Advanced Transition Metal Organometallic Chemistry

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Module - 11
Lecture - 54
Organometallic Catalysis Reactions: Fischer-Tropsch Mechanism

Welcome to this course on Advanced Transition Metal Organometallic Chemistry. We had been discussing an important topic which is C1 chemistry. It is a topic which deals with the industrial utility of carbon monoxides, particularly from the perspective of its reduction as well as oxidation. With regard to the oxidation of carbon monoxide we had earlier on spoken about water-gas-shift reaction which is nothing but oxidation of carbon monoxide to carbon dioxide in its reaction with water with the other product being the production of hydrogen.

So, it is the reaction of carbon monoxide and water producing carbon dioxide and hydrogen which is extremely important as a source of fuel and also for this Haber, Born-Haber synthesis for producing ammonia. So, that had been the case with regard to the oxidation of carbon monoxide which is a part of the C1 chemistry that we are talking about and has been discussed early as a part of water-gas-shift reaction.

Continuing further on this topic, we had discussed the complementary reduction of carbon monoxide reaction which is popularly known as Fischer-Tropsch synthesis which is mainly represented by the reduction of carbon monoxide with hydrogen to give alkanes and water. Now, the main, these reactions have been affected under heterogeneous catalysis conditions and one requires extremely harsh drastic conditions to perform these reactions.

In this context, we had discussed about new rhodium carbonyl complex which is homogeneous catalyst counterpart of Fischer-Tropsch synthesis. And which can carry out Fischer-Tropsch synthesis using hydrogen and carbon monoxide producing ethylene glycol. Now, in the earlier class we have also discussed about a possible pathway that involved the in this Fischer-Tropsch synthesis.

One of the main characteristic of Fischer-Tropsch synthesis is the fact that, this is a reaction which represents reduction of carbon monoxide to alkanes. However, the product selectivity of this Fischer-Tropsch synthesis is extremely low. And as a result, one not only produces alkanes, alkynes, but also one produces alcohols, glycols, ketones and so on and so forth. So, large array of product is produced under Fischer-Tropsch synthesis which not only, which simply indicates that Fischer-Tropsch synthesis is produced, a reaction is performed in multiple product pathways.

Now, keeping that in mind, we had discussed the mechanistic pathway that govern Fischer-Tropsch synthesis. And here we had seen, this pathway was a combined pathway for heterogeneous catalyst as well as for homogeneous catalyst. And we had seen that the reaction proceeds by activation of carbon monoxide through by coordination to the metal centre followed by reaction with hydrogen in 2, 3 different pathways leading to the formation of methanol, methane and the ketone type compounds.

Now, these multiple reaction pathways thus indicates how these different forms oxygenated alcohols, oxygenated alkanes or alkanes are produced. Now, the next the question about the pathway for Fischer-Tropsch synthesis offers is that, how does this alkane or methylene group so produced in the reduction of CO with H 2 polymerised to give rise to higher order alkanes.

So, this is a interesting question as to not only that hydrocarbons be formed, but then these hydrocarbons are sort of stitched to each other to produce higher order hydrocarbons. And that is crucial or an insight to that is crucial in proper understanding of the Fischer-Tropsch synthesis. So, then the next layer of mechanism thus points towards understanding how the polymerisation of methylene group occurs at the catalyst surface.

