Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts
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Lecture 29
Metallocene and Post-metallocene Catalyst: Homogeneous to Heterogeneous and Lab to Industry

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Welcome to our class Metallocene and Metal-carbene based catalysts for advanced poly olefin synthesis and so far we have discussed about the various metallocene and very advanced post metallocene catalysts mainly for homogeneous catalysis we have studied, we have understood the mechanism, we have understood the advantage over Zeigler-Natta catalyst, we have learned the monomers scope and to tune its properties.

Today, we will discuss some practical issues on the metallocene and post-metallocene catalyst actually in general will try to understand in general and then we will try to apply this concept to the metallocene post- metallocene catalyst for polymerization, why this is important because we know that 2 type of catalyst, one is the homogeneous and one is the heterogeneous. And both have advantage, both have disadvantage. Homogeneous the catalysts are very good in laboratory skills, their activity is very good, to understand the mechanism, that is the most important, that otherwise we cannot develop a new catalyst.

We have to understand, what is the mechanism for bond breaking, bond making? However, for heterogeneous catalyst the mechanism is complex but it is more practical on the issue of recyclability, because in homogeneous catalysis we it is very difficult to recycle the catalysts, but for heterogeneous it is easy to recycle the catalyst, so once we develop for homogeneous catalysis to make catalyst to make a valuable products or very important for very important synthesis to make it in industrial viable process, we have to convert this homogeneous to heterogeneous.

Why it is important? How it can be done and what are the strategies, that will be discussed along with some very important and industrially important some heterogeneous catalyst, we try to understand how does it work, and then we will try to apply to our the target systems that is metallocene and post metallocene.

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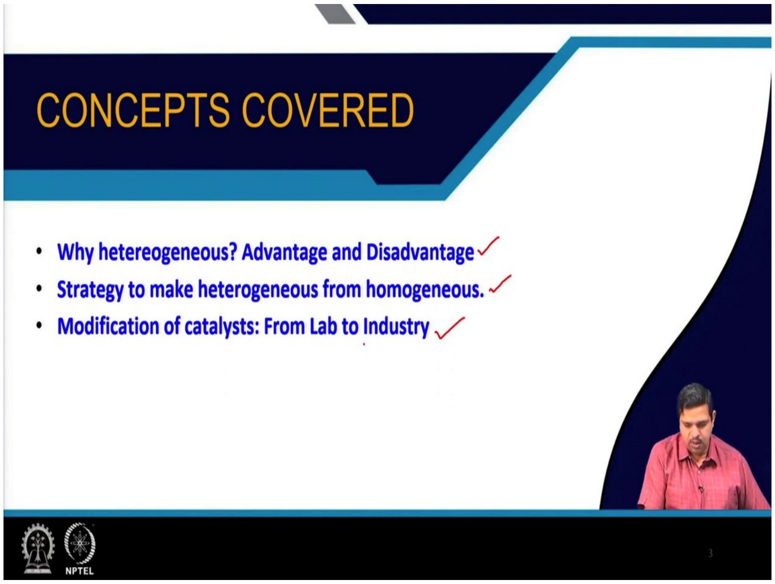

So let us try, start. So the concepts will cover that about the heterogeneous, what is the advantage, what is the disadvantage, strategy to make the heterogeneous from homogeneous catalyst system, and how to modify, and how to transform transfer the lab technology, lab to the industrial technology, that is very important. Because we if I want to synthesize in a bulk we have to consider the cost of the catalyst, otherwise the process will not be viable and not cost effective. So it is very much important for the, to make it successful industrial process.

