Transition Metal Organomettalics in Catalysis and Biology
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Lecture - 50
Olefin Polymerization (Part 11)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. We have been talking about olefin polymerization in the last few lectures and in this regard in the immediate past few lectures, we have focused on the development of Ziegler-Natta catalysts particularly with respect to polyethylene as well as polypropylene. In this regard, let me just briefly talk about the highlights of what we have covered so far.

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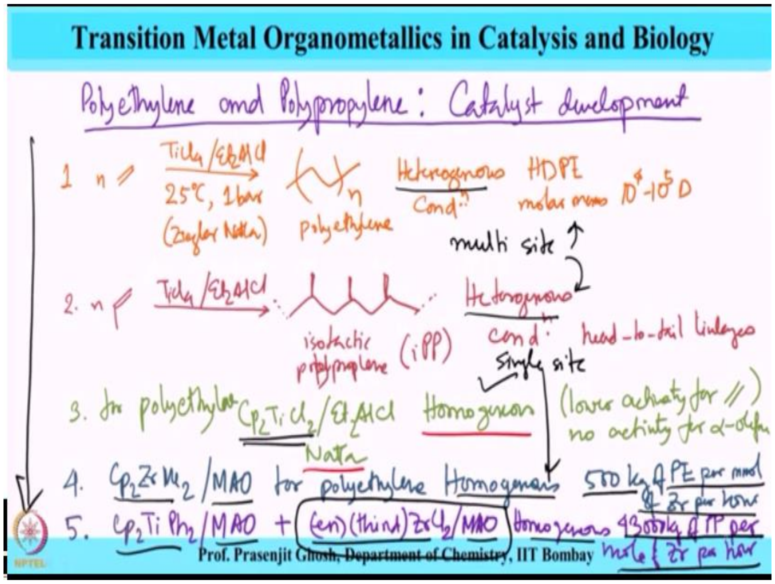

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Polyethylene and Polypropylene: Catalyst development

1 n $\xrightarrow[25°C,\ 1 bar]{TiCl_4/Et_2AlCl}$ polyethylene (Ziegler Natta) Heterogeneous Cond^n HDPE molar mass 10^4-10^5 D

multi site

2. n $\xrightarrow{TiCl_4/Et_2AlCl}$ isotactic polypropylene (iPP) Heterogeneous cond^n head-to-tail linkages

Single site

3. for polyethylene Cp_2TiCl_2/Et_2AlCl Natta Homogeneous (lower activity for ethylene, no activity for α-olefin)

4. Cp_2ZrMe_2/MAO for polyethylene Homogeneous 500 kg of PE per mmol of Zr per hour

5. Cp_2TiPh_2/MAO + $(en)(thind)ZrCl_2/MAO$ Homogeneous 43000 kg of PP per mole of Zr per hour

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In this context, the first we spoken about is ethylene TiCl4 25 degree centigrade 1 bar pressure. This is a Ziegler-Natta catalyst, gives a polyethylene and these is under heterogeneous conditions produces HDPE of molar masses 10 to the power 4 to 10 to the power 5 Dalton. Subsequently, we saw that for polypropylene, it gave isotactic polypropylene or IPP and this is also heterogeneous and this also has head to tail linkages.

The first in this advanced focusing more on polypropylene, the first catalyst for polypropylene was Cp2 titanium dichloride with Et2AlCl. This is for polyethylene, sorry ethylene this catalyst is homogeneous, but lower activity for ethylene and no activity for alpha olefin and this was reported by Natta. So the first homogeneous catalyst was reported by Natta. Then subsequently, Kaminski produced Cp2 zirconium Me2 MAO.

So for polyethylene homogeneous and extremely active 500 kg of PE, polyethylene per millimole of zirconium per hour. So post this, what was reported is the fifth one, which is Cp2 zirconium Ph2, sorry, Cp2 titanium Ph2 MAO and this ethylene en thind zirconium Cl2 MAO. This we had discussed. That is again homogeneous and was producing 43,000 kilogram of polypropylene per mole of zirconium per hour.

So what is the point to note is that, this is sort of timeline of development. So the first is heterogeneous for polyethylene, then heterogeneous for polyethylene and then first homogeneous came with this DCP system, homogeneous for polyethylene. Now this DCP system with MAO gave extremely high activity of polyethylene per millimole per hour and then subsequently DCP system with MAO and this ansa system with MAO gave extremely high isotactic polyethylene per hour.

And we had looked at this system, at this ansa system in much more detail in our previous discussion and what we saw that as we move from homogenous to heterogeneous in these cases the catalysis are as we move from homogeneous to heterogeneous, this is martensite for this heterogeneous and for the homogenous ones these are all homogeneous. These are single site catalysis.

