Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

Professor Sanjib K. Patra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture 30
Metallocene and Post-metallocene Catalysts: Homogeneous to Heterogeneous & Lab to Industry (Contd.)

(Refer Slide Time: 0:33)

NPTEL ONLINE CERTIFICATION COURSES

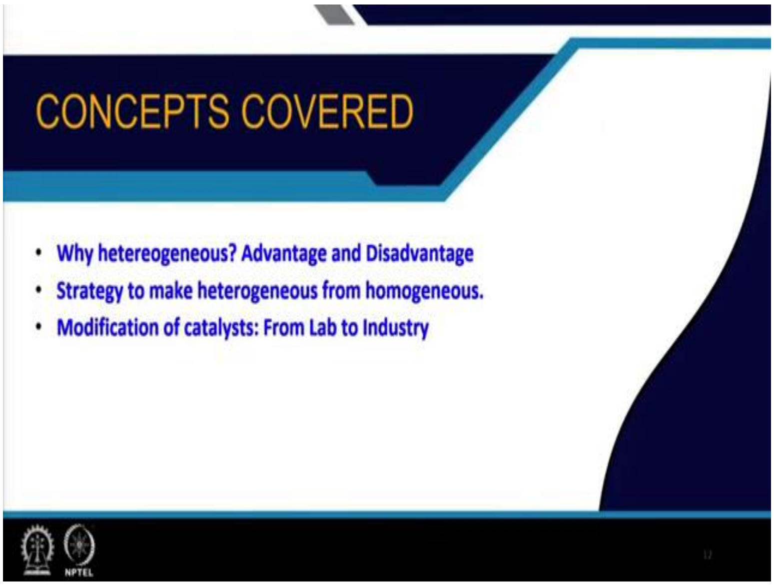
Lecture 30: Metallocene and Post-metallocene Catalysts: Homogeneous to Heterogeneous & Lab to Industry

Hi, welcome once again, so we shall continue our discussion on the homogeneous to heterogeneous transformation and from a lab to industrial journey and in the last class we have discussed about the basic concept of the heterogeneous catalyst system.

And we have also tried to understand in a comparative way what is the basic advantage and disadvantage from homogeneous to heterogeneous and also we learned that what are the very important and like a path breaking heterogeneous catalyst systems which are accepted in industries and still it is used heavily.

So, today when we will discuss about the first part, we will discuss about the mechanism how does it work in heterogeneous catalyst and then we will try to discuss that what are, how we, what are the strategies to make the homogeneous metallocene catalyst to heterogeneous catalyst for practical implications in industries.

(Refer Slide Time: 1:37)

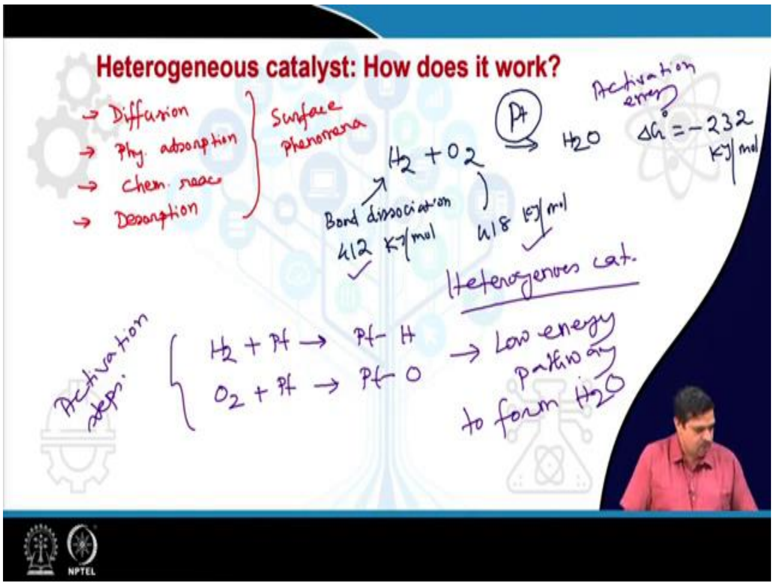


CONCEPTS COVERED

- Why hetereogeneous? Advantage and Disadvantage
- Strategy to make heterogeneous from homogeneous.
- Modification of catalysts: From Lab to Industry

So, the concepts are similar as our last classes because we are continuing the discussion so here mainly we will be discussing the mechanism and the metallocene catalysts on support how to do it.

(Refer Slide Time: 1:59)



Heterogeneous catalyst: How does it work?

So, if you recall in the last class we have discussed the important steps that is the diffusion because I, as we discussed it is a surface phenomena, then physical adsorption and then we will the chemical reaction and then the last step is the desorption, these are the and all you see that heterogeneous is a surface phenomena so the nature of the surface of the catalytic system plays a vital role in heterogeneous catalysis.

