Transition Metal Organometallics in Catalysis and Biology
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Lecture – 58
Non-Group IV Metal based Olefin Polymerization Catalysts

Welcome to this course on transition metal organometallics in cattle catalysis and biology we have been talking about non-group IV metal based olefin polymerization catalyst this is indeed a very interesting area that we have been focusing upon. And to say the least that they started actually the whole field of olefin polymerization catalysis actually originated from our non-group IV metal based phenomenon, and this is what is the famous nickel effect that led to identification of group for metal based transition metal complexes which are extremely active for olefin catalysis.

And then subsequently search in areas which are beyond group IV transition metals they eventually took place and in that context we have spoken about the lanthanum transition metal complexes also we have spoken about iron and then in the last lecture we had seen how palladium took the center stage first nickel and then palladium for nickel the story has been that it has been like coming to a full circle.

Because it is the nickel effect which had indeed led to the start of these polymerization of olefins and then later on it is the Brookharts who had developed catalyst which was sort of useful for olefin polymerization.

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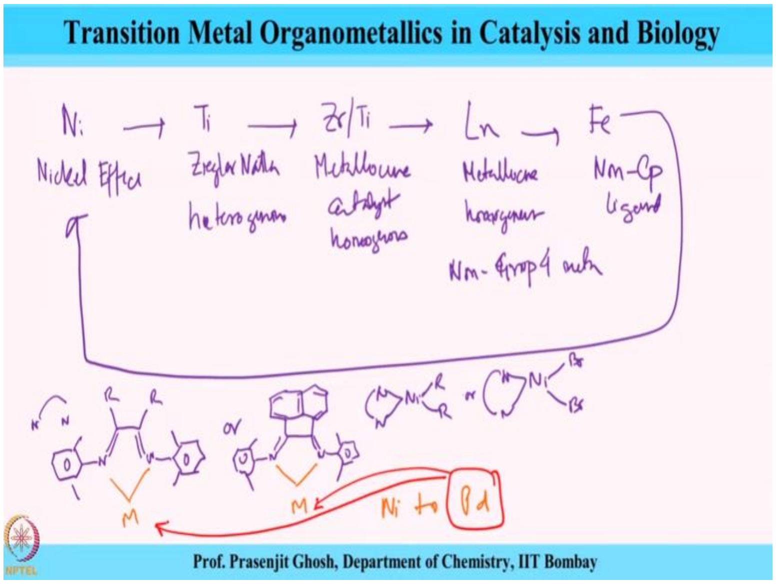

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So let me just run it down so we started with nickel in so called nickel effect led to titanium Ziegler Natta which led to zirconium as well as titanium metallocene catalyst this was heterogeneous, and these were homogeneous that led to lanthanum metallocene again homogeneous. Now this is a non-group IV metal then we went to iron and this was non cp ligand and then finally from iron with Brookhart we went back to nickel which was these famous nickel catalyst that of this type.

Or the ligands which are used are or and they mainly are of this type the catalyst represented our or bromides now with nickel this could produce long-chain linear polymer as well as oligomers depending on the substituent. So then the nickel followed by the work by Bazan which we have discussed about in the tandem catalysis where they could produce ethylene 1-butene copolymer using a single monomer.

So now there is another interesting discovery which sort of change the field in a dramatic way is that when this metal when the metal bound to this ligand is changed from nickel to palladium then there is a startling discovery and the startling discovery is that when this metal is a palladium then one can do polymerization of olefin with functional co monomers.

So this is really an very interesting discovery because olefins with functional group sort of poisons the catalyst and such kind of copolymerization with olefin with functional monomer absolutely was a real tough challenge at that point of time and this was overcome by substituting nickel which happily did ethylene propylene polymerization or ethylene alpha olefin copolymerization with palladium that sort of could carry out it ethylene polymerization with polar functional monomers.

