing or doing some extra design of the catalyst so what are they, so here you will see some of the examples this is the very famous catalyst that is the Dow's CGC catalyst that CGC means we will discuss that is the constant geometry catalyst the CGC catalyst and other one is the Lova catalyst that is also very famous and in all the cases you will see that one CP is missing so one CP ring is there and other CP ring is has been replaced by the amine or amidotype of ligands.

And one CP is replaced by imino ligand so and others are as usual whether the titanium or the zirconium so these are specifically these are very effective and famous catalysts that is why I am discussing with these 2 examples and these are you can see basically half sandwich complex very easy to understand in other complex you will see there is 2 metallocene and here one metallocene is gone so that is why the half sandwich complex.

And it is a more open because you will see steric hindrance is less, less steric hindrance here at this side so that is why the more open in nature that means here so this side is more open and that is why the monomer can approach and but however there is another disadvantage the activity is very high because there is lot of space monomer can easily come there is less steric hindrance but we have to sacrifice the stereoregularity.

So we discuss what is the reason so but these are perfect for ultra high molecular weight polyethylene that is the advantage and so you can get some branching using the copolymerization we will discuss what is the co-polymeration so we can make high molecular polyethylene, we can make the LLDPE that is a linear low density polyethylene using the co polymerization so ethylene and another alpha olefin as example hexane butane like that because as it is more open that means bit it can little sterically hindered alkene or longer chain of alkene also can coordinate very nicely even not only the alkene secant it can also can coordinate like a (())(29:34) so it is can polymer is the (())(29:36) molecules it can also not bonding you can understand that so much sterically hindered monomers also can be polymerized by this kind of catalyst.

So but as I told that stereoregularity is a issue and you can, you will have a less stereoregularity and as example like if we quantify this kind of ligands will give the maximum of 0.7 ratio of the m m m m that is the this one is basically quantifies the how much stereoregularity is there so that we have to sacrifice and with the same condition if you take any achiral metallocene catalyst that stereoregularity will be much higher in that case the m m m m fraction will be more than 0.9 or something like that so that is the one disadvantage but this is the reactivity wise this is much more than the normal metallocene compounds.

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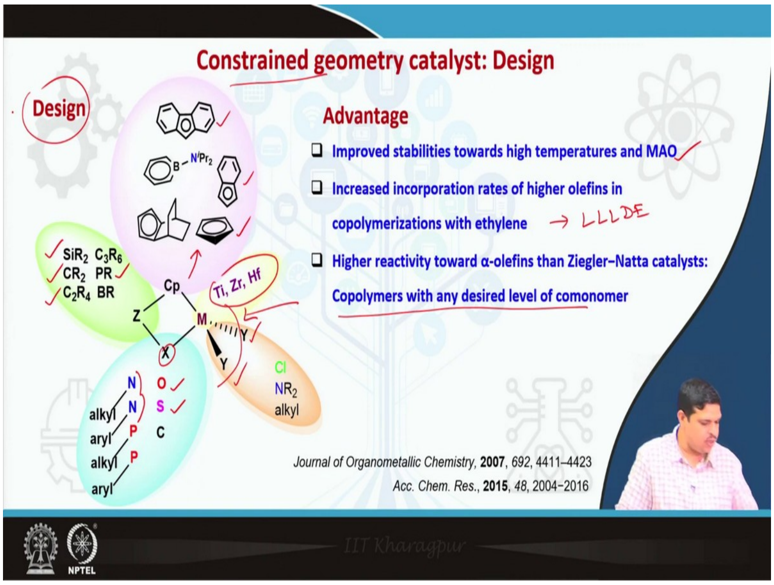

Constrained geometry catalyst: Design

Advantage

- ☐ Improved stabilities towards high temperatures and MAO
- ☐ Increased incorporation rates of higher olefins in copolymerizations with ethylene → LLLDE
- ☐ Higher reactivity toward α-olefins than Ziegler–Natta catalysts: Copolymers with any desired level of comonomer

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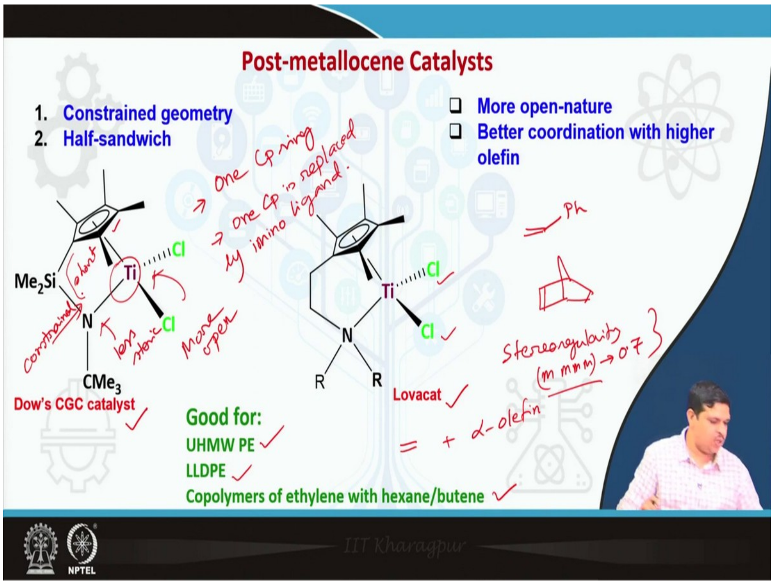

Post-metallocene Catalysts

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Dow's CGC catalyst

Lovacat

Good for:
- UHMW PE
- LLDPE
- Copolymers of ethylene with hexane/butene

So what are the constrained geometry so this is the why because you see that this CP rings this is the CP rings and this the titanium and this one is actually very short bridging so this due to the short bridging this is very constrained, this is very constrained and that is why the name is constrained geometry and due to this constrained this space is quite open so different type of ligands are possible and has been developed with different catalysts of this kind of category that is the constant geometry.