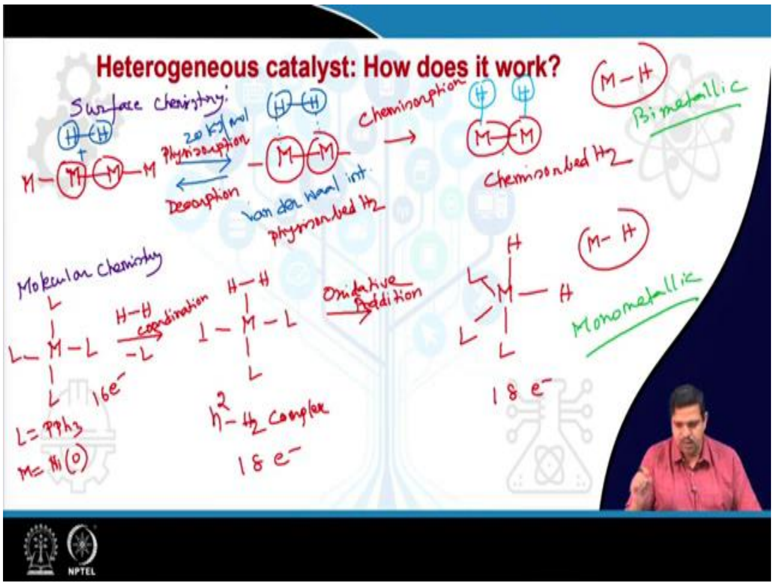
One very classical example I want to give it is a text book example but it's very important and very interesting to discuss like this the classical reaction plus H_2 plus O_2 is H_2O as you know this is thermodynamically favorable reactions theoretically because the delta G 0 is any idea how much is, is yes spontaneous minus 232 kilo joule per mole. However, the bond dissociations energy of the HH that is the bond dissociation energy is very high and almost similar similar in H_2 and O_2, this is 412 kilo Joule per mole and this is 418 kilo Joule per mole is very much similar.

So, if you keep H_2 and O_2 in a sealed glass container you will see nothing happens, there is no reaction at all but theoretically this reaction is feasible because you see the delta 0 is quite negative minus 232 kilojoule per mole. But this reaction only happens in presence of the platinum gauge or platinum catalysts heterogeneous catalyst, platinum catalysts so and this is also one example of the heterogeneous catalytic system, heterogeneous catalysts.

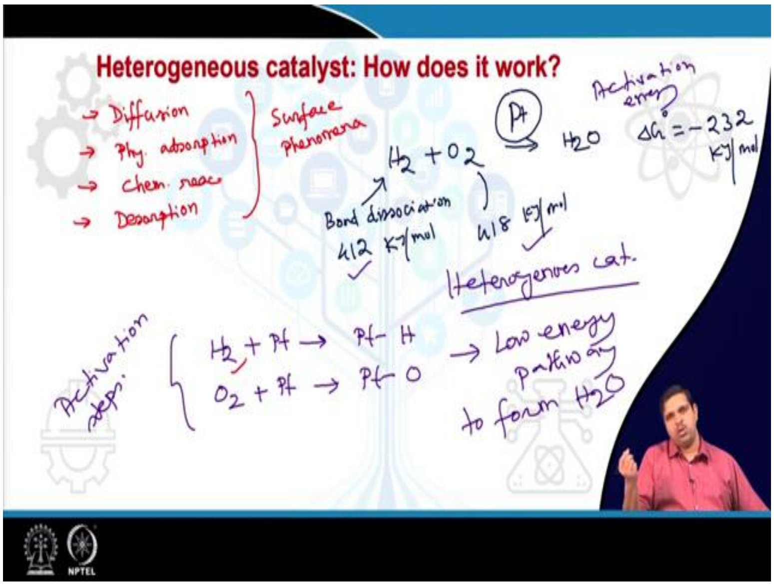
Here is a heterogeneous this is very interesting system. And how does it happen? This is activation energy is very high in this case because you see the dissociation energy is quite high here but in presence of the platinum it takes a different path so it actually first activate the small molecules like hydrogen and oxygen and to make the platinum hydrogen, platinum hydride and the O_2 Pt is Pt O, so it is basically you see these are the activation steps, so and then it undergoes through a low energy pathway to form H_2O.

So, this is a very classical example of, one example of heterogeneous catalyst system, most of us we are aware of that one because it is text book chemistry. In the next one I will try to discuss or try to give some highlight what are the basic steps of any heterogeneous system that is applicable for any kind of heterogeneous catalyst whether it is a polymer supported, whether it is a silica supported or whether the catalyst is itself is a heterogeneous like oxides, many oxides, alkyl oxide, transition metal oxide, lead transition metal oxide, lanthanide oxides are also acts as a catalyst for various reactions.

(Refer Slide Time: 6:48)



Heterogeneous catalyst: How does it work?



Heterogeneous catalyst: How does it work?

So, we it is we know that this heterogeneous catalyst is actually the surface chemistry, that we have already discussed. Now I will discuss or show the basic difference in a very qualitative way in a pictorial diagram so that it is it you can easily understand what is the main difference, fine.

So, suppose I am doing some hydrogenation reactions or activating the HH as example in the last here you will see so this is basically the activation of the dihydrogen or H2 normal H2 gas which has a quite high bond diffusion energy of 412 kilojoule per mole. So, let us take a similar type of very, I am the I will discuss in a very general way so this is suppose is let us say is a metallic one metals and like that a metallic surface, it may be oxides, this may be elementary metals or alloys anything.

And here and let us say that I am passing hydrogen through this one. So, what will happen? Hydrogen is like this one so there will be now like that it will be some kind of interaction and this is called I will discuss what kind of interaction it is like that and you will have so some kind of weak interaction and this is called is a generally this the interaction is Van Der Waal interaction in nature, Van Der Waal type interaction is a very weak interaction at around 20 kilojoule per mole and that is why it is a reversible in nature.