And the single site catalysis means that polymer has narrow polydispersity index and low PDI and polymers are much more well behaved in terms of their properties. So let us now focus on this ansa complex that we had discussed, which is extremely good activity for polypropylene.

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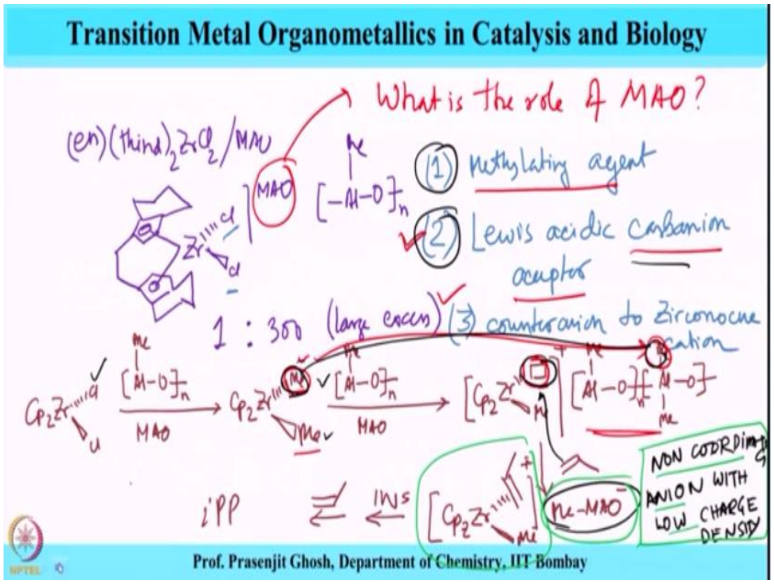

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So this ansa complex is en thind zirconium Cl2 MAO. Structure wise the complex looks something like as is shown over here, maybe the structure as is shown over here. This is bound to zirconium with MAO. So this is the structure of this complex and the ratio of these to MAO is about MAO can be represented as AlO methyl. So this ratio is 1 is to 300 means large excess of MAO is required and then the question comes that what is the role of MAO?

The question subsequently come is, what is the role of MAO? It seems like that MAO is a magical reagent, which enhances the activity of this catalyst, this homogeneous catalyst to the extent that it even surpasses the original heterogeneous Ziegler-Natta catalyst. The answer to that is that MAO has three functions. MAO has three functions that MAO acts as a methylating agent.

That MAO acts as a methylating agent that means that these halides get replaced to becoming methyl. So they convert zirconium halides to zirconium methyls and second function is that it has a Lewis acid carbon ionic acceptor. Lewis acidic acceptor, this is an important function of MAO. The first is its methylating it and then making it dimethyl and still there is large excess of MAO, which are highly electron deficient Lewis acidic species.

Now after they have methylated the halide, they abstract one of the methyl. So it is not only a methylating agent, but also it is a methyl anion acceptor. So that is why it is called this a carbon ion acceptor. So not only it is making methylating it, but converting a halide to methyl and then subsequently it is also accepting abstracting the metal snatching the methyl and the third role of MAO is that and serves as a counter anion to zirconocene cation.

So it has three role and this can be a suitably explained in this series of chemical equation as is shown below. For example, Cp2 zirconium chloride methyl MAO. So this is the first function that we had seen the methylating agent. Now the second function is that it acts as a methyl abstraction. So this can be represented as methyl with MAO giving Cp2 zirconium. One of the methyl gets abstracted, the other is a vacant site plus.

So only one methyl gets accepted and then ends up becoming a vacant site over here and then the anion. So this is the second role. This is the what portrayed out here is the second role of methyl abstraction and then this methyl group ends up in the carbon ion of MAO as is shown here Al Me O n Al Me Me O. So this methyl group which gets abstracted from here ends up on the aluminum as is shown here and then both the second.

And then subsequently, this acts as a counter ion to this zirconocene cation and what happens subsequently is, in this vacant site the polypropylene lands up occupies, polypropylene comes and Cp2 zirconium methyl, this cation and Me MAO minus anion, which undergoes insertion subsequently with many propylene as it shown to give isotactic polypropylene. So the role of MAO is greatly explained that it has three.

First is it works as a methylating agent. So this gets converted to methyl, second it has anion abstractor, so one methyl gets converted, gets abstracted and then there is a vacant site hole and then subsequently to this hole the olefin comes binds and so this now serves as a non-coordinating anion with low charge density. So this is an interesting observation that this MAO has several roles.

