Transition Metal Organometallics in Catalysis and Biology

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Module No # 07
Lecture No # 35
Oligomerization of alkenes and alkynes (Part -1)

Welcome to this course on transition metal organometallics in catalysis and biology today we are going to be talking about oligomerization of alkenes and alkynes. This is an interesting are which has emerged out of Ziegler Natta catalysis and it as its own domain. Now we have discussed these alkene and alkynes oligomerization reactions earlier in the context of applications of organometallics catalysis in large scale synthesis.

In this context what noting we have spoken about important industrial process which is called shell higher olefin polymerization process which was developed in 1950's to make it use of various fragments of alpha olefin oligomers for commercial purpose. Now this story is sort of goes back to 1950's when shell was trying to develop methods for using alpha olefin's from the range of C8 to C14. So we had discussed this in great detail in our earlier lecture on very applications of organometallics catalysis.

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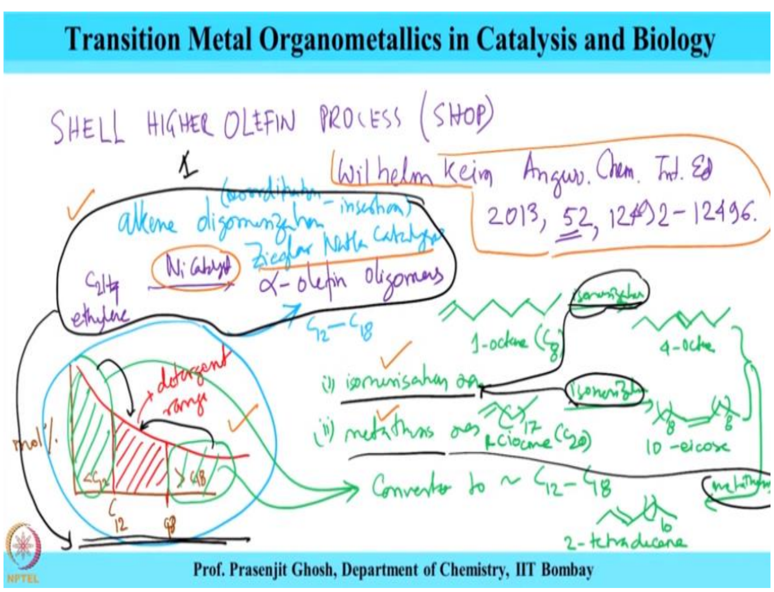

And a nice review of these process shell higher olefin process or shop has been nicely reviewed in this article by Wilhelm Keim in Angiew Chem edition in 2013 52 12492 to 12496. We have looked into this process whereby alpha olefin's where prepared by Ziegler Natta method C2H4 ethylene using nickel catalyst produced alpha olefin oligomers and that had huge distribution as it shown over here of different fragments mole percent from C12 to C18 and this is greater than C18 and this is less than C12 and the distribution goes something like this of which the range of alpha olefin's from C12 to C18 this range was used for making detergents.

And this was what provided the impetus for looking into use of other 2 fragments which at that point of time were not being used one is the fragment which was less than C12 and the fragment which is about C12. So these fragments are that point were usable and were trying to find some use to make this unusable fragments. Now these oligomerization if alpha olefin was produced by these process which is called alkene oligomerization using Ziegler Natta catalysis that means that coordination insertion method.

So all these alpha olefins the whole thing was produced by this process of having have to use nickel catalyst for alpha olefin's but of these various fragments only usable fractions was C12 to C18 was usable. Now in this shop a parallel development in which they used isomerization reaction as well as metathesis reaction to use these fraction C12 and C18 to convert to around something between C12 to C18 and hence can be utilized.

So this was done using Ziegler Natta catalysis and nice example is given over here in the following reaction. For example 1 octane this is C8 was isomerized to give the isomerized product which is 4 octane as well as CH2 17 this is 1 ei cosine this is C20 fragment isomerization to give 8 you get 10 ei cosine and these 2 together was done metathesis to give C10 or 2 tetra decane.

So what we have seen that these shop includes 2 process 3 process mainly the first is this coordination insertion process this is number 1 process which generates all these range of alpha olefin generated from here and then the 2 other process 1 is isomerization process over here as well as over here isomerization process and the second one is metathesis process which is over here. So these 2 process together would help these fraction which are less than C12 and C18 together to come into a range which is usable.

So for detergent purpose so mainly a couple of process to came together to look at to find use for this wide range of alpha olefin a part of a shop process. Now in our discussion so far what we have done is we had already discussed this reactions earlier on isomerization as well as metathesis as well as this distribution cart as a part of olefin metathesis by forwarding the utility of olefin metathesis industrial scale.

