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

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Lecture 22

Coordination polymerization of olefin by Metallocene Catalysts: A new avenue in polyolefin catalysts (Contd.)

Welcome once again. So, we will continue our discussion about the coordination polymerization of olefin by metallocene based catalysts.

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CONCEPTS COVERED

- Metallocene as catalysts for olefin polymerization
- Role of initiator and co-initiator
- Mechanism

In the last class, we discussed about the initial development of the metallocene catalysts by (())(0:48) and Kaminsky sin. And we discussed in the last class that what are the catalytic system, and we realized that there is one catalyst who is called initiator, and another co-catalyst is required that is the co-initiator. And then we show that what are the structures and category of the catalyst system and what is actually the co-catalyst.

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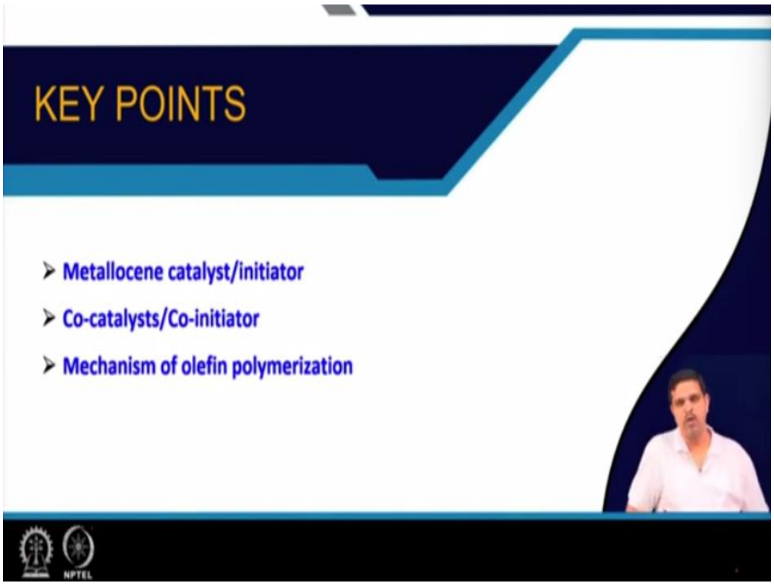

KEY POINTS

- Metallocene catalyst/initiator
- Co-catalysts/Co-initiator
- Mechanism of olefin polymerization

So, we will continue our discussion about the role of the co-initiator and the initiator, and we will try to understand the mechanism.

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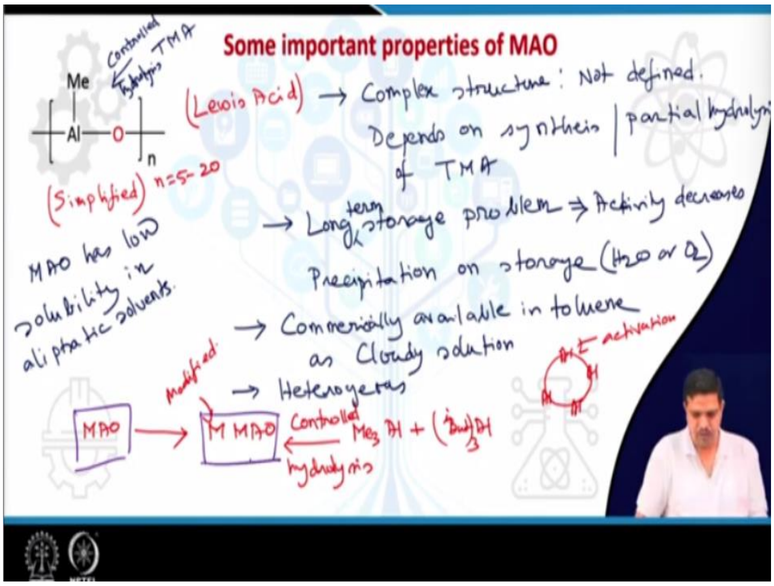

Some important properties of MAO

(Lewis Acid) → Complex structure : Not defined.
Depends on synthesis | partial hydrolysis of TMA

→ Long term storage problem ⇒ Activity decreases
Precipitation on storage (H_2O or O_2)

→ Commercially available in toluene as Cloudy solution

→ Heterogeneous

(Simplified) n=5-20

MAO has low solubility in aliphatic solvents.

MAO → MMAO ← Controlled hydrolysis $Me_3Al + (^iBu)_3Al$

So, in the last class we discussed the synthesis of and the what are the basic structures which we believe about the MAO and this MAO in the last class, you learned that this may be linear, this may be three-dimensional, this may be cyclic, although most of the scientists believe that it is a cage-like systems, network systems.