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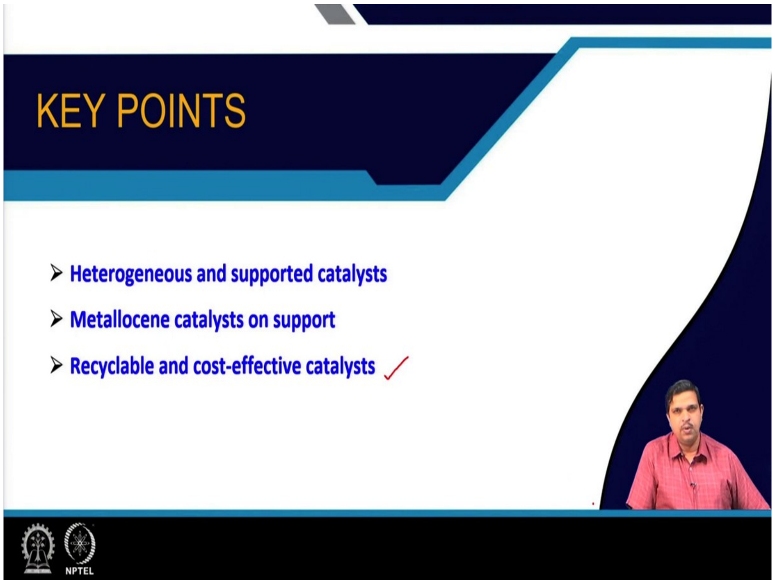

So key points will know the heterogeneous and supported catalysts and we will try to know that how it is recyclable, what is the advantage, what is the cost effectiveness, and how important it is, and also try to understand the mechanism, and try to understand the difference in mechanism between homogeneous and heterogeneous catalyst.

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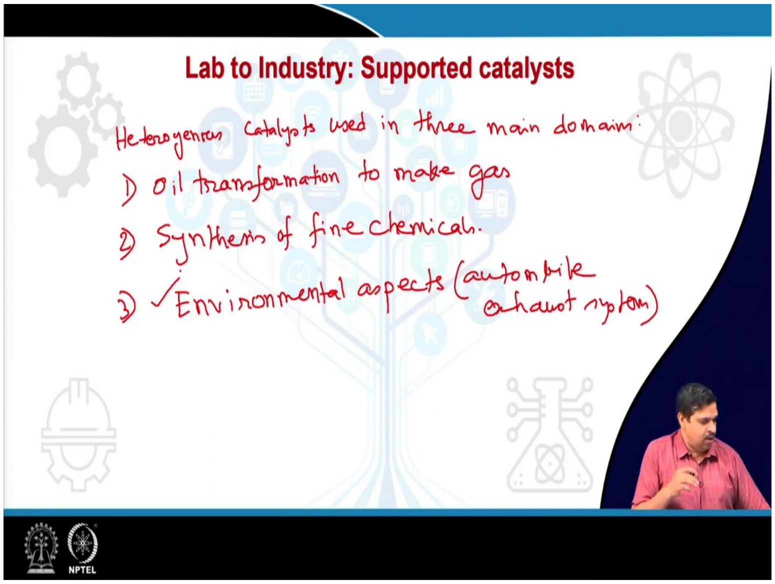

Now various process I am sure you have learned in your earlier courses or even some process are so in popular that some heterogeneous and supported catalysts which are industrially accepted from the last 5 decades or so are also in a textbook you have I, as example you know the synthesis of sulfuric acid by V205, all we know, the Haber process that is the synthesis of ammonia from Iron from nitrogen and hydrogen with the iron as a heterogeneous catalysts, those are very famous heterogeneous systems.

If you divide all the heterogeneous systems catalytic systems for industrial process you can divide into these applications into 3 domains. So I will divide the following way heterogeneous catalysts used in 3 main domains, I mean application domains, if you consider, if you know any heterogeneous catalysts and you think it you will see that those will fall at least one or two of these categories. As example one is the oil transformation to make gas, gas means which are valuable not only for fuels and also for to synthesize the value-added organic compounds and others.

Synthesis of fine chemicals and number 3 is the environmental aspects. If you recall, the environmental aspects I am sure all you know that every vehicle has the catalytic converter and this what is the function of this catalytic converter is basically to remove or to transfer the toxic gases produced for the incomplete compression of the fuels. I will discuss in more detail. So these are basically like for to solve the problem of the toxic gases in automobile exhaust system and also for others like for industrials to solve the problem industrial flue gases and other aspects of environmental concern.

So the supported catalyst the heterogeneous catalysts are very much used in our daily life as example you will see, here in the automobile thing, auto automobile applications and all the cards will should have a very efficient catalytic converter, otherwise that will not pass the quality check and that cannot be cannot run in the market.