So, basically you can again H2 can be released in a very fast and easily so that is why it is a reversible nature and this is called the physisorption, this step is called the physisorption, this step, so this is the physisorption and this is called the physisorbed of H2 on metal surface. And now next you have when these are in a close proximity to the metal center that is the active center.

Then what will happen there will be the chemical reactions as you have seen for the small molecules in a molecular chemistry like oxidative addition, reductive elimination that we have seen for the small molecule chemistry we have discussed in case of homogeneous catalysis system.

So, this is you can tell this step is the chemisorption and this interaction is high much higher than the physisorption and this is called the chemisorbed H2. And you see here the, here first what is happening this is a physisorption is happening and the reverse step you can tell this is called the desorption the reverse step this is very low in energy that is why it is a reversible in nature.

And then chemisorption and then you see what is happening M H bond is forming as you have seen like for small molecular chemistry I will also give one example so that you can understand now for the molecular chemistry what happens I am taking again a very general structure like L may be phosphine if you want to be specific L may be phosphine, M maybe nickel 0, N may be nickel 0, sorry this one, fine.

Now, you will see that what will happen for if you so this is a molecular chemistry, this is the surface chemistry and the first one and this is molecular chemistry. Now, what will happen here? The, let us say this if it is nickel 0 that is the 16 electron system so it can first undergo the coordination.

So, one L will come out and then it will be the classical eta 2 hydrogen so it is basically the is first coordination here H and this is basically eta 2 H2 complex and if you calculate it will be

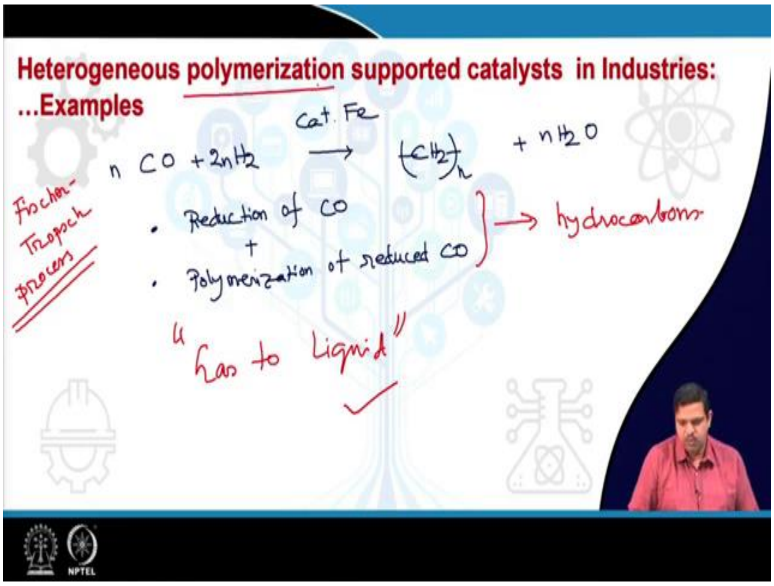
18 electron if we consider M is nickel 0. Now, this is the now bond making step that is the oxidative addition we are all familiar what is oxidative addition so here what is happen what will happen the geometry I am again writing very hypothetical it may be square planar it may be triangular bipyramidal depending on the ligand depending on the metal center.

So, if one triphenyl phosphine goes away then it will be square planar so here you will see this is again the 18 electron system and you will see that there is a formation of again M H bond. So, in this case also M H, in this case also M H bond you will see, but the basic difference you will see here that here it is the addition of hydrogen is a bimetallic in nature and for molecular chemistry it is generally mono metallic.

But in a some cases it may happens for as a bimetallic also as example for dimeric compounds like a die gold complexes, silver complexes, of any other bimetallic complexes that the psi oxidative addition in mono metallic in bimetallic pathway also possible but in the normal cases the in a molecular chemistry you will see that that formation of the M H or new bond it is in a mono metallic nature and for the heterogeneous system that is that follows the surface chemistry has been a bimetallic nature like here you will see.

So, the basic difference you will see here in the surface chemistry that is the heterogeneous system, physisorption and then chemisorption and in a molecular chemistry coordination then oxidative addition and then others like reductive eliminations all those things as example for heterogeneous happen like disruption releasing the product. So, these are the steps in a very I am discussing in a very simple way so that it is understandable to everyone, I am not going in more detail about the kinetics.

(Refer Slide Time: 15:56)



