Transition Metal Organometallics in Catalysis and Biology

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Module No # 08
Lecture No # 36
Oligomerization of alkenes and alkynes (Part – 2)

Welcome to this course on transition metal organometallics in catalysis and biology we have been discussing about various oligomerization of olefin's and alkyne reactions. And in this context we have looked at the first and the fore most of this type of reaction which is shell higher olefin process in great detail and look at shop from the context of olefin oligomerization giving alpha alkenes.

Now this shop process was very important process which was practiced in industrial scale for producing detergents and this primarily had so retained for making alpha olefin oligomer alpha olefin's for applications in surfactant and detergent and this initially where obtained by cracking of crude oil however later as Ziegler Natta catalyst is evolved nickel catalyst was found to produce alpha olefin's from C oligomers from C2 C3 all the way to C20 and above.

And the only drawback about this olefin oligomerization under shop process was that the Ziegler Natta coordination insertion olefin oligomerization was non selective that it could produce a bunch of oligomers with various distribution ranging from smaller oligomers of dimer timer to large oligomers having more than 18 or 20 monomer unit. Now in order to make us of this large distribution of oligomers to other process.

For example olefin isomerization followed by olefin metathesis they were put in place to make use of the low molecular weight oligomers as well as high molecular weight oligomers which individually had not much used as detergent. So this is a combined shop is a combined process that involves alpha olefin oligomerization, isomerization and metathesis put together to make crude material for producing detergents.

So we have covered this in great detail in our previous lecture and also we have looked into the alpha olefin oligomerization catalytic cycle and the thing that comes out is that the active species is usually a nickel hydride species.

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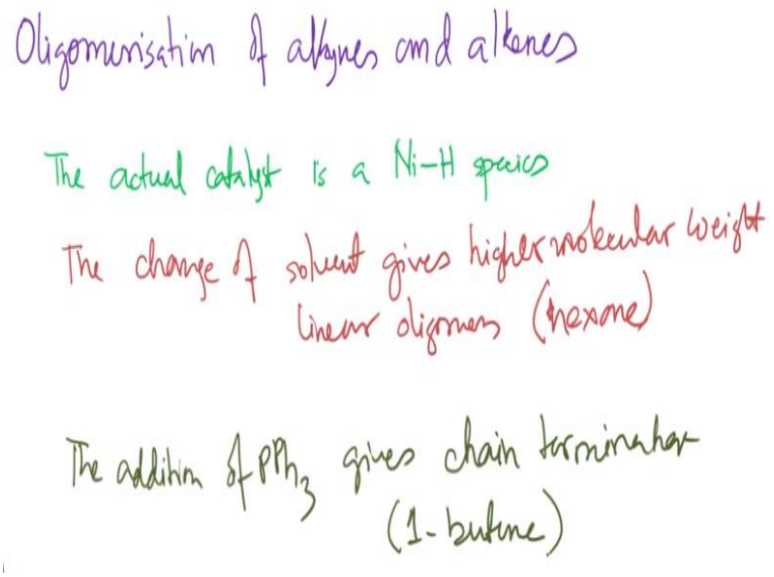

The active species also what has been observed that change of solvents gives high molecular weight higher molecular weight linear oligomers. And this was done in solvents is for example hexane for the shop process what was found that addition of tripheyl phosphine gives chain termination. For example 1 butane these obtained so even though this was oligomerization of olefins was very useful process which help develop shop process all together.

However criticism of this process lies in its lack of selectivity because a large number of oligomers of various chain link are obtained in different ratio's during the process of oligomerization using the nickel catalyst. So selectivity was itself issue now in this context another important example needs what mentioning is about ethylene trimerization.

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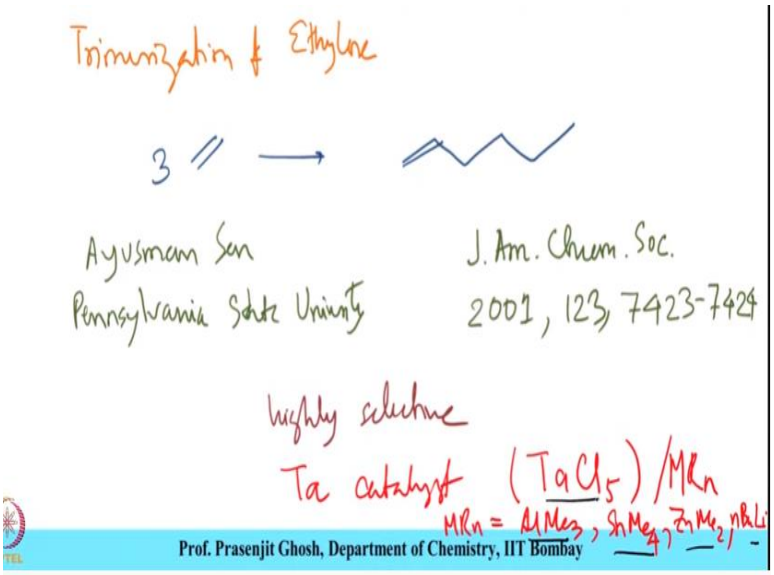

Trimerization of ethylene now so the process indicates conversion of ethylene to 1 hexane now the process is important with respect to alpha olefin products and oligomerization in shop is with regard to selectivity of these reaction. So this reaction is highly selective in producing 1 hexane. Now this discovery has a Indian impact on it and is made by the group of professor Ayusmam Sen and has been reported by professor Ayusmam Sen of Pennsylvania state university and it was reported in journal of American chemical society in 2001 very recently in that 123.