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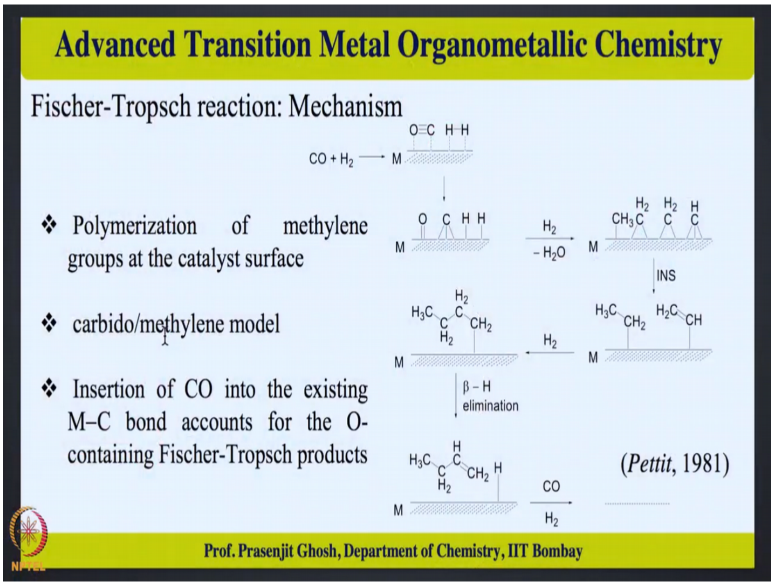

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Fischer-Tropsch reaction: Mechanism

- Polymerization of methylene groups at the catalyst surface
- carbido/methylene model
- Insertion of CO into the existing M–C bond accounts for the O-containing Fischer-Tropsch products

(*Pettit*, 1981)

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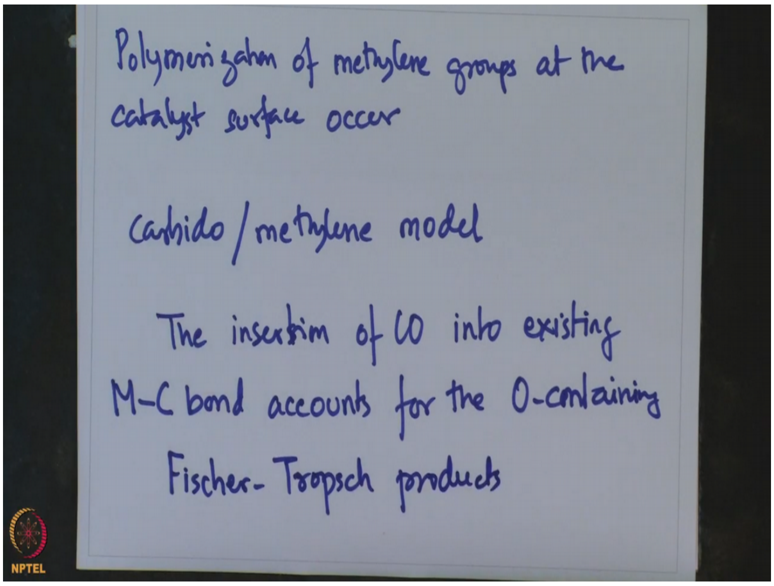

Polymerization of methylene groups at the catalyst surface occur

carbido / methylene model

The insertion of CO into existing M-C bond accounts for the O-containing Fischer-Tropsch products

And these polymerisation mechanism has been modelled on a metal heterogeneous metal surface. And that is popularly called as carbido or methylene model. And this also happens by insertion of CO into the existing metal carbonyl bond that accounts for the Fischer-Tropsch products, oxygen containing products. And this is illustrated by the following schematic representation this visual being shown over here. So, let us take a look at this methylene polymerisation of methylene at the catalyst surface using this carbido methylene model.