Heterogeneous polymerization supported catalysts in Industries: ...Examples

Fischer-Tropsch process

$$n\,CO + 2nH_2 \xrightarrow{Cat.\ Fe} \left(CH_2\right)_n + nH_2O$$

- Reduction of CO
  +
- Polymerization of reduced CO

→ hydrocarbons

"Gas to Liquid" ✓

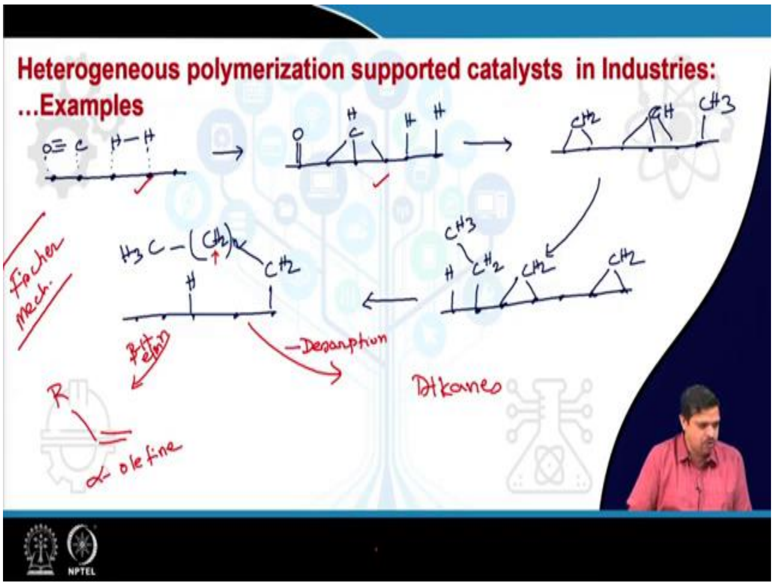
So, here I will now discuss about one example which is very much followed in industries that is the Fischer-Tropsch synthesis or Fischer-Tropsch process and what is that this is very important and it has you will understand why it is important so you can basically form the carbon monoxide and hydrogen very simple substrates easily available and what you will get, you will get the hydrocarbons not actually the polymers and non-toxic byproducts the water.

So, if you consider like valance CH2n and here n H2 O and what is this is actually the catalytic iron so here what is two steps actually what one is the reduction of carbon monoxide and then polymerization of reduced CO and this is this process called the Fischer-Tropsch process this is very very important, one of the heterogeneous reactions and it is a million dollar market.

And here you see that this is what we are getting, we are getting basically from here hydrocarbons which can be feedstock for many value added materials as example for the fuels, the works, the oils, etc. And this is called popularly, this reaction is gas to liquid so you will see here you are using two gases and you are getting a liquid that is like low molecular weight alkanes. So, that is also popularly we call is gas to liquid one of the very important industry, heterogeneous industrial process for heterogeneous catalyst.

So, this is a you will see that heterogeneous polymerization supported catalyst in industries and how does it happen, the reactions. Here this is very complex system however, there are a lot of mechanisms are involved however I will just try to show you in the original mechanism proposed by the Fischer and how does it happen I will show you.

(Refer Slide Time: 19:44)



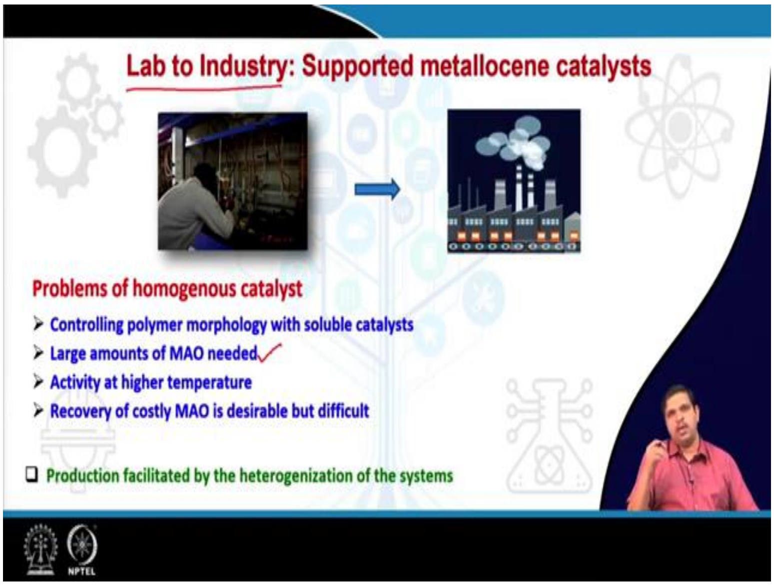
Heterogeneous polymerization supported catalysts in Industries: ...Examples

So, you can consider that this is the iron surface and here is carbon monoxide, fine and here hydrogen and this is weak interaction the Van Der Waal interaction as we have learned now previous discussion and as I told that heterogeneous catalysis mechanism is very complex to understand so C here and here, here formation so this is you can see Van Der Waal this is the physisorption and then the chemisorption happens and then in presence of H2.

So C H2 and this is CH and here CH3 and then so these are let us say the iron active centers so this is CH3 this is, and this is CH2, this is CH2 like that, fine. Now, here you see it will continue and you will see like CH2, CH2 n like CH3 like H like that now is interesting, it can desorption and desorption will produce the alkenes and it can also undergo the beta H elimination so this hydrogen will be beta and it can give the alpha olefin as a minor products.

So, this is a very simplified Fischer mechanism as I told that there are different mechanisms have been postulated by different groups, these are one of the examples, simple examples, so you can see understand that this is the physisoft H2O carbon monoxide, this is the chemisoft carbon oxide H2 and then this similar way the reaction the polymerization reactions happens and you will get the lower alkenes but here you will not get the high molar growth you will get like a small molecular weight the alkanes, octane, heptane, (())(23:41) like that and also to some extent some alpha olefin also you will get, fine.