And however we have not looked into these oligomerization process in nickel catalyst and in today's lecture we are going to focus on this alkene and alkyne oligomerization using Ziegler Natta catalyst is a part of the shop chemistry. And all of it is nicely reviewed by Wilhelm Keim article given in Anguew Chem 1952 12492 to 12496 and I request all the students who have who are all took this course to go through this review which is which explains the story and the development at that time very elaborately and would benefit the reader very much.

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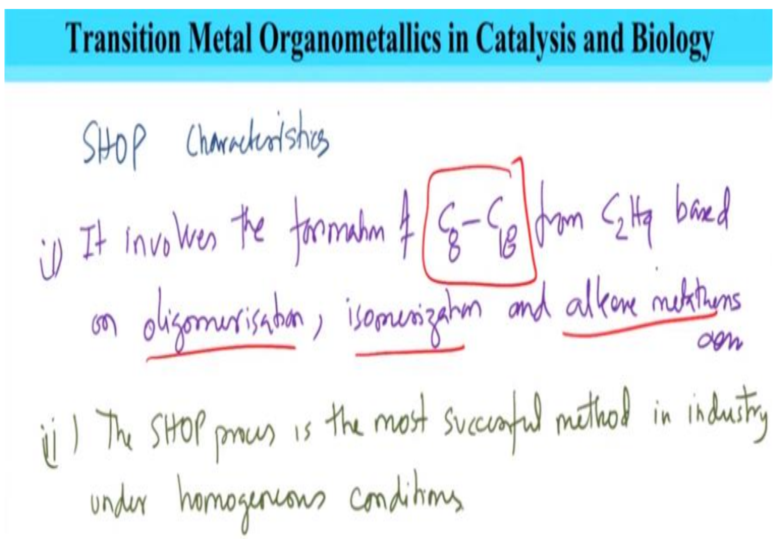

So shell higher ellucian process characteristics one it involves the formations of C8 to C18 from ethylene based on oligomerization, isomerization and alkene metathesis reaction. Now these we have discussed in detail in our previous slide where we had shown you diagrammatically where with example where each of these reactions play a role to produce this C18 to C8 to C18 fragments which are the application for detergent usage.

So these 3 reactions are to be discussed under this shop shell higher olefin process reactions family of reactions. Now the other characteristics of shop is the shop process is the most successful method in industry under homogenous conditions. And usually these polymerizations are carried out in polar solvent so this is one of the powerful method in which this oligomerization reactions to produce this alpha olefin using Ziegler Natta catalysis is concerned.

So shop is very successful method in industry and it is primarily used for producing alpha olefins from ethylene as a alternative method for producing alpha olefin’s from petroleum or by cracking of natural crude oil. So let us now take a look at the mechanism for this alkene and alkyne oligomerization reaction.

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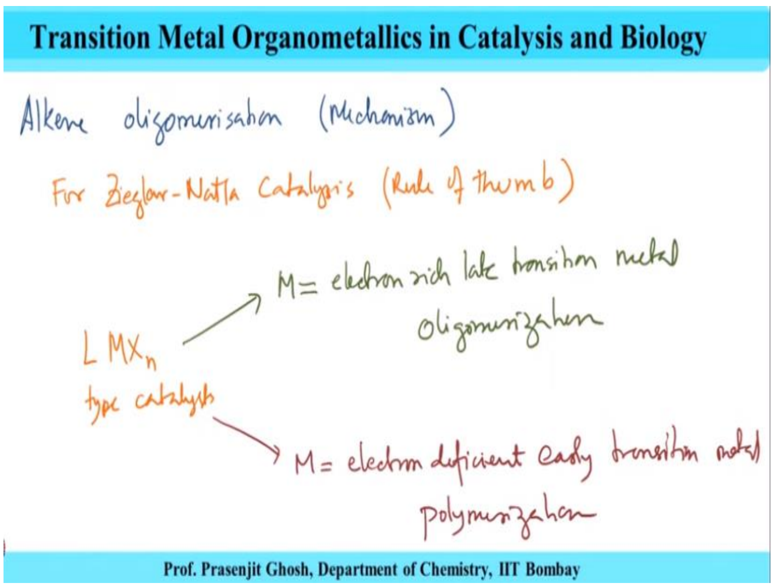

Mechanism now the rule of thumb is that if it is electron rich metal of them oligomers are preferred whereas if it as electrons deficient metal like early transition metal then this polymers are preferred. So for Ziegler Natta catalysis the rule of thumb is for MXn type catalyst in equals electron rich late transition metal then oligomerization is favored even alpha olefin’s. Whereas when n is electron deficient early transition metal then polymerization is preferred.