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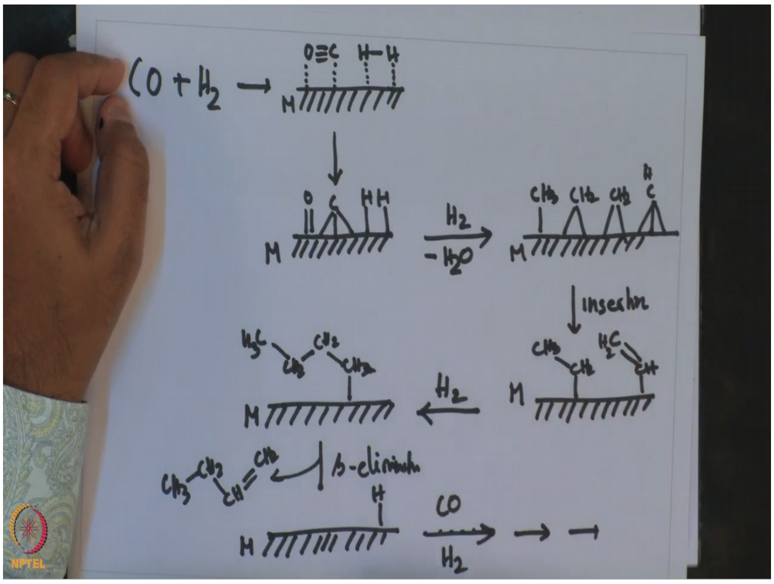

So, the reaction starts with CO + H 2 and the metal is given as M. And this is the metal surface. So, CO and H 2 binds to the metal. So, initial binding leads to the activation of CO. And as a result, the CO is split into metal oxide and metal carbido. Metal carbido which then reacts with hydrogen and eliminates water to give the metal methylene compounds, a variety of metal methylene compounds which can be written as methyl CH 3 methylene CH 2 another methylene CH 2 and C H.

So, that undergo insertion. This methyl into the CH 2 group to give this ethyl higher homologs of methylene or methyl. So, ethyl CH 2 CH 3 is obtained. And similarly, insertion of this to this gives this CH C H 2. That with hydrogen results with metal. Now, this in presence of hydrogen further inserts into this. And this polymerisation of methylene occurs. C H 3 CH 2 CH 2 CH 2; this undergoes beta elimination to give CH 3 CH 2 CH CH 2 and a metal hydride.

Now, this metal hydride then again undergoes CO and hydrogen insertion. And the reaction just proceeds the way. So, this is a beautiful model which sort of explains the polymerisation of the methylene group. And this is a step wise sequence that occurs first by adsorption of carbon monoxide and dihydrogen on the metal surface followed by the breakage of the carbon oxygen bond to give metal oxide, metal carbido and metal hydride bond sticking out on the surface.

The reaction with the hydrogen produces water which is eliminated or which leaves off the surface along with the generation of methyl methylene or C H moieties. Now, once they are formed they undergo insertion to give this resultant higher homologs like ethyl or vinyl moieties, which in presence of hydrogen undergoes further insertion to give butyl moieties which eventually will beta eliminate giving an olefin and a metal hydride.

And then the same sequence continues. So, this is a wonderful model which sort of explains the formation or polymerisation of methylene groups or the catalyst surface and sort of gives a provides a key insight as to how the reduction of carbon monoxide to methanes so formed can develop into higher alkanes through the course of this reaction. Now, the first example of these the reduction, experimental evidence for the reduction of coordinated carbon monoxide where hydrogen was provided by Barco in this beautiful example of this zirconium complex.

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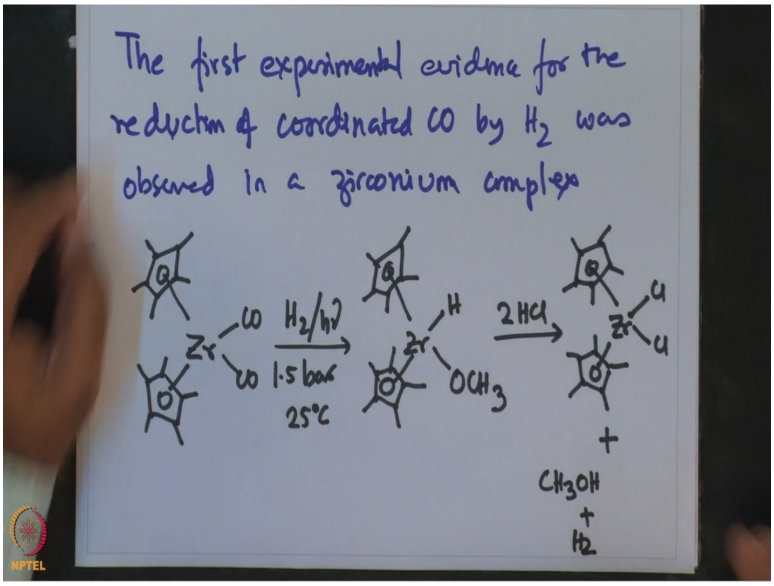