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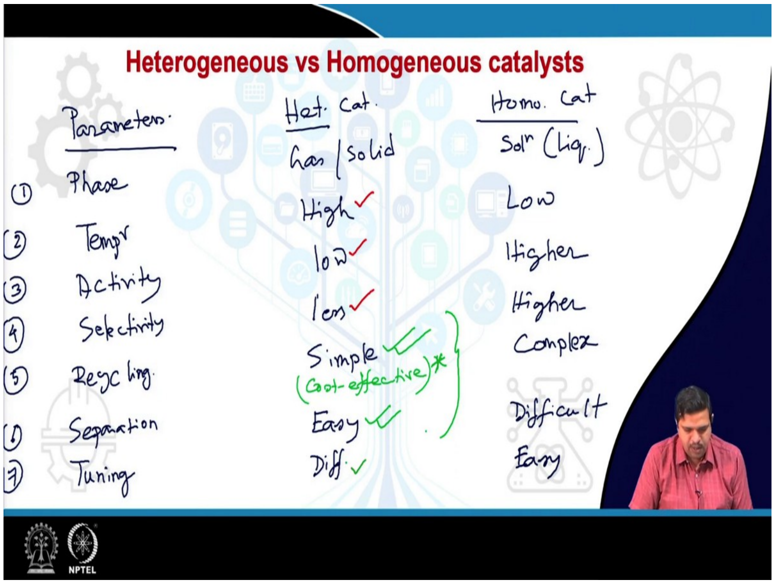

So these are I will discuss some of the very basic the difference between the homogeneous heterogeneous before coming to some of the examples of the heterogeneous system. This is very important to understand, that what is the basic difference in the between these 2 categories of catalysts. So let us you some pick some parameters or issues and here I am writing heterogeneous and heterogeneous catalysts and here I am just writing as a homogeneous catalyst.

So we will try to understand in a comparative style, so that it is easy to understand. So let us try first, the phase all we know that for heterogeneous, the phase will be not a single phase, generally it is gas or solid or sometimes liquid or solid. And homogeneous catalyst is mainly solution that means the liquid phase most of the cases like we do in our laboratory the normal reactions, we all use a solvent or sometimes we use neat that is the, that the substrate itself acts as a solvent.

Now temperature generally for the heterogeneous we need a high temperature and the homogeneous is generally low temperature but depending on the substrate depending on the bond energy, bond diffusion energy of the substrates and also depend on the catalytic systems. But generally heterogeneous catalyst needs higher temperature most of the cases. Activity, activity is for heterogeneous lower and for homogeneous is higher and reason is obvious because for the heterogeneous system the some sites are hindered so substrate cannot approach easily for the heterogeneous catalyst, because it is supported to some support material, I will discuss what is the supporting materials, so this is disadvantage of heterogeneous.

Selectivity, it is less and it is higher for selective device and for recycling is it is very simple and it is very complex for homogeneous catalysts and also this is due to the simplicity, this is cost effective and that is the biggest advantage for the heterogeneous catalysts.

And similarly this is very related to the fifth point, that is the separation. Again it is easy and for the homogeneous catalysis it is very difficult, because the phase is same, so it is very difficult to separate the catalyst after the reaction. So it is very difficult to reuse the catalyst again, so that is one of the very one of the very the biggest issue and the tuning of, tuning means tuning of catalytic properties. Here it is difficult and here it is comparatively easy.

So here you can see for from this, these are the many other points are there but here you will see for heterogeneous catalysts the temperature is generally higher activity is low selectivity is less and tuning is difficult but all the reverse you will see that here is very simple. Separation is very easy and most importantly it is cost effective. So this is basically is the winner, you can tell and that is the reason industry domain will always like heterogeneous rather than homogeneous.

Homogeneous is good to understand the mechanism but if you consider the cost effectiveness always heterogeneous catalyst is the winner. I hope it is very clear now.