(Refer Slide Time: 23:53)



Lab to Industry: Supported metallocene catalysts

Problems of homogenous catalyst

- Controlling polymer morphology with soluble catalysts
- Large amounts of MAO needed
- Activity at higher temperature
- Recovery of costly MAO is desirable but difficult

☐ Production facilitated by the heterogenization of the systems

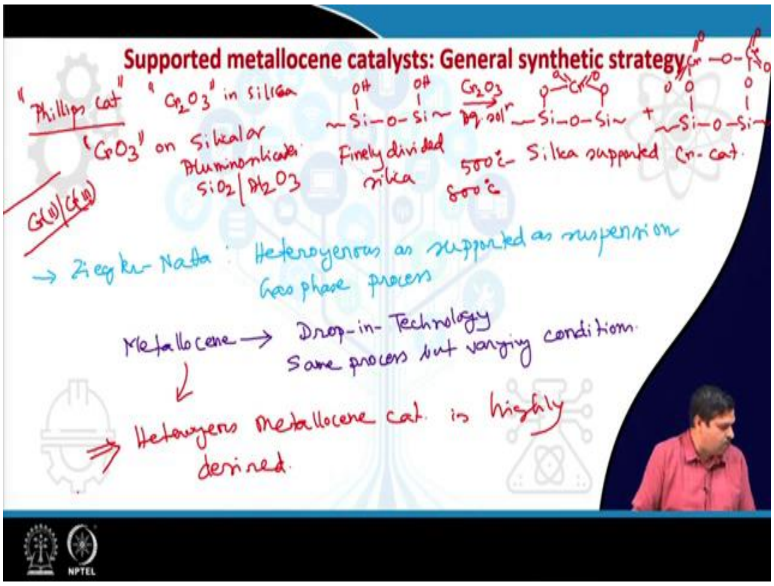
So, now we understood that there to make its industrial process, to make is a practical implications we have to transfer the homogeneous very active homogeneous catalyst to most practical heterogeneous catalyst, so obviously there is a strong relation between lab and industry so we have to make the active catalyst, we have to check it, we have to understand the mechanism then we have to transfer to the lab, so very close relation between lab to industry, academicians and industrialists, fine.

And how will do it and that I will discuss. And we now very familiar what is the advantage and disadvantage I am not going more detail but for the metallocene based catalyst some specific problems in homogeneous like controlling polymer morphology with soluble catalysts that is a very active catalyst sometimes it is difficult to control its reactivity large amounts of MAO needed.

That is another very disadvantage we have already discussed that sometimes the MAO has to be taken thousand times more or sometimes like 10 to the power 3 or 10 to the 4 times more compared to the actual metallocene catalysts. So, co initiator has to be taken in a large excess. Recovery of costly the MAO and the metallocenes is very difficult because the process is not simple.

So, obviously to make the cost effective, economic and industrial acceptance we have to transfer the our homogeneous active metallocene catalysts to the heterogeneous catalyst system, although there may be some sacrifice in the activity, in selectivity but overall it will be more economic in nature.

(Refer Slide Time: 27:08)



Supported metallocene catalysts: General synthetic strategy

"Phillips cat" "Cr_2O_3" in silica

'CrO_3' on Silica or Aluminosilicates SiO_2/Al_2O_3

Cr(II)/Cr(III)

Finely divided silica

500°C – 800°C

Silica supported Cr-cat.

→ Ziegler-Natta : Heterogeneous as supported as suspension Gas phase process

Metallocene → Drop-in-Technology Same process but varying condition.

⇒ Heterogeneous metallocene cat. is highly desired.

So, what we have to do it that is we will try to discuss now. What are the synthetic strategy? The synthetic strategy is or what are the basic issues we have to take care, that is we will try to discuss now here. But before that I just want to mention about some few points of the Philips type catalysts and we already discussed what is the Philip type, Phillips catalyst.

This is also used as for ethylene polymerization and this is basically the chromium based catalysts Cr 2O3 generally used in silica, in silica, fine. So, what is that? This is if you just consider this is a silica surface just a one unit of the silica, so if you react with Cr 2O3 you will get like this and also so it is very complicated, very difficult to, very difficult to know exactly what actual system it is.

And then this is oxide, this is oxide, fine. So, this will be not there, so here you will see that silica supported chromium catalyst and these are highly used so this is basically you see that Cr O3 on silica or aluminosilicates sometimes both can be done. And how it is prepared? It is prepared basically finely divided silica and this is the aqueous solution and when you heat it around 500 degree centigrade to 800 degree centigrade this is only for this one but the temperature will depend or the other condition will depend on your other, the other catalysts.

And you will get this one the as I told that the polymerization mechanism is different because is very complex both chromium 2 or chromium 3 can be involved so this not very well understood what are the actually mechanism but this I want to show tell that this is how a polymerization catalyst this is one of the oldest catalyst for ethylene polymerization that is the Phillips catalyst are converted for two heterogeneous from homogeneous.