And after abstraction, what is possible is that you know it stabilizes this zirconium to species cation, zirconium cation being a non-coordinating anion with low charge density. Now what it sort of implies that this can be achieved with any other non-coordinating anion with low charge density and that should also be equally effective and the ingenuity of organometallics chemist comes into play where indeed such a well-behaved catalyst were developed with other non-coordinating anion and which were extremely good for polymerization.

So this shows, how the structure activity relationship, how understanding helps in developing the catalyst or helps in improving the catalyst and this is done by Tobin marks, professor of North Eastern University, who had used non-coordinating anion to develop this zirconium species, which is extremely active.

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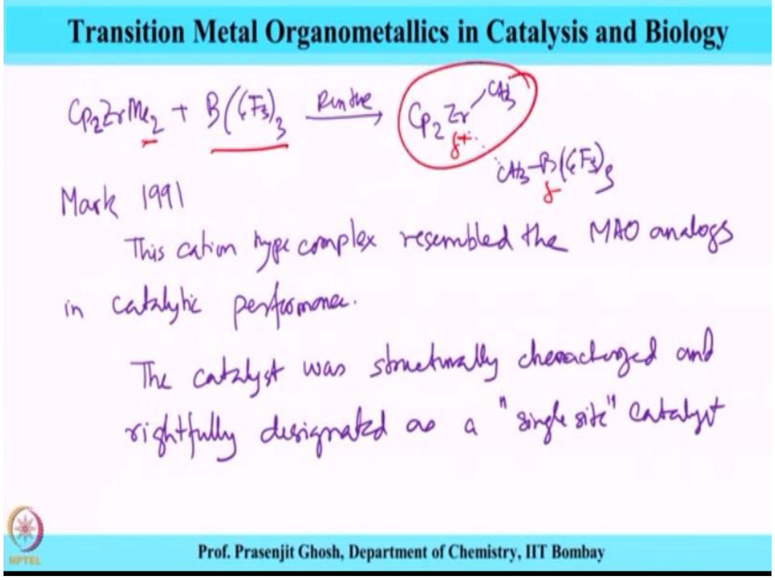

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$Cp_2ZrMe_2 + B(C_6F_5)_3 \xrightarrow{\text{Pentane}} Cp_2Zr^{\delta+}(CH_3) \cdots CH_3^{\delta-}\text{–}B(C_6F_5)_3$

Mark 1991

This cation type complex resembled the MAO analogs in catalytic performance.

The catalyst was structurally characterized and rightfully designated as a "single site" catalyst

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So what Marks did is, we took this Cp2 zirconium dimethyl and used this Lewis acid of boron. So now instead of aluminium, it is boron C6F5O3 in pentane gave Cp2 zirconium methyl, the loosely interacting with CH3 BC6 F5 whole 3. So this is a ion pair separated species with zirconium being in positive and this boron being negative, after abstracting this methyl from zirconium methyl.

This famous nice example was reported by Marks in 1991 and this complex, this cationic complex resembled the MAO analogues in catalytic performance and this was structurally the catalyst. This was structurally characterized and is rightfully designated as a single site catalyst so this was a fantastic improvisation by Mark, where development of replacement of MAO using this boron trifluorophenyl reagent.

Which abstracted one of the methyl and also behaved as a non-coordinating anion in stabilizing this zirconium CP methyl cation, which carried out the polymerization of polypropylene with equal efficiency as that of the MAO counterpart. So that this shows how understanding a suitable, a proper understanding of the catalyst mechanism helps in improving the catalyst greatly.

And that is why the structure activity relationship is so important in developing the efficiency of the catalyst. So with this I come to the conclusion of today's lecture, where we have seen how these catalysts for polypropylene improved from the heterogeneous Ziegler-Natta titanium tetrachloride diethyl aluminum chloride based catalyst, a multi-site catalyst to the focus shifted towards developing single site catalyst that was advantageous.

But the inherent difficulty of this homogeneous single site catalyst was their activity was inherently low, which was however overcome by advent of MAO by Kaminski in 1981 and subsequently even MAO got replaced by contribution from Mark, who could develop better similar catalyst bearing boron based non-coordinating anion, where the boron triphenopentaphenyl C6F5 could serve as a metal abstraction as well as non-coordinating anion and stabilize this single site catalyst.

So with these, I come to a conclusion of today's lecture. We are going to be looking at these catalyst development and some more interesting aspects about how to achieve the syndiotacticity, isotacticity, at will and the rationale that went in developing this catalyst, as we discuss the topic in more detail in the next lecture. Till that time, goodbye and thank you for being with me in this class. See you in the next lecture.