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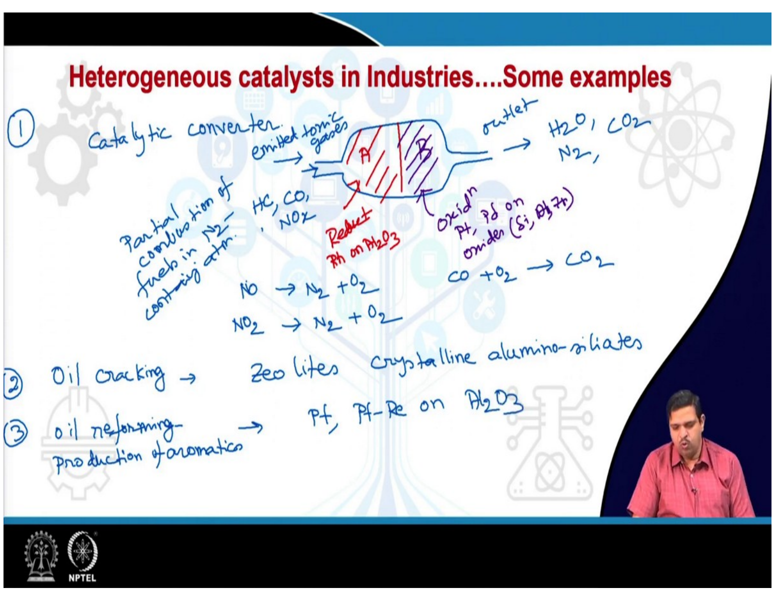

Now I will… So some of the very well known heterogeneous catalysts in which are popularly used and many industrial industries follow the process and most of the this heterogeneous catalyst catalytic catalyst process are being used let us say at least from the last 50 years or so till today. So let us list some of the very common heterogeneous catalyst before coming to our system to understand that why where we stand for. So as we I already discussed about the environmental aspects in just two three slides back.

So if you see that in the automobile exhaust catalytic converter I do not know how many of you have seen it, but it is actually like this one like a flat like that and this actually here the emitted toxic gas as example like hydrocarbon, carbon monoxide and the NOx maybe NO or maybe NO2 and this then convert to less toxic or non-toxic gases, as a as example the nitrogen, water, and carbon dioxide.

And here you will see that we use some catalyst chamber here, so this is basically nothing but a catalyst chamber. And generally it has a 2 parts, one is let us say part A and other one is the part B, 2 Chambers, let us say this is B. So this is basically the oxidation chamber and the A is the reduction chamber. So you we use the reduction some catalyst, 2 type of catalyst which are, which acts as a reducing agent reducing catalyst as example here like for the reduction rhodium on supporting materials like alumina and for oxidation is here like platinum or palladium on oxides.

So I am supporting oxides to make heterogeneous catalysts and generally these catalysts are kept you know like a plate to energy to increase the surface, so that the efficiency is more. So here what happens, 2 type of reactions are happens, in this case in the oxidation chamber. So like in their CO and plus O2 it is CO2 and in this case the reduction chamber NO and plus here, what happened the N2 plus O2 or NO2 and N2 plus O2 like that.

And how does it form that, so no or NO2 is basically the, this form due to the partial or incomplete combustion of fuels in nitrogen containing atmosphere, because we know that we have already around 78 percent nitrogen, so due to that one and those are in that NOx is sometimes called NOx, those are really toxic. So we have to remove or we have to convert this toxic to the non-toxic or less toxic gases.

So you see that these are one of the example which are used in and we are very familiar on that one, if you are more if you are very interested you can check in any car that there will be this kind of a flat, the chamber will be there, this is nothing but the catalytic converter and this is just before your final exhaust tube of the automobile.

So this is your outlet and this is the inlet from the engine combustion. So you will see that, this is how we use the heterogeneous system in our very common uses. Now for industrial we use the oil cracking huge use in petroleum industries and in this case we use a catalyst called geolights, this is also a very famous, and you have, am sure you have read this in even in school level, I mean you are familiar with this term and the geolights and also in our previous courses and this is nothing but a crystalline alumino silicates.

I will not go in detail about the structure, I just want to mention some of the very famous heterogeneous catalysts. Then the oil reforming and production of aromatic compounds valuated aromatic compounds and here we use platinum or platinum rhenium alloy on again the alumina Al203, we will discuss later how we make the supported catalysts.