So, this one is a very simplified, you can tell, very simplified and generally you represent the MAO like this one. So, this is simplified representation of the MAO, and n is generally kind of 5 to 20 like that. And obviously, this one is a very good, very good Lewis acid that is needed as a co-initiator. So, we will discuss some of the important properties of the MAO which will be useful to understand the mechanism and to understand the mechanism of polymerization as well as the mechanism of activity, the main catalytic part.

So, I just tried to discuss in a very simple way that we now learn it is very complex structure. So, it is basically not defined and quite unclear, how, what are the structures. There is a combination of, it is quite possible that there is a combination in the same system there is a combination of the cyclic linear system and this actually depends on the how you are synthesizing, depends on synthesis, that is the how was doing the partial hydrolysis of TMA.

TMA recall, so, this actually seen, we do TMA and this is the controlled hydrolysis. And it is basically depend this, the different contribution of the structures. The statistical distribution of the structure actually depends on this synthetic strategy.

And it is the problem of long storage, the long term storage problem. That means, with time, it undergoes this system is decreases with time. This information I am giving particularly for the industrial personal so that they may be careful while using this co-catalyst and also obviously for the general perspective.

So, it has a problem, the long storage and you see that it undergoes the precipitation on storage and it actually activity decreases. This is commercially available in following, generally with defined strength as cloudy solution. So, this is actually the heterogeneous system and it does not, it is not really fully dissolving solvent. And because MAO has this, MAO has low solubility, in aliphatic solvents.

And we do not use generally the other than hydrocarbon solvents in olefin polymerization because there may be some other reactions with the active catalyst because you know that the metallocene disc systems are very reactive and so, we use always the innocent solvents like the aliphatic solvents. And that is why these MAO is commercially available in toluene as a cloudy solution.

So, only problem is that you cannot really store for a long time, and particularly, if you use it again and then seal and again use it like that. So, in because there is a chance of insertion of water or the oxygen in the storage flask. So, you have to be really very careful on that one.

And also, as it is a heterogeneous system, so it is a heterogeneous because your, it is not solvable in your pollination condition. So, most of the, so the activation mechanism is also really very complex system to understand. Most of the reactions that happens, if it is like a cage like structure and if it is like aluminium here, so most of the activation happens on the surface.

However, this MAO has been now modified to the M MAO. This M stands for the modified MAO, which has better solubility compared to the normal MAO. So, this is actually how do we prepared, we prepared from the Me3 Al and is tri-iso-butylaluminum. So, butyl, isobutyl aluminium. And if you do the controlled hydrolysis, so you get a system where on aluminium, both methyl is there and in some aluminium, in the same cage like structure of polymer structure, there will be butyl group.

And so, what will happen? So, what is the effect? So, solubility will increase and you will get the better system, homogeneous system because use that metallocene based systems is basically homogeneous system. So, if all the parts are homogeneous, definite the mechanism, the activity of the polymerization will be much higher. So, that is the MAO. So, MAO is also, we you also use in industry and academically, we use MAO, and sometimes we also use the modified MAO.

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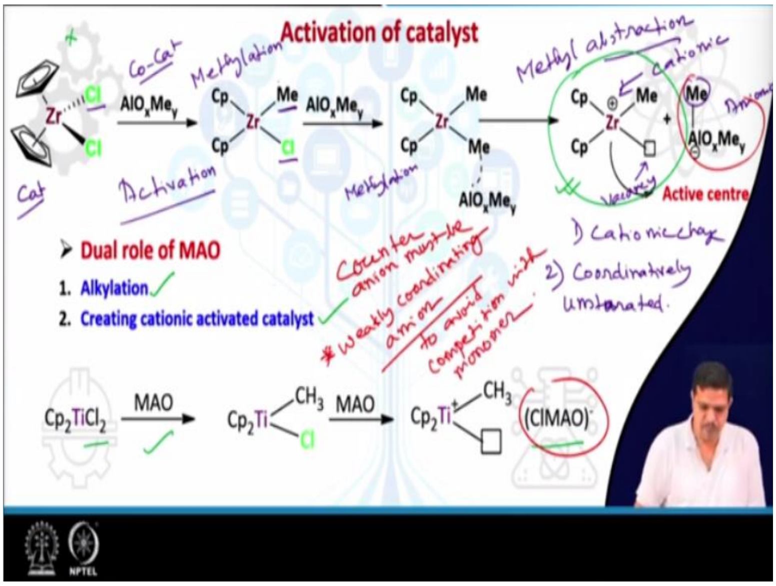

Activation of catalyst

- Dual role of MAO
  1. Alkylation ✓
  2. Creating cationic activated catalyst ✓

So, now we are very familiar with the, what is my catalyst system? Main catalyst system that is the catalyst. And this is my co-catalyst. Now, as I told that, what is the role of the co-catalyst? This is basically to activate my catalytic system, main catalyst that is the metallocene. So, this is what we are doing. We are this is basically the activation to make the main catalytically active species for olefin polymerization.