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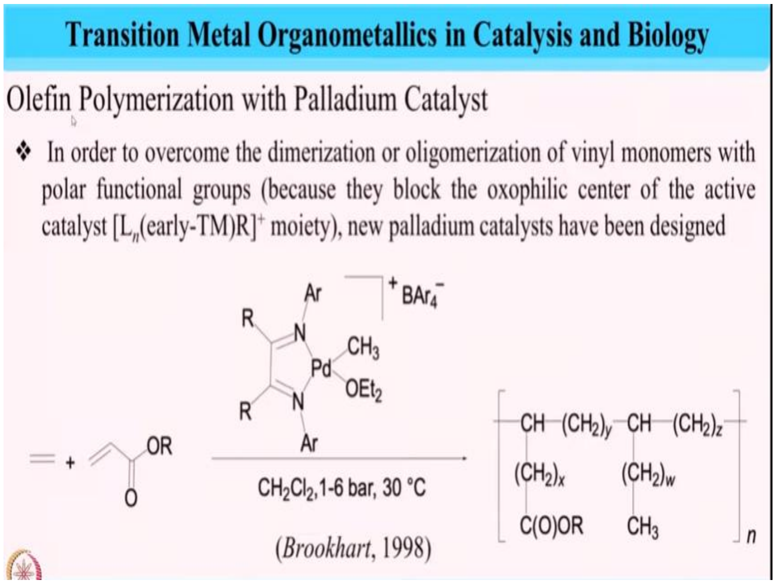

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Olefin Polymerization with Palladium Catalyst

- In order to overcome the dimerization or oligomerization of vinyl monomers with polar functional groups (because they block the oxophilic center of the active catalyst $[L_n(\text{early-TM})R]^+$ moiety), new palladium catalysts have been designed

CH_2Cl_2, 1-6 bar, 30 °C

(*Brookhart*, 1998)

So this is a very interesting story it was again developed by Brookhart JACS 1988 paper.

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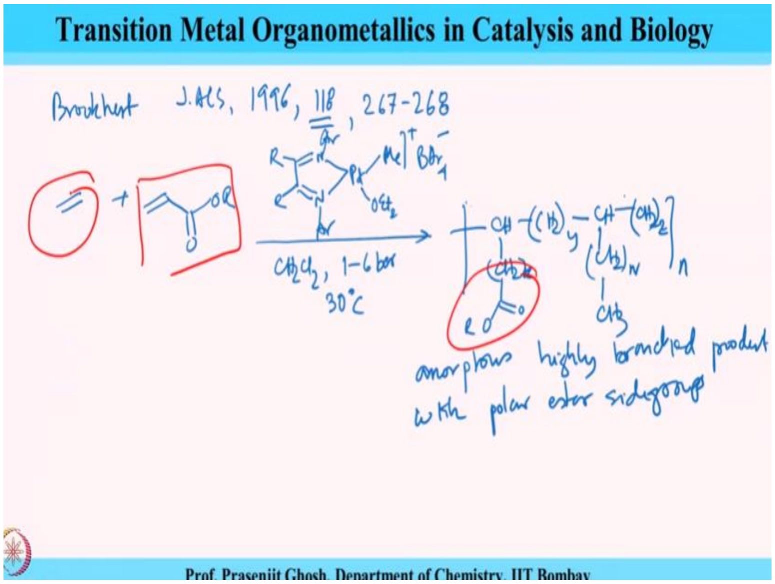

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Brookhart J.ACS, 1996, 118, 267-268

CH_2Cl_2, 1-6 bar, 30°C

amorphous highly branched product with polar ester sidegroups

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They request the interested students to look these reference up and the co polymerization was shown over here olefin plus vinyl monomers functionalized monomers in presence of the catalyst of this type palladium ethyl oet plus and BAr - non-coordinating anion in dichloromethane 1 to 6 bar pressure 30 degree centigrade. So almost a room-temperature reaction could give this much wanted CH CH2 x OR CH2 y CH2 w CH3 CH2 z N.

So this is amorphous highly branched branch product with polar ester groups polar ester side groups. So this is a very interesting discovery which could copolymerize and that there is a polar functional side group now present on the polymer backbone. So this was sort of the breakthrough first provided by Brookhart in being able to carry out polymerization of polar functional monomer with olefin. Subsequent that there were other groups like grubs and so on and so forth could report some other complexes as well as Bazan report other complexes that could successfully carry out such a polar polymerization.

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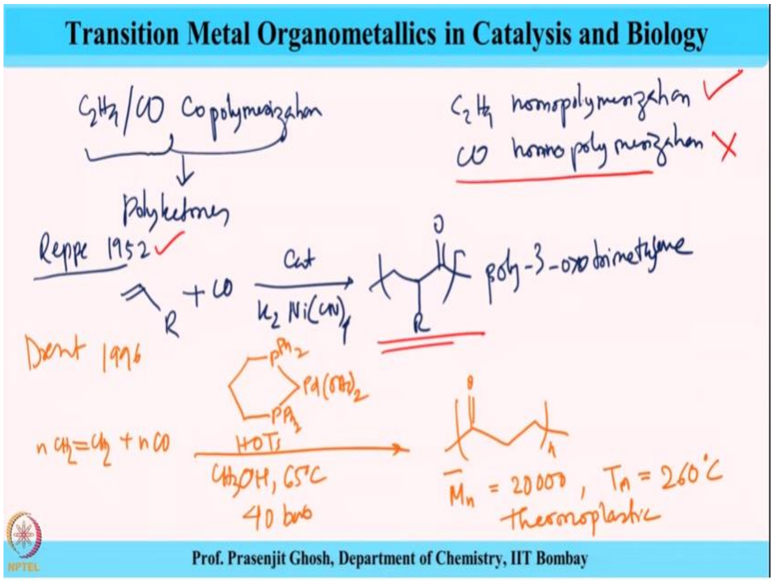

