Transition Metal Organometallics in Catalysis and Biology
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Lecture – 57
Non-Group Iv Metal based Olefin Polymerization Catalysts

Welcome to this course on transition metal organometallics in catalysis and biology. We have been discussing the evolution of olefin polymerization catalyst and in that way, we have drifted quite a bit. We started with Ziegler Natta heterogeneous titanium zirconium group for transition metal based catalyst which are martensite catalyst with extremely high activity for ethylene homo polymerization as well as propylene homo polymerization.

And then gradually drifted towards metal group for transition metal based metallocene type single site catalyst which were extremely a well behaved in terms of provide being able to polymerize homo polymerize ethylene as well as at propylene and also show extremely high activity depending on the modification of the transition metal group for metallocene catalyst and then subsequently we went into went at was looking for copolymerization of various kinds of olefinic monomer and subsequently copolymerization with monomer bearing functional groups.

Now in that aspect too we had moved over from group for transition metal catalyst titanium, zirconium hafnium and then went on to discussed about other metals for example lanthanide based olefin polymerization catalyst and which we had seen that even though they can polymerize olefins. But they cannot compare in terms of activity with respect to group for transition metals.

Now in this compression of looking for other non-group transition metal matching up to the activity of the group for transition metal contribution by Bruker’s and Gibson was discussed in the last lecture in which iron catalyst which is a non-group for transition metal showed extremely high activity in terms of olefin polymerization and it could give a range of products depending on the substituents going from oligomers all the way to the polymer.

And this was a tremendous discovery in terms of putting iron back into the polymerization map of in olefin polymerization and iron being the most abundant metal on the earth being cheap and economically viable this is a great news for people who are exploring iron based catalysis.

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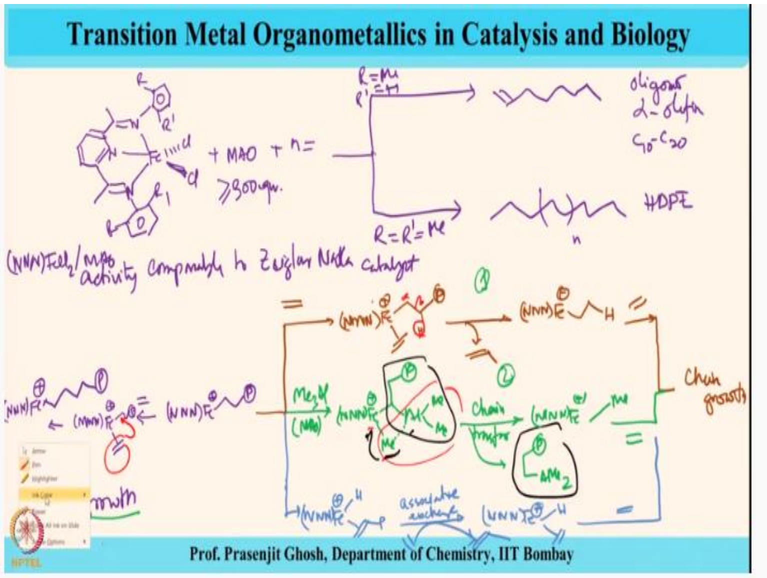

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So in the last class we had seen these; the catalyst which is grown over here methylene when R = methyl and R dash = hydrogen poly gamma alpha will be same C10 to C20 fraction produce high-density polyethylene. Now this activity comparable to Ziegler Natta catalyst. So this is a great news in terms of the chemistry and in terms of developing iron as a catalyst this in short is designated by NNN and Fecl2/MAO catalyst.

Now in this the interesting thing is that in this the chemistry a that chain termination competes with the chain growth and that is shown over here. So NNN Fe+ polymer with ethylene gives NNN Fe polymer and ethylene with iron in the plus state then this will come and insert which will then give NNN Fe polymer with Fe+. So this is a chain growth whereas this has 3 chain termination pathways as well.

So this is a chain growth chain growth reaction and it has 3 chain termination pathways as is shown here. The first one is this will bind to the ethylene and one can have NNN iron polymer bound to ethylene it has a hydrogen and it can beta hydrogen can eliminate and become a hydrate and that can insert into the thing so that can eliminate propene this moiety and then it can give

NNN Fe+ hydrogen which can again under grow ethylene to give chain growth. So this mechanism is sort of a chain termination mechanism but giving rise to chain growth.

There are other possibilities as well which is shown here. So this with Me3L tri methyl aluminum or MAO would give this complex NNN Fe+ polymer L methyl. So in this case what this is that tri fluoro tri (()) (10:02). Now this M methyl is interacting with iron and as a result there is a chain transfer that happens chain transfer and this kicks out polymer here ALMe2 and this methyl gets transferred to iron from aluminum.