The first experimental evidence for the reduction of coordinated CO by H_2 was observed in a zirconium complex

The first experimental evidence for the reduction of coordinated CO by H 2 was observed in this zirconium complex, in a zirconium complex. And this is beautiful given by this reaction of bis pentamethyl CP, CO, CO under hydrogen and H nu at 1.5 bar pressure 25 degree centigrade, produces zirconium hydride and methoxide, with HCl produces. So, methanol + hydrogen and the zirconium dichloride complex, + methanol + hydrogen.

So, this is beautiful experiment or experimental demonstration of the reduction of coordinated CO by hydrogen resulting in the formation of zirconium hydride and zirconium methoxide which when treated with HCl gives zirconium dichloride, methanol and hydrogen. So, this as we see that this be (()) (18:10) correlation to that of the methylene polymerisation reaction model reaction that we had seen in the earlier slide.

Where we had seen that activation of carbon monoxide does indeed happen by coordination to the metal surface, followed by the reduction of hydrogen leading to the formation of methoxide moiety. So, this is a nice experimental evidence for the fact of reduction of coordinated carbonyl by hydrogen for this particular zirconium complex. Now, following up this another example that involves the formation of ethylene glycol was also reported.

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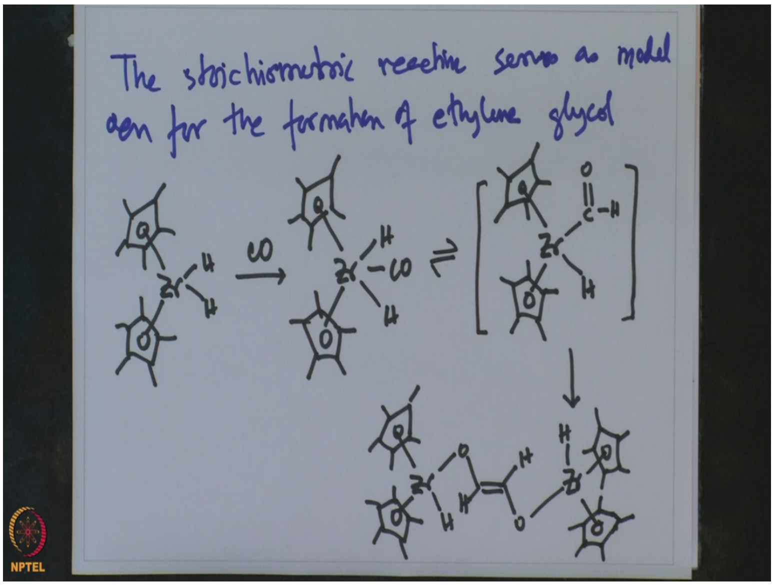

The stoichiometric reaction serves as model rxn for the formation of ethylene glycol

So, stoichiometric, the following stoichiometric reaction serve as a model reaction for the formation of ethylene glycol. So, this is another interesting example in a model example for homogeneous catalysis which serves as a model for the formation of ethylene glycol. So, this again is a bis CP star complex, dihydride complex of zirconium. This reacting with carbon monoxide giving zirconium dihydride carbonyl complex that sort of undergoes this CO insertion to give this zirconium formyl complex which sort of dimerises to give the glycol precursor, zirconium hydride.

So, this is a nice demonstration of the reaction that how the glycol can be formed in this course of Fischer-Tropsch synthesis. So, with this we come to conclusion of our discussion on Fischer-Tropsch reaction. And what we had observed is the fact that Fischer-Tropsch reaction is an important component of C1 chemistry. And that it affects the reduction of carbon monoxide to alkanes.