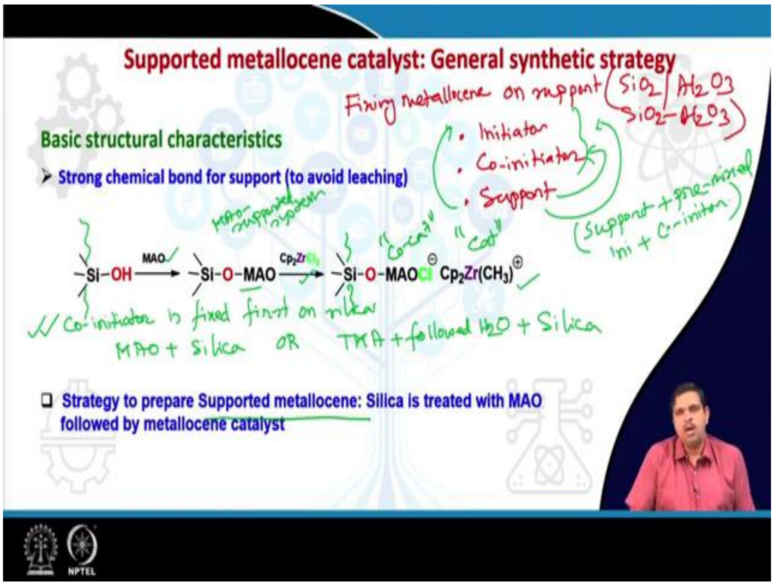
So, very similar approach from the previous knowledge we try to see that how can be done for the metallocene based catalysts. So, let us come to the our polymerization catalysts now we all know that Ziegler Natta is a heterogeneous catalyst and it is used as supported, as suspension or slurry in hydrocarbon liquids in polymerization reactor.

And this is the gas phase process, so the like ethylene gas is passed on this suspension and the polymerization happens. So, for the metallocene catalysts also the with the previous knowledge and the Ziegler Natta because Ziegler Natta was catalyst was very successful so metallocene, for metallocene also the similar approach can be done this is called a drop in technology, the industry people took it like a drop in technology.

Drop in technology means the same process we used to have a Ziegler Natta but we just vary the conditions, same process. So, it is basically the same process or same fundamental aspects but varying reaction conditions because your main active catalyst is different so we have to vary some temperature, the concentration, the stoichiometry.

So, and for that definitely the for that, that heterogeneous metallocene catalysts is highly desired to make it a industrial process because we will just follow the same process as we are successful Ziegler Natta in industrial process, so it is basically follow the concept of drop in technology with the metallocene catalysts as Ziegler Natta was the heterogeneous so we will also try to do make to, make transport the homogeneous metallocene to heterogeneous catalyst.

(Refer Slide Time: 33:43)



Supported metallocene catalyst: General synthetic strategy

Fixing metallocene on support (SiO_2 / Al_2O_3 $SiO_2-Al_2O_3$)

- Initiator
- Co-initiator
- Support

(Support + pre-mixed Ini + Co-initiator)

Basic structural characteristics

- Strong chemical bond for support (to avoid leaching)

MAO-supported system

$$-Si-OH \xrightarrow{MAO} -Si-O-MAO \xrightarrow{Cp_2ZrCl_2} -Si-O-\overset{\text{"Co-cat"}}{MAOCl^{\ominus}}\ \overset{\text{"Cat"}}{Cp_2Zr(CH_3)^{\oplus}}$$

Co-initiator is fixed first on silica

MAO + Silica OR TMA + followed H_2O + Silica

- ☐ Strategy to prepare Supported metallocene: Silica is treated with MAO followed by metallocene catalyst

Now, what how it can be done? What can be done? Basically the fixing metallocene on support, on support means either SiO2 or Al2O3 or maybe aluminosilicates both all these combinations can be done. And theoretically three ways can be done because see in our whole system what are there we have the initiator, we have the co initiator and we have the support, support means the silica or aluminosilicates.

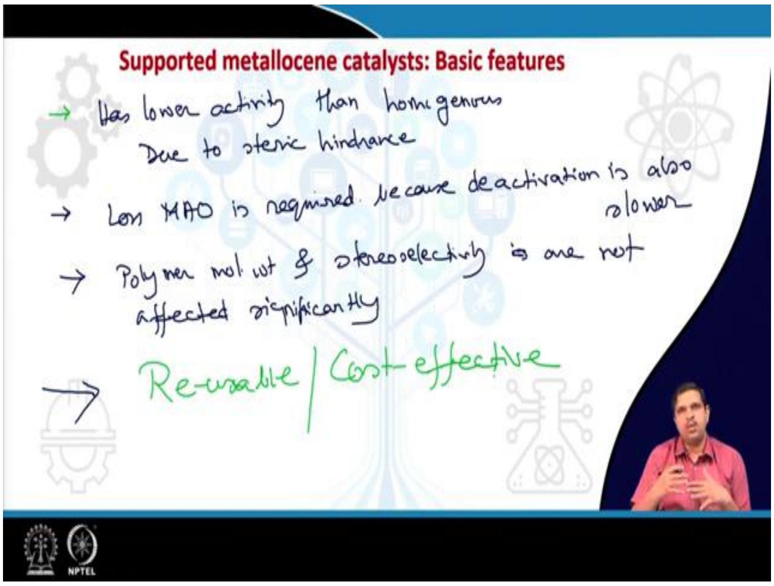
So, either you first react with support plus initiator or what I am trying to say that either this support with initiator, either support with co initiator or either you react to its support with the initiator and co initiator mixture, three ways possible. But the most successful are this one, what that co initiator is fixed cost on silica and how it can be done, it can be just reaction with MAO plus silica or trimethyl aluminum followed by the control amount of water and the silica.