So one beauty about this reaction is the selectivity highly selective as one compared to the alpha olefin produced by olefin oligomerization shell higher olefin process and interesting thing to note over here that for this reaction and all the transition metal tantalum or tantalum catalyst have been used as opposed to nickel catalyst which have been which are often used for producing alpha olefin's ethylene oligomerization reaction.

Now these to be precise tantanium penta chloride is the starting precursor in presence of some metal alkene MRn and these metal alkene can become can be several alkylating regions like trimethyl aluminum tetramthyltan, dimethyl zinc and mbutyllithium. So this the scope of this reaction in terms of generating active species is very broad where different types of alkylating reagent like methyl aluminum tetra methyl ten dimethyl zinc butyllitinum are used to alkylate this tantalum 5 compound tantinum petanfloride to get the active species which is actually a tantalum 3 species .

So let us this is very interesting discovery which has the mark of an Indian inventor professor Ayusmam Sen currently on role in Pennsylvania state university who had made this fine discovery. So let me just walk you through the catalytic cycle for these trimerization of ethylene reaction.

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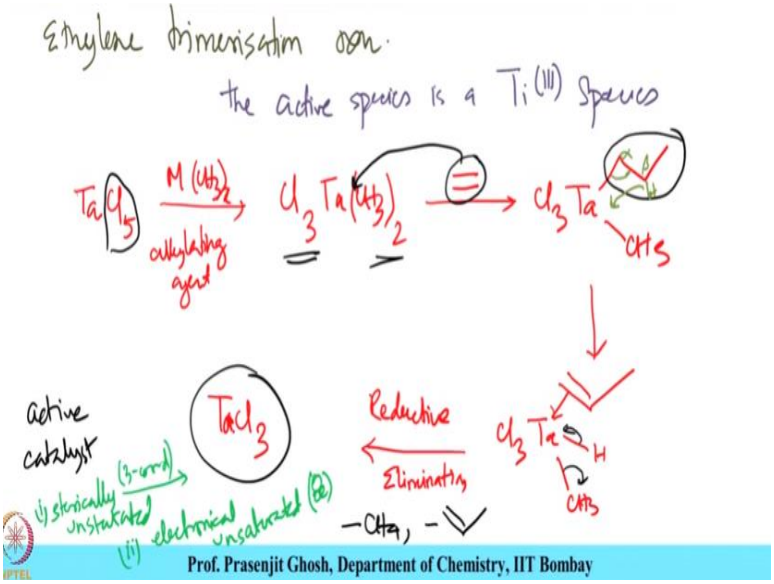

The first is the formation of the active species which is the active species suggested to be titanium 3 species. And this active species is produced from tantanum 5 compound precursor as it shown below in presence of M alkylating agent gives Cl3 tantanum dimethyl. So its partial alkylation that occurs of that tantalum 3 species penta 5 becoming 3 chloride and 2 so this is partial alkylation which occurs to get this tantalum 5 species then that reacts with ethylene to give contain long methyl species where the coordination insertion of where the coordination of the ethylene occurs one of the tantanium 5 tantalum methyl bond to produce this tantalum propyl moiety.

Now this tantalum propyl moiety because of electron deficiency of tantalum has beta hydrogen which sort of better eliminated to produce this titanium hydride methyl species with coordinated propylene. Now then under these ethylene bound tantalum or hydride species undergoes bit reductive elimination as is shown over here to eliminate methane as well as propane to generate the active species which is the tantalum trichloride.

So this is the active species active catalyst for ethylene trimerization one thing to note about this catalyst is that this species is both sterically unsaturated as well as electronically unsaturated. So this is a 8 electron and this sort of 3 coordinate 3 ligand so this species is highly active in terms of having very less of steric saturation of 3 chloride ligands bound to titanium and also electronically very unsaturated because it is a 8 valence electron 3 from chloride and 5 from tantalum.

So it is a 8 valance electrons species so it is also very electronically unsaturated and this is supposed to the active species for this catalytic exim trimerization reaction. So one beauty about Ayusmam Sen work is that here successfully demonstrated the use of an early transition metal like tantalum for producing olefin oligomers like one exim usually the common wisdom had been that early transition metal produces high molecular weight polymers whereas more electron reach lead transition metals produces oligomers.

But here we have a nice example from sense group where we are successfully used an early transition metal for producing trimmers of ethylene in form of one hexane. The second important feature about sense work is the selectivity that in alpha olefin oligomerization using nickel catalyst in shop process a wide range of alpha olefins bearing different lengths are produced whereas sen as showed that highly selective trimerization can proceed with this catalyst that only gives one hexane as the final product.