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Now moving on there was another focus was on obtaining being able to actually polymerize ethylene and carbon monoxide. Co polymerization it is important to note that c2H4 homo polymerization is possible. However CO homo polymerization is not possible, and these would result this polymerization would result in poly ketones. Now which have very important polymer properties are important for their polymeric properties.

Now for being able to carry out this ethylene CO of copolymerization the first report was given by Reppe in 1952 who sort of had observed that if one takes alpha olefins and carbon monoxide in presence of catalyst then one could get a poly ketone poly 3 oxo tri methylene in presence of a catalyst like K2NiCN4 in some product. So one could see its formation and that was first reported by Reppe in 1952.

The first breakthrough was however reported by Drent about more than 30 years later in 1996 you using a catalyst he could polymerize ethylene and CO using a phosphine based catalyst in HOTs methanol 65 degree centigrade 40 bar pressure it could make poly ketone molecular weight 200,000 TM = 60 degree centigrade and this is a thermoplastic material. So the breakthrough actually in being able to make poly ketone successfully in being able to polymerizing came much later in 1996 as a report from Drent.

Now there are two aspects to it the first observation was however made by Reppe in 1952. Now there are two aspects to it one is that the alternating addition of CO as well as ethylene to give poly ketone and they were knowing this poly ketone polymers showed that it was really indeed a alternating polymer where both the groups were inserting one after another and that is what which was confusing because though CO homo polymerization is not known but ethylene homo polymerization is quite known.

So there were chances that one may see 2, 3 ethylene insertion followed by one CO but to everybody's surprise what was found that the polymer really had one is to one incorporation of ethylene and CO which said that it is indeed an alternating insertion of CO and ethylene. Now based on the catalyst and the proposed mechanism and doing the end group analysis of a polymer.

So actually this is a very powerful method of finding out the insight about the polymer mechanic is by looking at the end groups which are present in the polymer and what they showed that they were 2 in groups one is carbonyl compound and another is ester compounds and the fact that the 2 in groups are provided obtained in nearly equal amounts which sort of said that both the polymerization were happening in equal way. So this is illustrated by this nice example of the mechanism shown over here.

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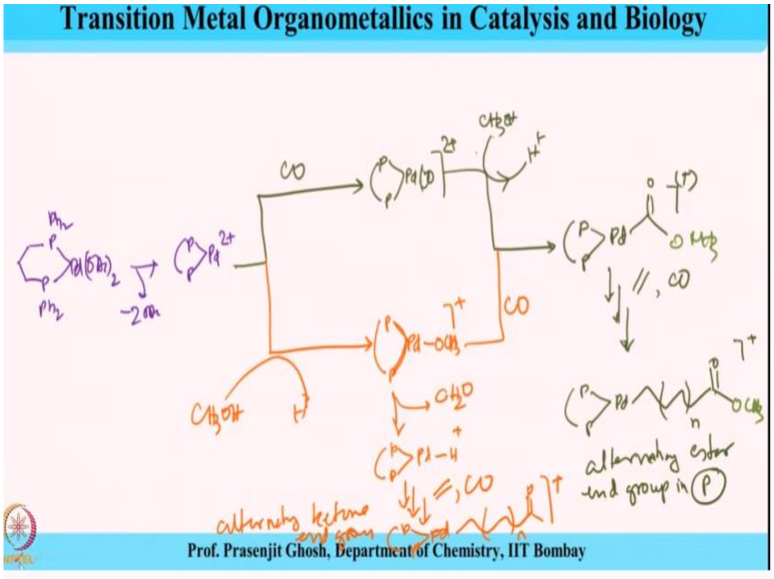

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So for example the catalyst which is in short is written by pp a palladium acetate or maybe I will draw it nicely. These catalysts would give catalyst precursor which is drawn by losing to acetate the catalyst precursor. So now there are two pathways one I am showing in green so it can add CO to give pd CO2 + and that can take methanol add methanol giving out H+ and resulting in the compound p,p,pd,CO+ and then once this is formed this can subsequently undergo various coordination insertion of ethylene and CO to give a polymer pd with the polymer with the in group being a ketone.