So, this is the most I mean followed method by various industries. However, the other method that is the co-initiator support plus initiator cost eventually it will give the same or the support plus pre-mixed, pre-mixed initiator plus co initiator also can be done. So, here you see what is happening so this is basically your silica support and we are now reacting with MAO and you will see this is my MAO supported system.

And now you are putting charging the main catalyst and you will see that it will MAO minus, MAO CL minus Cp Zr plus so it is basically you will see that now your main catalyst that is the this is the catalyst and this is basically co catalyst this will be electrostatically interacted and it will be on the support of the silica, so these are the method generally we follow to make the homogeneous to heterogeneous.

So, here you will see this is the strategy to prepare supported metallocene silica is treated with MAO followed by metallocene catalyst that is the method we generally use and experimentally it has been observed that this is the best one with a minimum leaching and other advantageous issues.

(Refer Slide Time: 37:58)



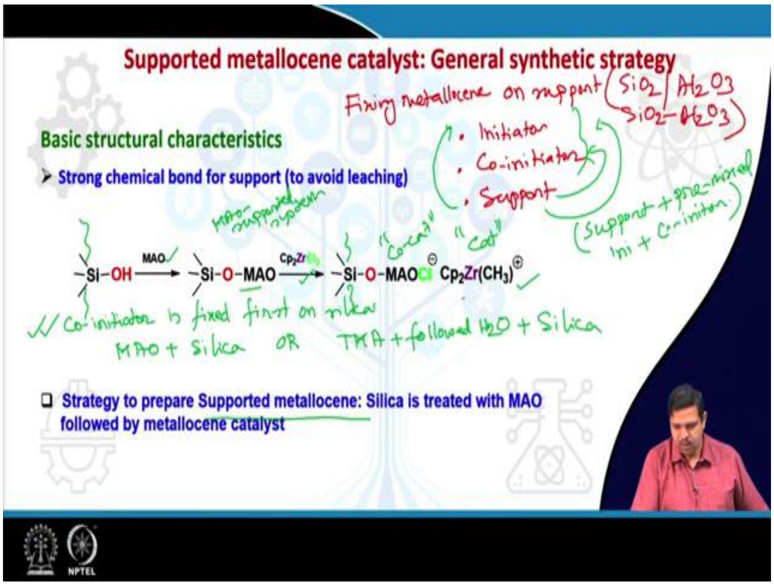
Supported metallocene catalysts: Basic features

→ Has lower activity than homogeneous
Due to steric hindrance

→ Less MAO is required because deactivation is also slower

→ Polymer mol wt & stereoselectivity is are not affected significantly

→ Re-usable | Cost-effective



Supported metallocene catalyst: General synthetic strategy

Fixing metallocene on support (SiO_2 | Al_2O_3 $SiO_2-Al_2O_3$)

- Initiator
- Co-initiator
- Support

(Support + pre-mixed Ini + Co-initiator)

Basic structural characteristics

- Strong chemical bond for support (to avoid leaching)

MAO-supported system

$$-Si-OH \xrightarrow{MAO} -Si-O-MAO \xrightarrow{Cp_2ZrCl_2} -Si-O-MAOCl^{\ominus}\ Cp_2Zr(CH_3)^{\oplus}$$

"Co-cat" "cat"

Co-initiator is fixed first on silica
MAO + Silica OR TMA + followed H_2O + Silica

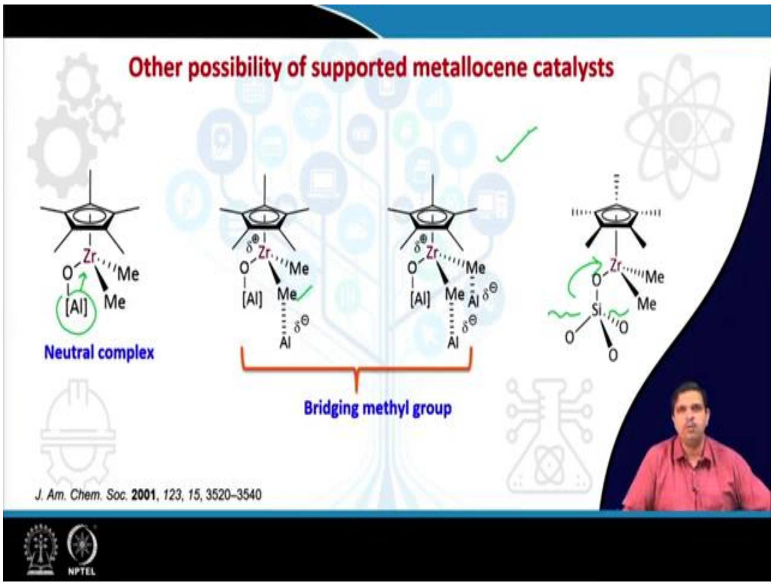
☐ Strategy to prepare Supported metallocene: Silica is treated with MAO followed by metallocene catalyst

So, some of the basic features you can tell that of this supported metallocene based catalysts we can I just list down that, has lower activity then homogeneous that is obvious because you are converting to homogeneous to heterogeneous, so you have to sacrifice some the activity and due to the, this is due to the steric hindrance, if you see the, this one so here you will see there is a silica means this is a polymeric network structure.