So these two are the key feature that sort of separates or that sort of separate for the sense work from the existing catalyst or which sort of sense work from the existing catalyst which have been known for olefin oligomerization. So now we are going to take a look at the mechanism as to how this active species titanium tetra fluoride carry out this trimerization of olefin's ethylene.

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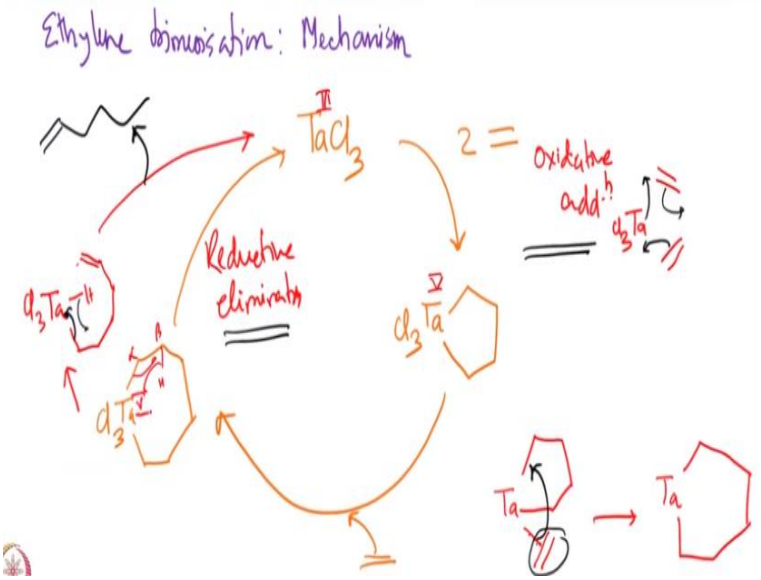

Tantalum chloride which is highly sterically unsaturated as well as electronically unsaturated reacts with 2 molecules of ethylene to form this tantalum metallocyle penta metollocyle penta cyclic metolocyle. So this is quite stable and it also has been shown by DFT calculation by others that this is a stable or stable product which will eventually form from 2 olefin's. Now the species which is formed is tantalum 3 Cl3 tantalum metallocycle where the oxygen state of tantalum has again increased from tantalum 3 to tantalum 5 and this is sort of an oxidative reaction which occurs oxidation which occurs by addition of 2 ethylene molecule.

And can be seen as such tantalum 3 to species with tantalum donating electron to the ligand to form these tantalum metallocycle which is shown over here subsequently the reaction of another olefin happens by coordination insertion pathway to give to this tantalum 7 membered ring and this happens by simple coordination followed by insertion of these into the bond to give that 7 membered pathway and finally the reductive elimination to give generate back via to generate back this tantalum 5 membered compound via beta hydrogen elimination these going to these and that undergoes reductive elimination giving 1 hexane to the side product.

So these also involves reductive elimination so what is happening over here one can see that this catalytic cycle initiates with oxidative addition and then tantalum becomes 4 and then goes to deductive elimination where again the tantalum oxidation state changes from tantalum 5 to tantalum 3. So this is the very nice piece of work by professor Sen where one could see that it tantalum 3 species being generated in the course of reaction.

And that is highly electron deficient as well as highly unsaturated compound which then successfully carries out these trimerization of ethylene to give 1 hexane first by oxidative addition of 2 ethylene molecules to give the tantalum 5 species which also then further undergoes one more insertion to give a 7 membered metellocycle of tantalum and that finally bta hydrogen eliminates as well as reductive eliminates to give one hexane as the product and regenerating back titanium trichloride.

So with these I come to the conclusion of today's lecture in which we have looked into first the various important attributes of olefin oligomerization particularly from the perspective of its active species which the nickel hydride species and the effect of solvents for example on going to solvents like hexane higher molecular weight polymers are obtained or the effective of phosphine's which sort of allows chain termination and facilitates lower oligomer formation.

And the second aspect that we have discussed is about a interesting reaction that involves highly selective trimerization of ethylene to 1 hexane and this has been reported by Ayusmam Sen of Pennsylvania state university in the JCS state article 2002 article which we have already referred to and request the reader to read it form with more detail and in these process Sen has nicely demonstrated that even a against the conventional wisdom that even a early transition metal can be used for successfully used for olefin trimerization in the very selective fashion.

In particular he have started with the tantalum penta fluoride using some alkylating agent he had generated a highly unsaturated and highly electron deficient tantalum 3 species which selectivity produces one hexane in the mechanism as is shown below. So very interesting work and it is also highlights the scope of organometallic chemistry for particular in terms of carrying out different kinds of transformation some of which may go beyond the wisdom of the conventional logic and nice work by Sen in this regard was discussed.

So with this i come to the conclusion of today's lecture on ethylene oligomerization and ethylene trimerization that we have discussed. We are going to talk a more on few more other examples of various kinds of olefin oligomerization reaction when we meet next in this lecture series till then thank you and good bye.