Now, what is important over here that this reduction of carbon monoxide to alkanes are important not only from the reduction, the ability to reduce the concentration of carbon monoxide, but also being able to productively use that carbon monoxide for producing fuels when alkanes are obtained. Now, one of the limitations of Fischer-Tropsch synthesis that we had observed is that, this reaction sort of produces a large number of products including alkanes, higher alkanes, alcohols, acetates, olefins and so on and so forth.

And as a result, the product selectivity is a weak component of, or is a weak factor for Fischer-Tropsch synthesis. Now, these another limitation to Fischer-Tropsch synthesis is the fact that it uses extremely drastic conditions and the reactions are performed under heterogeneous catalytic pathways. Now, on this front, what has been observed that by improving the catalyst to iron compound, that Fischer-Tropsch synthesis, some selectivity of the mixture of the product could be obtained, however that is not that quantitative.

Now, on moving from the heterogeneous system towards homogeneous system, the first breakthrough in this regard came for a rhodium carbonyl compound which could exclusively carried out carry out Fischer-Tropsch synthesis to produce ethylene glycol. Now, as far as this particular reaction which is an example, true example of homo, application of homogeneous catalysis, this rhodium carbonyl compound being able to produce ethylene glycol in Fischer-Tropsch synthesis.

The only limitation for this method was very high temperature and very high pressure was used. It was also noted that at lower pressure for the same reaction methanol was preferentially obtained as opposed to ethylene glycol which was obtained at higher pressure. A look at the mechanistic pathway for this Fischer-Tropsch synthesis for homogeneous as well as heterogeneous system involved activation of the carbon monoxide by coordination to the metal centre.

And subsequent reaction with hydrogen through multiple pathways that lead to the formation of alcohols, alkanes and other carbonyl CO inserted compounds. Now, another important key question that remained about the mechanism of Fischer-Tropsch pathway synthesis which produced by multiple pathways giving rise to multiple product; and that be the reason behind this low product selectivity.

So, the other important question was, how was higher homologs of alkanes obtained. And answer to that was given by another carbido methylene model which sort of explained the phenomenon of obtaining higher homologs of alkane by polymerisation mechanism of the methylene group that occur at the catalyst surface. So, another model which shows the, initially shows the formation of carbido methyl methylene groups on the metal surface followed by the polymerisation of the methylene groups leading to the higher homologs of the alkane was thus proposed to explain the higher homologs of alkanes that are obtained from Fischer-Tropsch synthesis method.

Now, as far as the mechanistic insights and the proposed metal are concerned, 2 main experimental evidence which support this CO reduction of the, of a hydrogen reduction of a coordinated CO was obtained by Barco when a bis cyclop CP star zirconium dicarbonyl compound when treated with hydrogen and light and subsequently by HCL, could undergo this CO reduction to produce methanol.

Similarly, another bis CP star zirconium dihydride complex in presence of CO gave the formation of dinuclear zirconium bridge bis CP star dihydride compound containing bridging glycol precursor. So, which sort of explained provided a model of formation of ethylene glycol through homogeneous catalysis in Fischer-Tropsch synthesis. So, with these, I would like to conclude our discussion on another important area of C1 chemistry which is the reduction of carbon monoxide as a part of Fischer-Tropsch synthesis.

In this, we had looked into the mechanism, how Fischer-Tropsch synthesis is affected and what are the experimental evidence and what is the state of our in terms of the development of Fischer-Tropsch synthesis. So, I would like to sincerely thank you for patiently listening to this lecture. And we are going to take up another interesting reaction in the next class which would be on carbonylation of alcohols.

This also is an important high throughput industrial process based on homogeneous catalysis. I sincerely thank you once again for being with me in this lecture. And I look forward to being with you in the next lecture. Till then goodbye and thank you.