So you are putting lot of steric hindrance in the nearby the active catalyst surface and that is why you will say substrate cannot approach as easy as it is possible for the homogeneous system. So, this is sacrifice you have to do but here the good thing is that here less MAO is required and this is because deactivation process is also slower due to the steric hindrance, the deactivation is also slower due to the steric hindrance.

And polymer molecular weight and stereoselectivity is, are not affected significantly so that is good. And most important issue is that this is reusable and cost effective. So, you can use the different batch of the polymerizations in industries.

(Refer Slide Time: 40:45)



Other possibility of supported metallocene catalysts

Neutral complex

Bridging methyl group

J. Am. Chem. Soc. **2001**, *123*, *15*, 3520–3540

So, these are the other possibility of the supported metallocene catalyst that here we have I have shown one strategy here you can see that you can directly attach the metallocene those are more advanced although it is not, still it is not well accepted in industries we have to take we have to do some tuning and other method, standard is that we have to standardize the method.

So, these are the very nice strategy so these aluminosilicates or silicates you can attach to the metal center like that way this one or you can use the bridging methyl groups like this one or you can here you will see these silicates you can attach directly to the metal centers like that one so you can design our supported metallocene catalysts how and we can develop in new strategies to make the supported metallocene based catalyst.

So, these are some of the other strategies which are definitely as I told that is not still applied to the industrial synthesis but maybe in future.

(Refer Slide Time: 41:50)

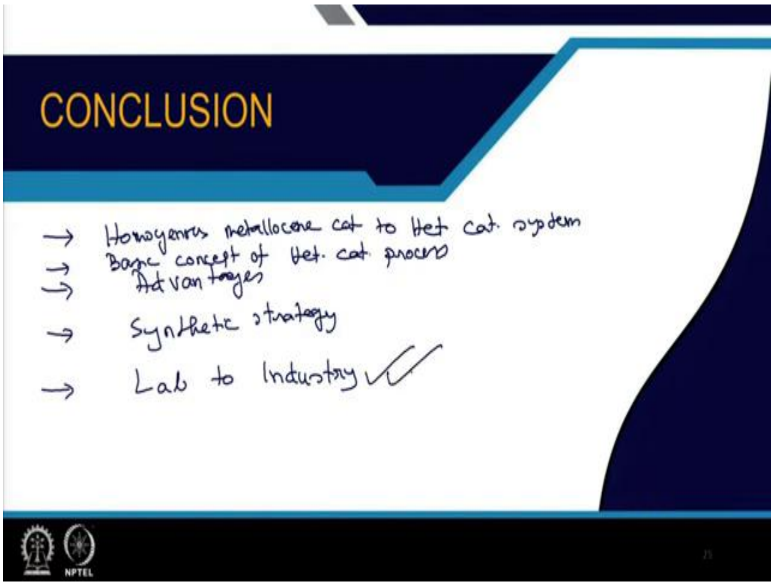
Challenges to overcome in future

- ☐ Maintaining the single-site characteristics of metallocenes upon heterogenization ✓
- ☐ Overcoming the significant drop in catalyst activity
- ☐ Preventing catalyst leaching ✓
- ☐ Eliminating separate feeding of MAO co-catalyst ✓

So, however, some of the challenge, though it is a cost effective but we have to sacrifice some of the points and still there is a challenge to overcome in future like prevent catalyst leaching. The maintaining the single site characteristic of metallocene upon heterogenation that is one for some cases or for some substrates.

This selectivity is a issue because we are hindering, so you are basically that surface the close the proximity of the metal center are hindered and that is why if it may be difficult to some of the monomers to approach to the metal center and that is why we have to sacrifice in issue of the activity and the selectivity. So, there is some challenge we have this, there is a steel scope to overcome and the research is going on in industry and also in academics.

(Refer Slide Time: 42:52)



CONCLUSION

→ Homogeneous metallocene cat to Het cat. system
→ Basic concept of Het. cat. process
→ Advantages
→ Synthetic strategy
→ Lab to Industry ✓✓

So, in conclusion today what we have learned, we have learned a very important issues or aspects of the metallocene based catalyst how to make the homogeneous metallocene and same thing can be approached for the non metallocene compounds also, homogeneous metallocene catalyst to heterogeneous catalytic system.

Advantage, synthetic strategy and obviously some basic concept of the, basic concept of heterogeneous catalyst because this is important otherwise knowledge will not be complete, heterogeneous catalytic process. And thus we now understood how one catalyst can be transformed from laboratory to industry. So, we now know the journey pathway the roadmap from lab to industry, this is very very important to make the process viable and industry useful.

(Refer Slide Time: 44:40)

REFERENCES

- Organotransition metal chemistry from bonding to catalysis by John Hartwig, University science books, 2010
- Principle of polymerisation by George Odian, Jhon Wiley & sons, 4th edition, 2004
- Organometallic Chemistry and Catalysys by Didier Astruc, Springer, 2007
- Polyolefins: 50 years after Ziegler and Natta II by Walter Kaminsky, Springer, 2013
- Basic Organometallic Chemistry by Gupta and Elias, University Press, 2010.

These are some of the references you can discuss, those are we have most of the our discussion we have taken from these references, except some are from some papers or we will that already we have cited in a respective slides.

So, with this thank you and in the next class we will be entering to a very interesting and well and very important aspect that is the depolymerization by the same catalysts and then we will enter to the field of metal carbene complexes for the polymerization synthesis. Thank you very much and see you in the next class.