And you will see here that the bridging is maybe the silicon based carbon based or multiple carbon based or the phosphine or borane but as I told generally these are short bridge not quite longer here this X may be oxygen may be sulfur based donor or maybe carbon based donor and mostly actually is the nitrogen based donor the amino substituted amino and here are these CP rings not only the CP that the varieties of substituted CP you will see here that this one the indenyl or fluorenyl the different cyclopentadienyl or fused cyclopentadienyl are possible and the metal centers are titanium zirconium hafnium and these are obviously the alkyl or the halides.

And the advantage are lots as I discussed that is improved stabilities these are quite stable then the zirconation metallocene compounds so that is really good and more economic, increased incorporation rates of higher olefin in co-polymerization with ethylene so that why because as it is more open in open so that means when you the co-polymerization with ethylene using other comonomer as example a hexane butane or heptane then the copolymerization rate will be much better and you will get the LLDP polymer so that is.

So and obviously the higher reactivity towards alpha olefin then Ziegler Natta catalyst and that is why it is used for co-polymerziation particularly for the linear low density polyethylene and also like for branched polyethylene and sometimes we purposely need the branch polyethylene as we discussed in the previous classes that property depends on the chemical structure of the polymer and depending the property the applications we are targeting for and that is why we have to design our polymer we have to take a the appropriate catalyst otherwise we will get not get the particular polymer we are targeting for.

So you will see there is a huge scope and use possibilities using different ligands, different (())(34:40) different (())(34:41) and like that.

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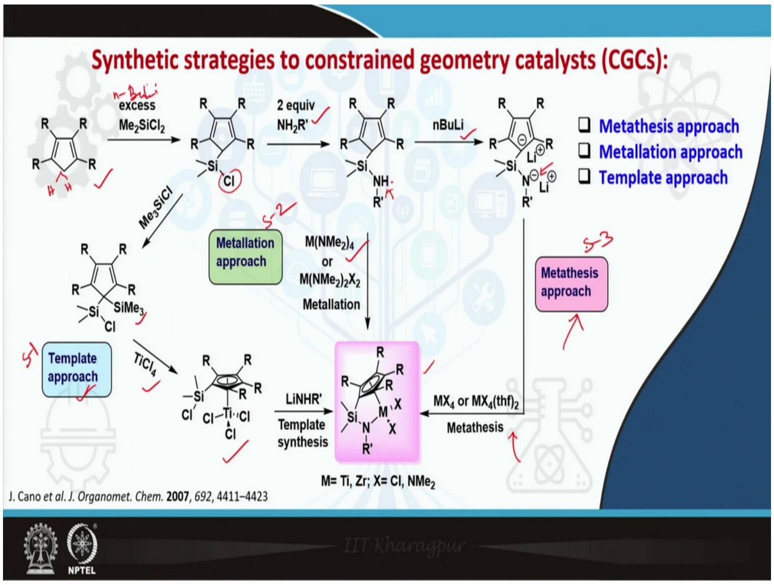

Synthetic strategies to constrained geometry catalysts (CGCs):

- ☐ Metathesis approach
- ☐ Metallation approach
- ☐ Template approach

M= Ti, Zr; X= Cl, NMe$_2$

J. Cano *et al. J. Organomet. Chem.* **2007**, *692*, 4411–4423

So in this case you see that the synthesis is very straight forward, you will see that multiple methods or strategies you can follow one example you see that you start from again the CP rings or substituted CP rings and then you use the butyl lithium and then the excess SiMe2Cl2 so here you have a H and you use n butyl lithium then it will be deprotonated and use XM dimethyldichlorosilane then you will get this SiCl that is very (())(35:32) and then you react with this one then you will get the this compound that is the template approach and then you then finally react with the TiCl4 then you will get this one, this is called the template approach.

The other one you see you start from here then you use the 2 equivalent of amine with what amine we are that is depending on you that what donor you will be selecting and then you are use the n-butyllithium to deprotonate this amine and then you have n minus and then you use the precursion like MX4 that is the ZrCl4 or TiCl4 then you get you will get your catalyst so this is called the metathesis approach because we are exchanging the metals of the lithium by the titanium or zirconium.

And one is the metallation approach here you will see you will get that this one and then you are using the dimethyleamino, Tetrakis dimethyleamino titanium or zirconium and you will get the direct metallation so here you will see 3 strategy, so strategy 1 strategy 2 and strategy 3 so sometimes it depend on the substituent, depends on the acidity of the involved proton attached with the amine and also depends on the substituent on the CP rings, so these 3 methods are generally followed to synthesize this kind of constant geometry catalyst.

So today we will discuss that how we are approaching from metallocene catalyst to the post metallocene catalyst and here we show that one CP ring has been replaced by the other donors as example imido or imino and then we show that some advantageous properties that is the mainly the reactivity and getting the high molecular polymers so we are trying to explore the catalytic properties to have our desired polymer.

So in the next class we will continue our discussion on the post metallocene catalyst and its development and obviously the mechanism and then we will try to understand the advantageous factors upon the Ziegler–Natta and also the Kaminsky type metallocene based catalyst, so thank you and see you again in the next class.