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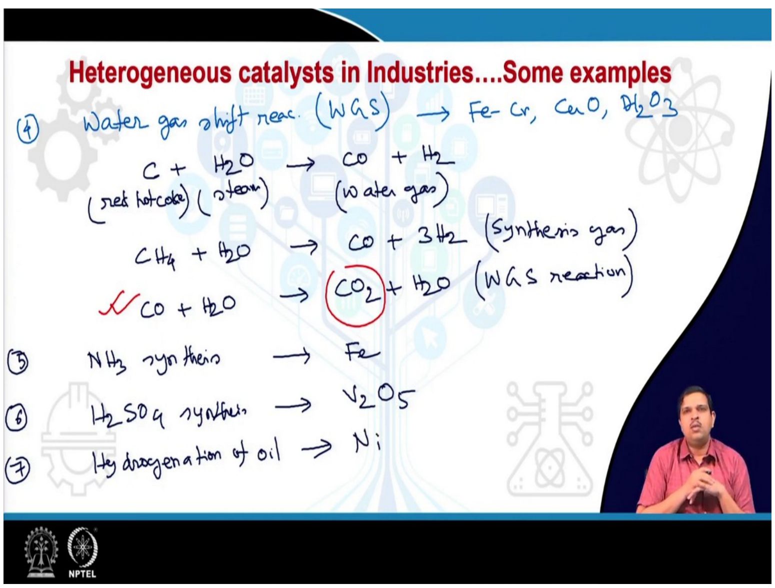

Now next one I will give a very famous example, all you have know the water gas shift reaction WGS. This is in nothing but to transfer the carbon monoxide to carbon dioxide and carbon dioxide is basically can act as a precursor compound for many evaluated organic compounds. What are the reactions? Water gas shift reaction, we call it WGS in short. And what catalyst we use, can you remember? This is iron chromium and support is the Al_2O_3 and if you recall these are one of the oldest heterogeneous catalysts which are accepted in industrial domain.

So what is that? This is here, so this is steam and this one red hot coke. So here you will see that all the cheap materials, the substrates are all are cheap and from here you can get carbon monoxide and hydrogen, this is called water gas, if you recall and then CH_4, and this one, so you will get more hydrogen CO plus $3H_2$, and this is called, can you remember, what is called this is synthesis gas, very popular synthesis gas, and from the produced carbon monoxide you will get the CO_2 plus H_2O and that is called the water gas shift reaction.

So these are very popular and very important as well so this one and you will get see the carbon monoxide here. This is used for various purposes to make the industry as well as the value added organic compounds. And the next one is the ammonia synthesis and you know how important in ammonia to not only to make the valuated nitrogen based compounds and also in fertilizers. And these are all you know because is a Nobel prize award-winning discovery, this is the iron and its Haber process, all we know.

The next is the H_2SO_4 synthesis, that also very famous and very well known and these are all the V205 vanadium oxide. And the next one hydrogenation of oil can you remember which catalyst, yes nickel, this is also very popular and still it is used.

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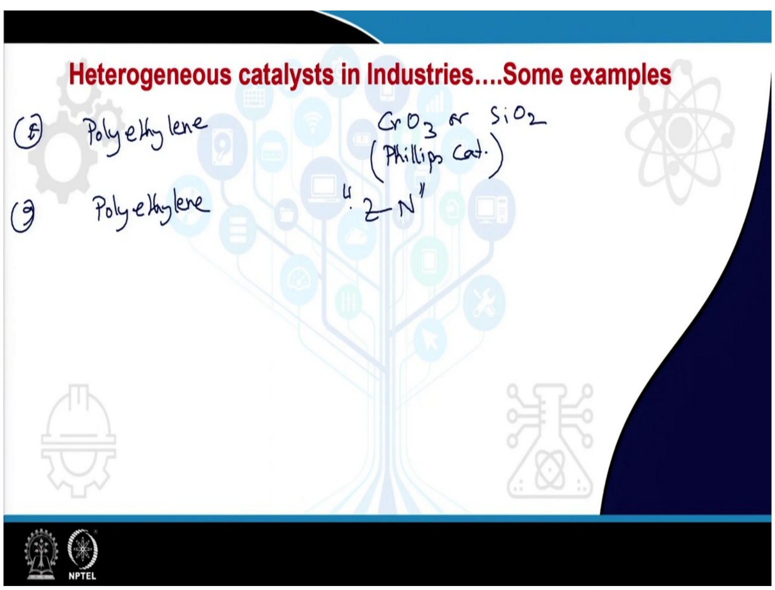

Now so and the last one I will show the polyethylene that and this is chromium oxide and on silica, it is if you remember this is nothing but Philips catalyst, I will discuss how does it work and how we can support this chromium oxide to the silica. So here you will see that this kind of are, obviously the another one in polymerisations, again the polyethylene is the Zeigler-Natta catalyst, so all we know now that Zeigler-Natta about the Zeigler-Natta, the how does it work, what is the advantage, what is the beauty of this Zeigler-Natta catalyst. So Zeigler-Natta catalyst is also heterogeneous catalysts for polyethylene synthesis.