And the unit which goes out is this as a result what stays behind on the catalyst is Fe+ methyl and that with ethylene again goes to chain growth and so what is interesting over here that here we have chain growth which leads to the growth of the polymer chain and here we have this chain termination mechanisms. This is mechanism number 1 this is mechanism number 2 both also leading to chain growth as a result the catalyst gives very high yield molecular weight polymers and then they this is not the second one there is also a third one which is a possible third pathway chain termination and that is given by this.

So these gives NNN Fe+ hydrogen polymer that undergoes associative exchange and as a result what happens is polycene comes in and propane goes out as its shown to give NNN Fe+ hydrogen and this in presence of olefin again gives chain growth. So what we have over here are 3 chain termination pathways this is pathway number 1 this is pathway 2 and pathway 3 all the termination pathway eventually in presence of olefin giving chain growth and this is in addition to the normal chain growth pathway.

So this is a wonderful catalyst which because of these reasons could match up to the activity of that Ziegler Natta system and could carry out polymerization and we have seen that how chain growth help in producing longer catalysts. Now we have moved from now we move and go beyond iron and we moved to nickel from here and we had seen that how the story sort of started with nickel how the stories are have started with nickel in terms of the nickel effect which sort of helped in discovery of the Ziegler Natta catalyst.

And then it went back a complete circle from nickel to titanium zirconium to lanthanum to iron and then it again goes back to nickel. Now we are going to be talking about how nickel can be used for producing poly olefin polymers.

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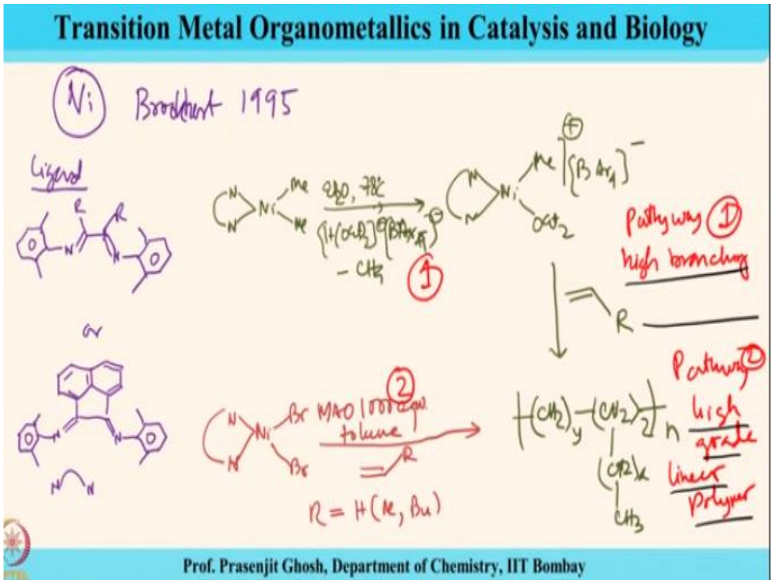
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And the credit goes to Professor Morris Brookhart who used a bulky system of the type shown that could produce polymer and how the ligand are of 2 types. One is this or this so this is a bulky system and we can in short, we can designate this as this ligand. What this list ligand does is that in its nickel complex in ethyl at -78 degrees centigrade in presence of H protonating agent F4 it eliminates methane to give this compound and then there is the ethyl solvent iterated here 4.

So this is the counter on and with propene it could give polypropylene of and the same he could also start instead of the methyl he could also start it from the nickel dibromide precursor using MAO 1000 toluene with isopropyl R it can R can be hydrogen, methyl, butyl it could also produce the same pathway. So the this is one can think of this as a pathway 1 and this is pathway 2 the polymer produced by pathway 1 are high branching hyper branching whereas polymer is produced in pathway 2 gives a high grade linear polymer.

And one can sort of control that if the grades of the polymer depending on the conditions used or pathway follows in one case one can get high grade a linear polymer. In other case one can be a highly branched polymer so this was a nice work where Brookhart also know put a nickel in the map for making polymers because nickel the whole business started off with nickel being in the nickel effect setting it off and then nickel known in shop where it was mainly used for oligomerization catalyst.

It is Brookhart work which made nickel to come into the map of olefin polymerization and it also convincingly demonstrated that how nickel can be used even to make polymers and nickel being a late transition metal it has a propensity to chain walk during the polymerization and that is what is explained by branching that is observed.