So, let us what we are doing here. So, here you see that this is the methylation here. So, this step, you can tell first step is the methylation. So, now while discussing that, how it is activation is going on. So, first is the methylation. So, here one core group is substituted by methyl, and this MAO is the Lewis acid is doing that one. So, it is basically obstructing one chloride.

So, you see here, so this is methyl is obstructing this methyl or this will be obstructing later. So, here what we will see that in this case, this is my MAO, it is now taking the chloride, first step and methylating here. So, this one chloride is substituted by methyl by the MAO. So, here it is acting as a methylating or methylation, methylating agent or methylation. And then another one second step, you will see this chloride is again substituted by one methyl. So, here is also again the methylation.

Now in the next step is you see that it is acting as a methyl. So, this step is a methyl abstraction. Now what is happening, it is becoming as anionic here, so this is becoming anionic and this is becoming the cationic. And you see that this, there is a backend space here. So, this is the backend space. Now, what we are doing, we are creating a cationic here, cationic centre, because the oxidation state of zirconium is plus 4. So, definitely there is a catatonic species.

The last step is basically acting as a methyl abstractor. And where we are doing, we are making a catatonic charge and we are making the coordinatively unsaturated species. And this is for what? This is, so that my monomer that is the ethylene can coordinate with the zirconium centre. So, this is my active catalyst for the coordinative, for the polymerization of ethylene.

So, here you see that this is not my catalyst actually, this is not my catalyst. The real catalyst is the active catalyst is this one. So, here, the two role of the MAO, that is one is the alkylation, and the other one is the basically the creating cationic activated catalyst so that the activity of the catalysis is more. If it is cationic, then the, it is acts as a much better pi acceptor for pi acceptor system for the alkene. And, on the top of that, we have realized that for zirconium system D0 cases, there is no loan pair.

So, this, anyway, it is acting as a pi acceptor. Now, if it is positive charge, the pi acceptor strength is much more. And also, there is a now coordinate the unsaturated species because there is a vacancy side, so ethylene can easily coordinate. So, electronically and sterically now this is ready to undergo the reactions with my monomer that is the alkyene.

Similarly, not only for zirconium, but titanium also the same happening. And you are getting the, if you take the titanium chloride, you are getting this one. The ClMAO minus, that is the your the counter anion. So, one thing you have to understand that this counter anion, this one and this counter anion or this counter anion, this counter anion must be weekly coordinating. And what is the reason? Because otherwise, there will be competition between my monomer and anion must be weekly coordinating anion. So, this is very, very, very important.

So, if you want to design other co-initiator, then this criteria should be in mind. Otherwise, what will happen that, if it is coordinating in nature, then this anion can bind here, the here and there will be competition with my substrate that is the alkene, that is the monomer. And this is to avoid competition with monomer. So, this is very clear.

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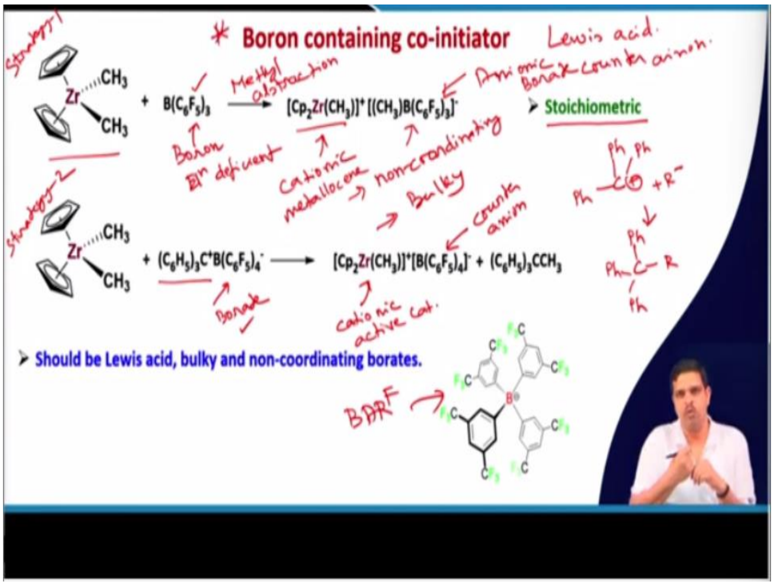