So these are some examples, not a complete list, just to understand about the position of the heterogeneous catalyst in industries and in the real life applications, so it is actually used the catalyst.

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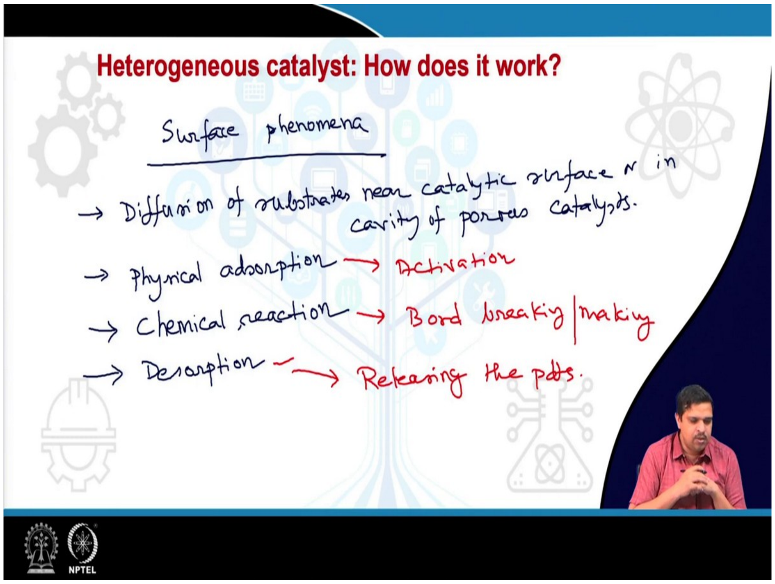

Now question is that, how does it work, heterogeneous catalyst. So we have or now we are we know that this heterogeneous catalyst are in a different phase mostly the gas solid or the liquid solid. So how does it work? There is a basic although the concept is same, that catalyst that we have already discussed about the catalysis, that how does it work. If you remember, in our previous classes we discussed that, what is a catalysis reaction, and what happens in presence of catalysts, the concept is same but however the mechanism and the bond breaking and bond making process are quite difficult for heterogeneous to homogeneous.

So that we will discuss in now. Now you will see that in heterogeneous catalysts this is actually the surface phenomena. So surface has a very big role on this heterogeneous catalysts. So first what happens, is first happens the diffusion of substrate near catalytic surface, mostly the metal oxides or the metal catalysts on a supporting oxide as example silicates or alumina or aluminum silicates or sometimes on polymer also sometimes for regime also near catalytic surface or in cavity of porous catalysts.

Now these are also very popular like for MOF, that metal organic framework which are porous in nature and also conjugated porous materials which are porous in nature and can perform selective catalysts which actually where the substrate actually enters in the cavity very similar as we have seen the in the geolites. In geolites also there is a different port size the one substance can enter and also the selectivity is also dictated according to the size of the pore and shape of the pore different selectivity we can get it as example for alkylation if generally for in geolites we get the linear alkenes or if you get a aromatic substituted aromatic we generally get the parasubstituted rather than meta or ortho. So this kind of selectivity is also possible for the porous catalyst systems.

Now next is, so first is the diffusion of substrates near the catalytic surface or in the cavity. Now next is the physical adsorption, and next step is the chemical reaction and the last one that is the desorption. If you recall that most of the cases, in like a homogeneous catalytic system the desorption is actually the reductive elimination or sometimes just a delegation. And here physical absorption is basically the activation step here. So this is the prime difference between the homogeneous and heterogeneous.

So here you will see, that this one the desorption is the last step and this physical adsorption this is basically, these are responsible for the activation. And this one is the bond breaking and making process. And this is basically the releasing, this is also bond breaking process, so releasing the desired products.

So in the next class we shall discuss continue our discussion on the heterogeneous catalyst and then we will try to understand how we can transfer or transform the metallocene based heterogeneous catalysts from homogeneous to heterogeneous for laboratory to industry journey. Thank you, we will see you in the next class.