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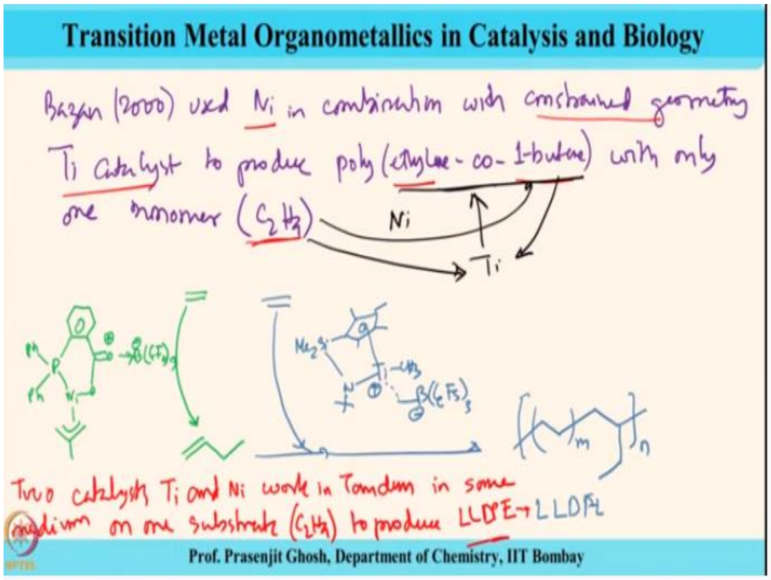

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Bazan (2000) used Ni in combination with constrained geometry Ti catalyst to produce poly(ethylene-co-1-butene) with only one monomer (C_2H_4)

Two catalysts Ti and Ni work in Tandem in same medium on one substrate (C_2H_4) to produce LLDPE → LLDPE

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Now continuing further a nice work by Professor Bazan took nickel to much higher heights where he used 2 catalyst working in tandem to produce high molecular with polypropylene. So this is a property which uses 2 catalysts transition metal one is nickel, and another is titanium to produce a polymer in a tandem fashion and this is nicely demonstrated illustrated over here.

So Bazan in 2000, demonstration showed used nickel in combination with constraint geometry titanium catalyst to produce polyethylene copolymer of 1-butene. The big good thing is that this is a copolymer process with only 1 monomer which is ethylene. So this is kind of a phenomenal work let me illustrate why first of all that it uses 2 catalyst 1 is nickel another is constraint geometry titanium catalyst 2 catalyst producing a copolymer of ethylene and 1-butene. But the catch is that there is only 1 monomer which is ethylene.

So one catalyst is used first to convert ethylene to butane and then the second catalyst the first catalyst is nickel which used ethylene to butene and then the second catalyst titanium sort of polymerizes the butene and ethylene to give this copolymer ethylene co 1-butene this is a beautiful elegant demonstration of organometallic chemistry. It also shows how clear thinking can lead to wonderful catalyst development where 2 catalysts are made to work in a tandem.

Let me illustrate this more specifically with the catalyst those were being used the first catalyst is obviously a nickel catalyst which has which is of the formula this. Now this is a nickel a little complex and that is activated with boron C6F5O3 this catalyst converts ethylene to 1 butene. Now this 1 butene then reacts with maybe I will do it different color 1 butene then reacts with another molecule of ethylene and undergoes copolymerization using a constraint geometric catalyst.

Titanium methyl plus this is boron C6F5 whole 3 - so this does the co polymerization to produce mn LLDP, so the good thing is that this in; this case 2 catalyst titanium and nickel work in tandem in same medium on single substrate on 1 substrate which is ethylene to produce LLDP which is this. So this is a tremendous demonstration of the capabilities of ergonomic chemistry in which this LLDP was produced and depending on the variation of the conditions one can control the chain length and the molecular weight and depending on the incorporation extent also 2 different by varying the nickel to titanium ratio.

It should also be mentioned that this catalyst nickel and titanium are not interfering with each other. So with this we come to the end of todays lecture where we had seen the catalyst development from iron Gibson’s catalyst to Brookhurst nickel. The focus shifting from iron to nickel and what it says that there lot of chemistry even left with the other transition metal other than non-group for transition metal and in this case nickel and iron indeed showed did prove their strength in terms of doing wonderful chemistry and the last example by Bazan over tandem reaction between nickel and constrained geometry titanium group for catalyst took polymerization to a different level.

So with this we come to an end of today's lecture we are going to dwell a bit more on non-metals non-group for transition metals when we take up the topic in more detail in the next class till then thank you and goodbye.