Boron containing co-initiator

$Cp_2Zr(CH_3)_2 + B(C_6F_5)_3 \longrightarrow [Cp_2Zr(CH_3)]^+[(CH_3)B(C_6F_5)_3]^-$

- Stoichiometric

$Cp_2Zr(CH_3)_2 + (C_6H_5)_3C^+B(C_6F_5)_4^- \longrightarrow [Cp_2Zr(CH_3)]^+[B(C_6F_5)_4]^- + (C_6H_5)_3CCH_3$

- Should be Lewis acid, bulky and non-coordinating borates.

So, now we know that the catalyst is fine, initiated that the co-catalyst is fine perfectly works. But, we discussed in the previous class that the main advantage of the MAO is that it is needed in a very large excess. So, definitely there is a not really very cost effective, the large excess is the really, it is a huge excess like 1000 to 1 or 10,000 to 1 in for the ratio of co-initiator and initiator.

So, after successful discovery of the metallocene and the MAO, scientists again were searching for another system, definitely Lewis acid system where you can avoid the use of excess amount of the co-initiator to make it more economic. So, after that, it was realized that the boron-based this because, this is also electron deficient system can also act as initiator for the metallocene as we saw for the MAO.

But here, the main advantage is that stoichiometric. So, you can use just 1 is to 2 amount, or 1 is to 1 amount, if you start from the di-methyl. So, that is one of the very beauty in this kind of boron containing co-initiator. So, now the recent trend of using the system is the metallocene plus the boron based co-initiator.

So, again, you have to keep in your mind that, here, that counter anion that is this one should be non-coordinating. And that is why you need to use a bulky, bulk anion so that it does not approach to the close proximity of the metal center. And that is why you will see the different, the bulky groups like C6F5 has been used and how is the reaction mechanism. So, it is basically acts as a methyl obstruction. Again, the same way the methyl abstraction and after abstraction of the methyl, this is my the cationic metallocene and this is my anionic, you can say the borate counter anion,

Similarly, you can, we can also use the anionic borate, which has the methyl abstracting power. As example, you know that this (())(20:55) is a very good methyl abstractor. So, it is basically, if you use this one, Ph Ph, this is one of the well-known methyl abstracting agent or (())(21:12)abstracting agent. So, if reacts with R minus, then what happens? So, it gets like this one. So, these are two strategy either you can use the electron deficient boron or you can use the borate with the methyl abstracting cationic unit. And you see that this is my, again, the cationic active catalyst site. And this is the counter anion.

So, this is, you can call the strategy 1 and you can call the strategy 2. I hope you understood the difference. So, here it is, the boron electron deficient, that is the borane, and here it is the borate with methyl abstracting catatonic unit. And later also, it has been reported that you can use this kind of a, this is called the BARF, you see this is more soluble and so perfectly solvable in many solvents.

So, you can see that not only the MAO, we can use the different, co-initiator with the abstracting, methyl abstraction capability. And one of the very interesting category is this one because you can use it with stoichiometric amount. So, this is really very interesting.

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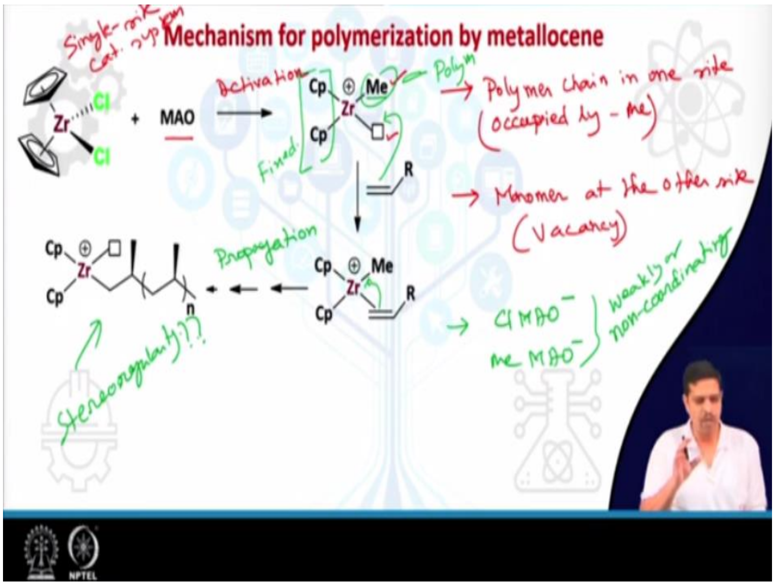