So alternating ester in group in polymer whereas the other possibility it might as well be it first takes methanol and gives out H+ to give p,p,pd, OCH3+ and that can eliminate aldehyde CH2O giving palladium hydride which again can do CO ethylene polymer to give a polymer which has a ketone end group. So alternating ketone in group now this species again can react with CO2 give the ester.

So now the glimpse of the mechanism can be obtained by the fact that one can get a alternating polymer with ketionian group or one can get our ending polymer with a ester in group depending on how in what sequence it reacts with the solvent and these also throws inside as to mechanism of this polymerization reaction and the chain propagation happens through alternating insertion step as is shown over here.

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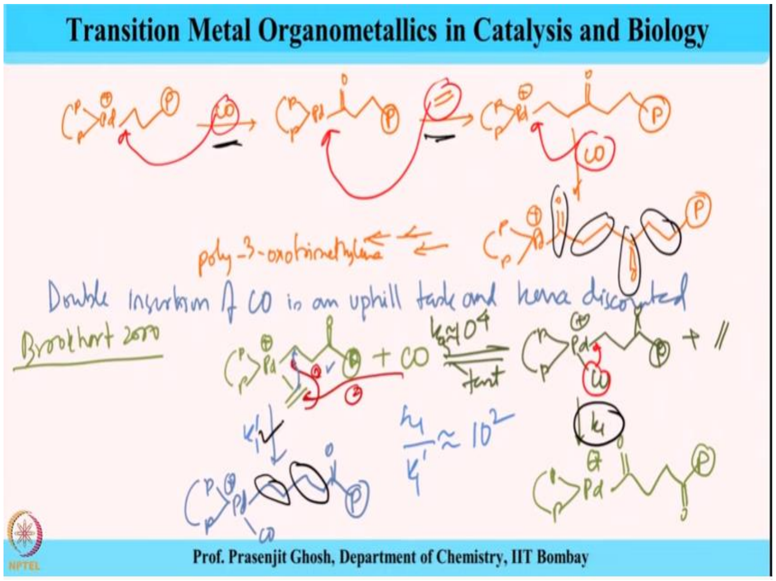

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Giving CO now this CO comes and enters over here to give the product how to give the product which then binds to an olefin. Now once the CO has inserted the olefin would also insert over here then the corresponding. The inserted product would be now again to this another molecule of CO will come which will come and insert over there to give the corresponding CO inserted product and that subsequently it will result in poly 3 oxo try methylene polymer.

So these are poly ketones now what is interesting about here is the fact that both CO and ethylene they are undergoing insertion alternatively. So for example here so it is sequential alternating insertion now which is happening. Now to sort of have an insight on this one has to consider the following for example there are chances that instead of having this alternative insertion there can be chances that double insertion of carbonyl can happen to insertion of carbonyl.

Now double insertion of carbonyl is an uphill and impossible task so that is discounted double insertion of CO is an uphill task and hence discounted that means that CO homo polymerization does not happen, and it is discounted and hence is not considered. So then one what is one left with the homo polymerization of ethylene or alternating current polymerization of ethylene and propylene.

Now homo polymerization of ethylene is energetically favored so has to be considered or taken into account and the finally the mechanism of this has been illustrated by Brookhart a very elegant example mechanistic study in 2000 which sort of explained provided evidence in favor of these alternative insertion of palladium. So what Brookhart did was he showed that this catalyst is present in or 2 forms for example this is the polymer chain where ethylene is coordinated.

So when that is formed it has two possibilities one is that it can insert to this or the one maybe I will illustrate this with thing one possibility will that this will undergo insertion and what is the this is possibility number 1 and the other possibility is that these coordinates may be replaced by a carbonyl which is more stronger binding. So this is possibility number 2 so if carbonyl displaces ethylene which is more fast then and this is a very first reaction and K equilibrium is about 10 to the power 4 10000 times faster.

Then it produces these palladium CO coordinated compound plus ethylene and this CO now then CO can insert into this olefinic bond to give the alternate CO polymerization as is shown over here and the other thing can be double insertion as we said that this possibility number 1 where these can insert into this then the double inserted product can also be pd CO this is pd+ and so what we find over here is that 2 insertions of ethyl olefinic unit has happened.