Now in our first discussion on the extent of the growing of the polymer chain we had said that extent of this chain link is very much dependent on the rate in which these the propagation step and the termination step they occur you know in comparative sense. If propagation is step is faster than the termination step then one ends up getting polymers and if the propagation step is comparable or slower than the termination step then one ends up getting oligomers.

And also what we see that these for electron deficient metal early transition metal polymerization is preferred in implying that the propagation it is higher than that of the propagation step. Whereas for electron reach late transition metal the propagation rate is comparable or slower than that of the termination one can implying that alpha olefin oligomers are formed. Now we are going to take a detailed look at the mechanism of these oligomerization reaction.

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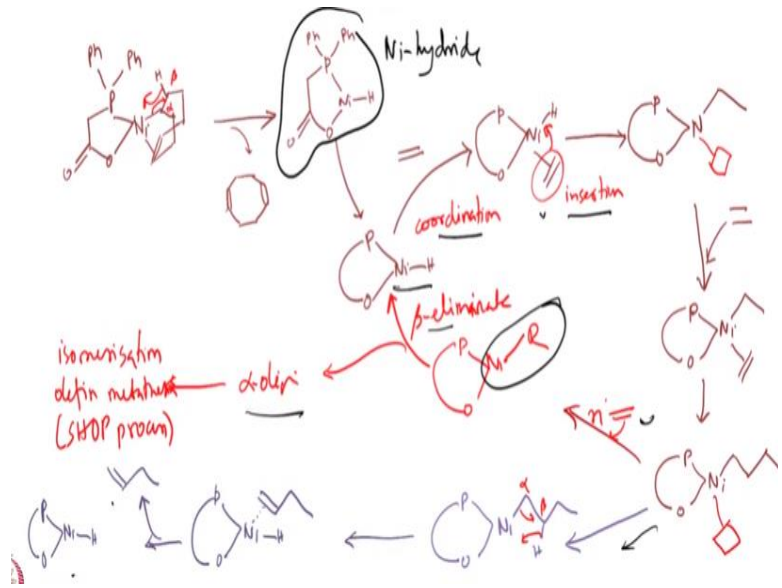

So this is the catalyst so these loses the hydrogen in data hydride elimination process this is alpha carbon this is data carbon. In a beta hydride elimination process giving an active species of nickel hydride along with nickel cod chloride so god is eliminated and the active catalyst is formed. So this is the active species which then enters the catalytic cycle and this is represented by this cartoon diagram as is shown here the nickel hydride then reacts with the olefin by coordination insertion pathway this is the coordination step and this is the insertion step as is shown here.

And now this olefin moiety will insert into the nickel hydride bond giving creating a vacant site as is shown over here and nickel ethyl moiety. Now second olefin will come and bind in the olefinic site coordination followed by insertion as it shown in the previous step. Now these can proceed in 2 direction from here the first is that it can beta eliminate can be shown over here this is alpha this is beta it can beta eliminate to give the catalyst nickel hydride coordinated to the alpha olefin which can eventually give nickel hydride species and the olefin going away.

And the other method is over here another olefin can come in times bind in the vacant site in times and undergo coordinative insertion to give a nickel alkyne species and this nickel alkyne species can beta eliminate to give the nickel hydrogen along with alpha olefin long chain alpha olefin. And this alpha olefin through isomerization and olefin metathesis is taken for producing the desired fraction by shop process.

So what it shows that this oligomerization mainly proceed by 2 method which is coordination insertion and in the shop process the late transition metal nickel is used for olefin oligomerization and usually the active sites is a nickel hydrides species is the active complex. Now nickel hydrides species can insert olefin and then coordinate olefin and then undergo insertion then the need can be to do the twice over and then there is possibility in the first possibility it gives 1 butane and nickel hydride or it can undergo subsequent olefin insertion to give a long chain nickel alkene which can then beta eliminate to give back then nickel hydride as well as alpha olefin's.

Now these alpha olefin's are then feed into the isomerization and olefin metathesis reaction as a part of the shop process. So with these we conclude our discussion on olefin oligmerization as a part of shop process in today's lecture and what we have done let me recapitulate what we have done is we have looked at the shell higher olefin process in its entirety and we have looked at 3 different applications of organometallic chemistry involving this alpha olefin oligomerization reaction using nickel catalyst.

And second the isomerization reaction and third the olefin metathesis reaction all come into to play in channelization the various lengths of alpha olefin obtained for producing something which is more important commercially particularly the alpha olefin's in C8 to C8 interactions which are used commercially. So with these we come to the end of the today's lecture we are going to be taking up more of olefin oligomerization when you continue with the discussion in the next lecture I thank you for being with me in this lecture and I very much look forward to being with you in the subsequent lecture when we talk more on olefin oligomerization reaction in more detail till then good bye and thank you.