Mechanism for polymerization by metallocene

Single-site cat. system

Activation

Fixed

Polym

→ Polymer chain in one site (occupied by - Me)

→ Monomer at the other site (Vacancy)

Propagation

→ Cl MAO⁻, Me MAO⁻ } weakly or non-coordinating

Stereoregularity??

So, now I just try to emphasize that what is the main, main points in this polymerization of the metallocene. Now we call it as single site catalyst system. Let us try to understand why and why it is so specific. And the mechanism and to understand the mechanism is also very clear and very simple, not very complex as we have seen for the (())(23:52). So, let us try to understand.

So, here you see that polymer chain, so in one site that is basically occupied by methyl, I will tell you just a second occupied by methyl. So, here why I am telling this one. So, here you see the MAO, what MAO is doing. So, it is basically doing the activation. And in the earlier slide we have discussed that what are the, how, what are the activation steps. So, here after activation, this is my you see, this is my methyl group, and this one is the basically, monomer at the other site. That is the, actually the vacancy.

Now I try to understand, try to discuss that what I am going to tell. So, here you will see that I have one side the methyl, so this is fixed. So, this is fixed. The role of this one is to make the stereoregularity that will discuss in the next classes. Now here you see that this one I have one methyl group here, one site and another site there is a vacancy. And you see here, this vacancy site is basically for the monomer because you see that the, this monomer actually attacks in this vacancy site, and then it is under undergoes the inception reactions here.

So, that is why you will see polymer chain in one site in which site is basically, so this is my is actually the, where is the methyl group is there, here is basically the polymer chain will be there after the insertion. So, two site; one is the polymer chin site that is actually occupied by methyl group at the initial, and another site that is the vacant site where the monomer will interact with the metal center.

So, but the condition is that your, the counter anion that is the coming from the MAO, either this one or methyl MAO, this should be the weakly or non-coordinating. And as these are the weakly and non-coordinating in nature and this actually gives the advantage that this vacant sites are occupied by the monomer and undergoes the polymerization on a specific site of the metallocene. And that is why it is called the single site catalytic system.

So, the polymerization, you will see that how the propagation, so this is basically my the propagation step, and this is the activation step. And, later we will discuss that how the stereoregularity is maintained. That is, we will discuss with the help of the symmetry. But today, I am trying to understand the mechanism involved in polymerization by metallocene catalysts.

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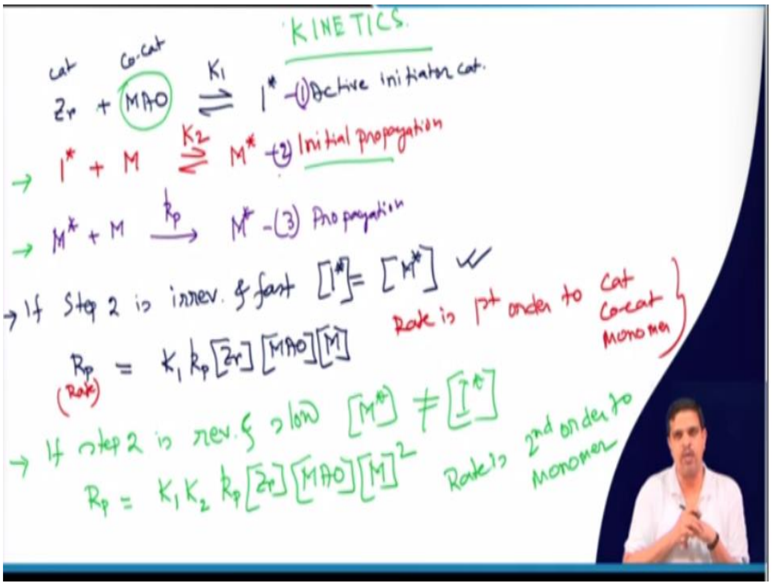

KINETICS.

$\underset{\text{cat}}{Zr} + \underset{\text{Co-cat}}{\boxed{MAO}} \overset{K_1}{\rightleftharpoons} I^*$ -(1) Active initiator cat.