One is this and other is this ,this and this let us say is given by k1 dash so the ratio of a k1/k1 dash is approximately 10 to the power 2 100. So overall as let me summarize as this is bigger much greater than this as well as this equilibrium constant is 10 to power 4 times in favor of this. So it is what we see is favored alternating insertion of ethylene with polyethylene is what is favored. So now with these we come to the end of the catalyst development story the non-group IV the metals and let me just summarize the overall findings of this work which has been discussed so far.

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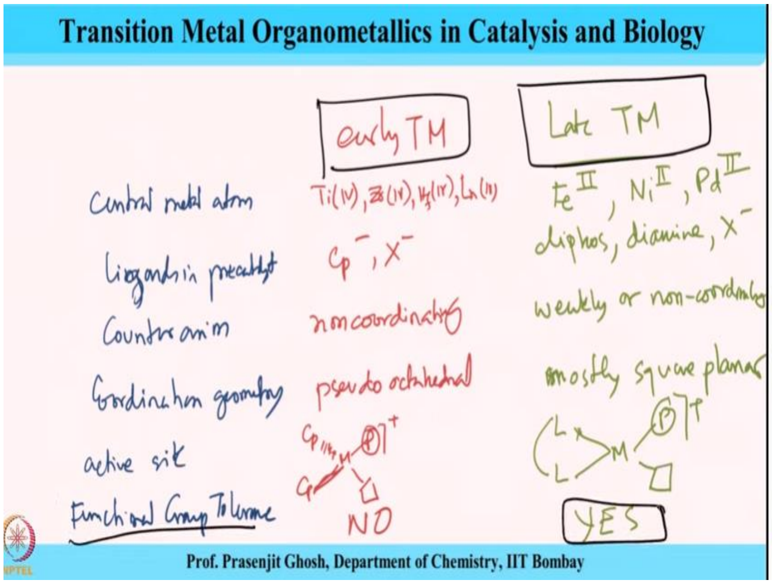

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	early TM	Late TM
Central metal atom	Ti(IV), Zr(IV), Hf(IV), Ln(III)	Fe^{II}, Ni^{II}, Pd^{II}
Ligands in precatalyst	Cp^-, X^-	diphos, diamine, X^-
Counter anion	noncoordinating	weekly or non-coordina
Coordination geometry	pseudo octahedral	mostly square planar
active site		
Functional Group Tolerance	NO	YES

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So there are actually 2 types of metals first is the early transition metal and we had also this is how we started the story with and then we had seen that the central metal and metal atom for these early transition metals usually are titanium IV zirconium IV, hafnium IV, lanthanum III then the ligands which are used for these ligands in pre catalyst usually had been cp- halides counter anion.

For these case the counter anion had been non-coordinating coordination geometry is pseudo octahedral active site is of this geometry and functional group tolerance and in this case absolutely none and what we saw that as we evolved from early transition metal to something of late transition metal in the course of catalyst development what was found that the metals which really did well are iron 2 then nickel 2 and palladium 2.

Actually they sort of did the trick whatever was complementary or challenge for these early transition metal they were made by the late transition metal. The ligand used by die fast these are non cp type ligands diamine or halide x- type of ligand counter anion however is the same weekly or non-coordinating counter anion in terms of active site is almost similar of what we had seen coordination geometry is probably alder like that first.

Coordination geometry is pseudo square planar mostly a mostly square planar and that is inconsistent with a d8 configuration of nickel and palladium and the active site is shown over here and there is the vacant site and functional group tolerance yes that is a big yes for late transition metals that they are indeed functional group tolerant. So here is the summary which brings out the comparison between the early transition metal and the late transition metal and which may sort of differentiates between the two is this functional group tolerance and that sort of helps this late transition metal to carry out copolymerization of ethylene with polar functional monomers.

So with these we come to the conclusion of today's lecture and hereby in this lecture we complete our discussion on the transition metals in catalysis aspect of this course where we have seen a lot of important industrial large-scale processes that are carried out by organometallic catalysts right from rapid synthesis method this is polymerization so on and so forth and then we move on to another very interesting aspect of organometallic chemistry that is bio organometallics or the applications of organometallic chemistry in biology.

This aspect actually is still in the developmental stage and we have a few very exciting developments to talk about in the context of applications of organometallic chemistry when we meet next and I once again thank you for being with me in this throughout this course. Particularly I enjoyed a lot talking about various important processes of organometallic chemistry kind of showcasing the proudest powers of organometallic chemistry and the features of organometallic chemistry.

And we move on to the other aspect of organometallic chemistry particularly a bio organometallic chemistry. So with this once again I thank you and I look forward to take up the bio brown metallic chemistry in details when we meet next till then goodbye and thank you.