→ $I^* + M \overset{K_2}{\rightleftharpoons} M^*$ -(2) Initial propagation

→ $M^* + M \xrightarrow{k_p} M^*$ -(3) Propagation

→ If Step 2 is irrev. & fast $[I^*] = [M^*]$

$\underset{\text{(Rate)}}{R_p} = K_1 k_p [Zr][MAO][M]$ Rate is 1st order to Cat, Cocat, Monomer

→ If step 2 is rev. & slow $[M^*] \neq [I^*]$

$R_p = K_1 K_2 k_p [Zr][MAO][M]^2$ Rate is 2nd order to Monomer

What I will do now, I will discuss the kinetic of, sorry, very simple way of this metallocene based polymerization catalyst. Suppose I am, so this zirconium I am writing is a just zirconium catalyst, and I am first doing the activation. So, this is my catalyst and this is my co-catalyst. And so, what I am now, this is the initiator that is the activated of the catalyst; active initiator catalyst.

Now this, let us say this was the equilibrium constant K1, and now next I am going, next step is my I start that is the initiator and the monomer that is, let us say ethylene. And what will happen, it will be M star, that is the initial that is the first propagation. So, let us see, this is the K2. And the next one is, and there will be kp, that is the propagation. And, so this is the propagation. I am just giving the number, this equation 3, this is 2 and this is 1.

Now we have to consider, I am just trying to understand that what are the very basic properties of the kinetic of this kind of metallocene based polymerization of the olefins. (())(31:29). So, now first considered the first case. If 2 is the step 2, if step 2 is reversible, is, irreversible and fast that means what will happen, that you can consider that I star is equal to consider that I star, concentration of I star and concentration of M star is same, because it is fast and irreversible.

Then what we can write the polymerization rate, that is the Rp that is the polymerization rate. So, what will be happening, so this is the K1 that is the from the first equilibrium constant, it is coming and this is the kp and so zirconium concentration. Then MAO concentration and the M concentration because here I star and the M star concentration is same here. So, here you see that the rate is that is the rate. So, rate is first order to my catalyst, to cocatalyst and to monomer.

Now, you take the second scenario. So, let us, the first one, second step, that is the, this one we thought as a irreversible and fast. Now what happens if this step is reversible? So, if step 2 is reversible, and slow, so in this case, what will happen? M concentration will be not equal. So, in this case, what will be the rate of the polymerization? Will be this one. So, we have to consider the K1 and K2. So, K1, K2. And so Zr, then MAO and then will be M square.

So, here you will see that, so what is the difference here? You will see that this, the rate is second order to monomer, although it is first order to catalyst and co-catalyst, but second order to monomer, if we considered that step 2 is reversible and slow. So, this one you have to this second step has influence how the order of the polymerization rate will be. Now here all the cases we used as a, we used as co-catalyst, MAO as a co catalyst.

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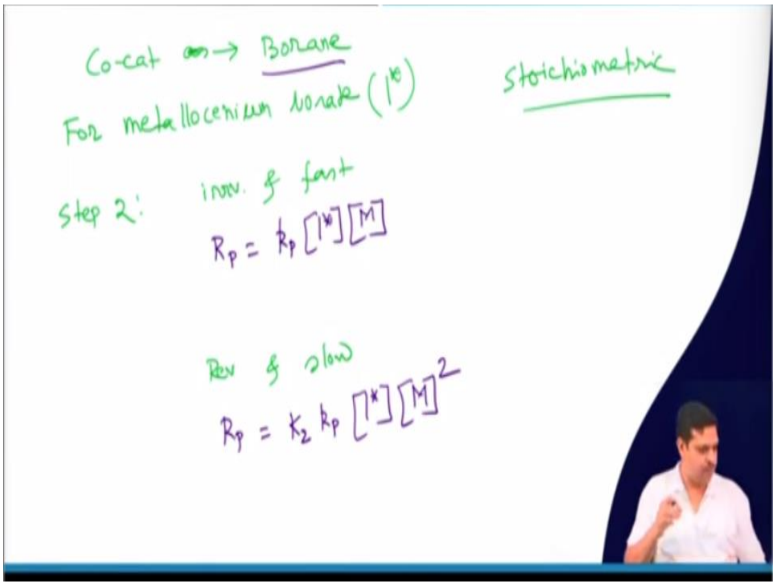


Co-cat → Borane

Stoichiometric

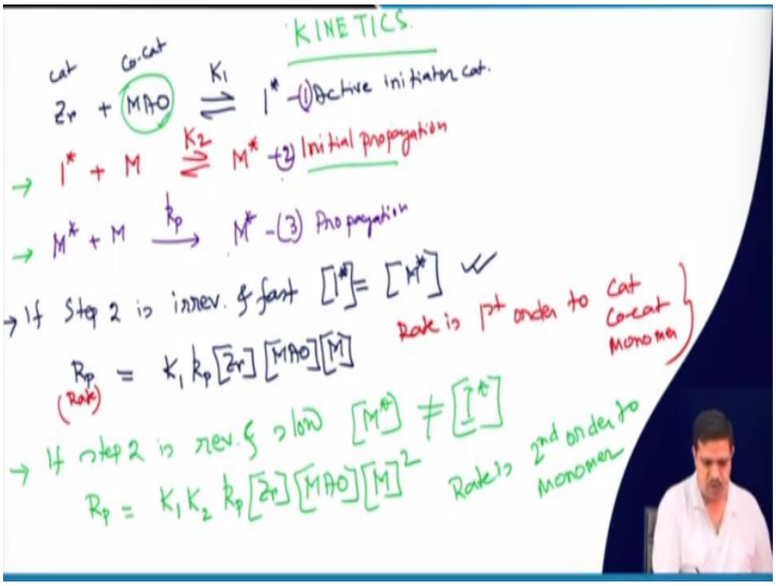
For metallocenium borate (I^*)

Step 2: irrev. & fast

$R_p = k_p [I^*][M]$

Rev & slow

$R_p = K_2 k_p [I^*][M]^2$



KINETICS

$$\underset{\text{cat}}{Zr} + \underset{\text{Co-cat}}{MAO} \overset{K_1}{\rightleftharpoons} I^* \quad \text{– (1) Active initiator cat.}$$

→ $I^* + M \overset{K_2}{\rightleftharpoons} M^*$ – (2) Initial propagation

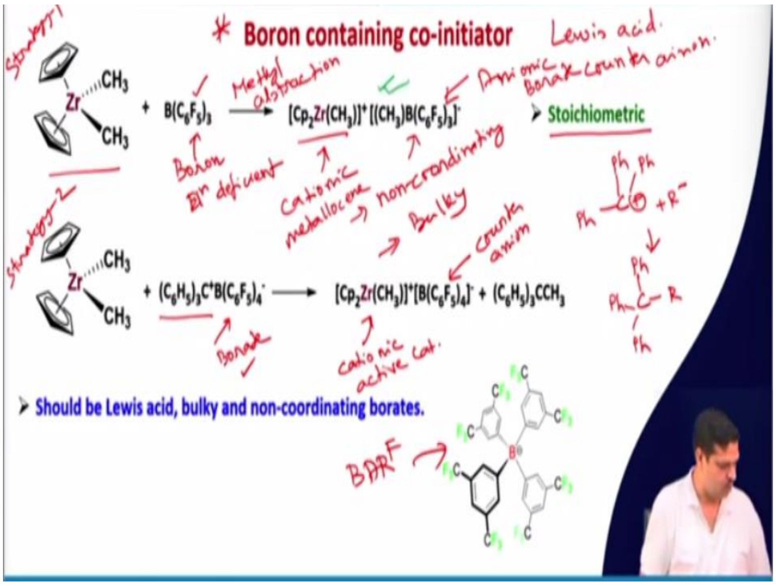
→ $M^* + M \xrightarrow{k_p} M^*$ – (3) Propagation

→ If Step 2 is irrev. & fast $[I^*] = [M^*]$ ✓

$\underset{\text{(Rate)}}{R_p} = K_1 k_p [Zr][MAO][M]$ Rate is 1st order to cat, Co-cat, Monomer

→ If step 2 is rev. & slow $[M^*] \neq [I^*]$

$R_p = K_1 K_2 k_p [Zr][MAO][M]^2$ Rate is 2nd order to monomer



* **Boron containing co-initiator** Lewis acid.

Strategy 1

$Cp_2Zr(CH_3)_2 + B(C_6F_5)_3 \rightarrow [Cp_2Zr(CH_3)]^+[(CH_3)B(C_6F_5)_3]^-$

- Stoichiometric

Methyl abstraction

Boron e⁻ deficient

cationic metallocene

Anionic Borate counter anion.

→ non-coordinating

→ Bulky

Strategy 2

$Cp_2Zr(CH_3)_2 + (C_6H_5)_3C^+B(C_6F_5)_4^- \rightarrow [Cp_2Zr(CH_3)]^+[B(C_6F_5)_4]^- + (C_6H_5)_3CCH_3$

Borate ✓

counter anion

cationic active cat.

$Ph_3C^{\oplus} + R^- \rightarrow Ph_3C{-}R$

- **Should be Lewis acid, bulky and non-coordinating borates.**

BArF

Now what will happen, if my, if I take as co-catalyst as the borane? Now let us see what will happen. So, for metallocenium borate that is the, this one here. So, in this case, you see that here it is MAO. Now I am considering the, this one, this one, understand. Now in this case, what will happen here, you will see that as it is a stoichiometric, then this, the rate of the reaction will be different than the MAO where we using the excess.

So, here, the in the first case, where the step 2 is irreversible and fast. And another case we consider reversible and slow. So, in these two cases, what would be the difference? The R, this will be like I star and M and in this case will be K2 kp and I star and M2. In this case of the borane as a co-catalyst. So, this is good to know because the, we should have a clear concept about the kinetic of the polymerization, the rate of the polymerization, who are the, who influences the rate of the polymerization rate and accordingly, we can change our, the condition and thermodynamic parameters.

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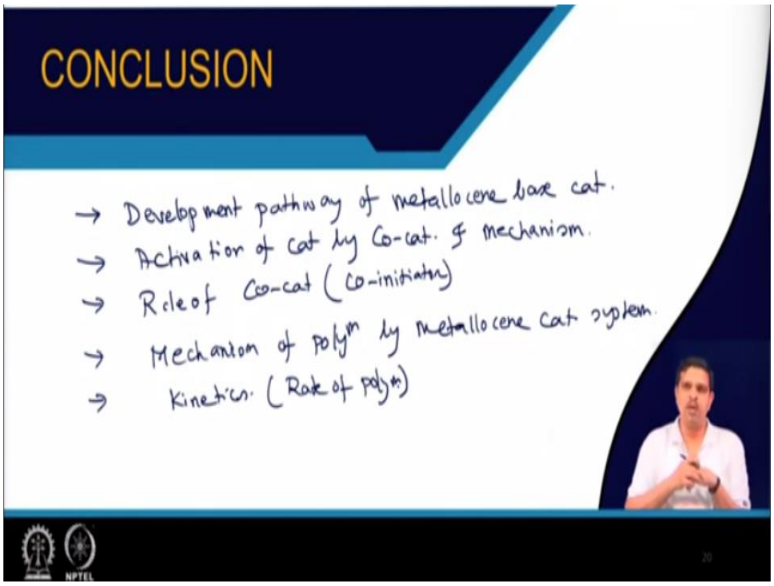

CONCLUSION

→ Development pathway of metallocene base cat.
→ Activation of cat by Co-cat. & mechanism.
→ Role of Co-cat (co-initiator)
→ Mechanism of poly^n by metallocene cat system.
→ Kinetics. (Rate of poly^n)

So, as a conclusion in this class, what we have learned, we have learned that the development pathway of metallocene-based catalyst, we now discussed that activation of catalyst by co-catalyst and mechanism, the role of co-catalyst or we sometimes we call co-initiator.

And the mechanism of polymerization by metallocene catalytic system and brief way and a very brief and qualitative, the kinetic, the rate of the polymerizations of the, when we use the metallocene and the co-catalyst. Here I have, we have discussed with the two widely used co-catalytic system, that is one is the MAO aluminium-based and the other one is the boron-based.

So, I hope you have enjoyed these classes, and you have now excited that yes, the metallocene based catalyst actually gave Renaissance in the polyolefin polymerizations and has been now used as widely used in different polymer industries to make a different type of polyolefins.

Now, as I told the different type of polyolefins. So, what are the different type of polyolefins with that we will discuss to in the next class. And you will see this is not the end, there is a various number of reasons why this metallocene-based catalyst are so popular because you can use and tune the stereoregularity by using the symmetry concept of the metallocene that is more exciting for the in metallocene-based catalytic system in alpha olefin polymerization.

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REFERENCES

- Principle of polymerisation by George Odian, Jhon Wiley & sons, 4th edition, 2004
- Polyolefins: 50 years after Ziegler and Natta II by Walter Kaminsky, Springer, 2013

So, you can read these books that is the Odian and the second book that is by Kaminsky, the discussion, what we have done in what we have done in the last two classes. Thank you and see you in the next class where we will be discussing the correlation between the symmetry of the metallocene and my output polymers. Thank you very much.