

**Advanced Transition Metal Organometallic Chemistry**  
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**Module - 11**

**Lecture - 52**

**Organometallic Catalysis Reactions: Water-Gas-Shift Reaction**

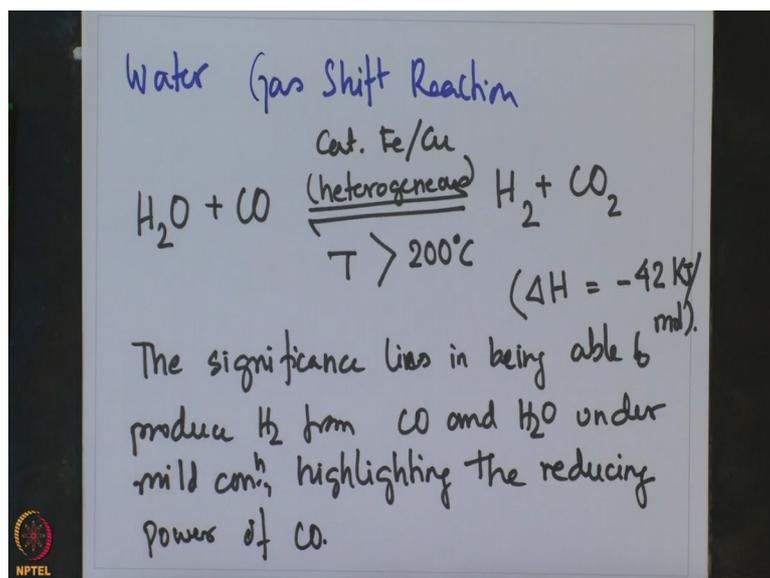
Welcome to this course on Advanced Transition Metal Organometallic Chemistry. As a part of our ongoing discussion on organometallic catalysis reaction, we had been looking at C1 chemistry particularly that of carbon monoxide utilisation chemistry from an industrial standpoint in the last 2 lectures. Now, what we had observed is that, though olefin oxidation reactions are important and are being used on an industrial scale.

For example, the Wacker oxidation of ethylene to acetaldehyde is being used in industry for more than a century now or that of Halcon/ARCO oxirane epoxidation reaction in which propylene is converted to propylene oxide in about 6 million tons a year, annually. There is a need to develop this CO utilisation chemistry, particularly this C1 chemistry which is more popularly known as.

Now, with respect to this, we have been talking about these 2 reactions: the water-gas-shift reaction and Fischer-Tropsch reaction. And what we have discussed is that the water-gas-shift reaction is a reaction that affects the oxidation of CO to CO<sub>2</sub>. Whereas the Fischer-Tropsch reaction affects the reduction of CO to hydrocarbons. So, in a way, both of these reactions are important and are a need of the day as the concentration of CO continues to grow in the environment and has become a global nuisance and hazard.

And there has to be remedial steps required to cut down on CO emission. So, from this perspective, this water-gas-shift reaction becomes important. In our past discussion, we have also looked at the various methods which contribute to the CO gas in synthesis gas.

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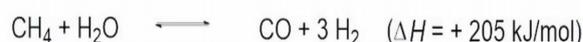


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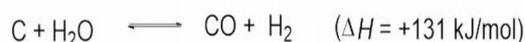
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#### Synthesis Gas: CO

- ❖ The CO can be obtained from
  - Controlled combustion of crude oil
  - Reforming of natural gases



#### Coal gasification



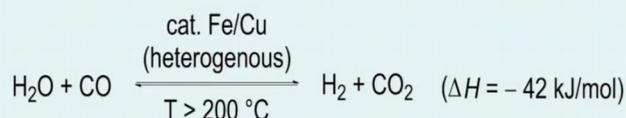
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And they are generally from 3 sources which are mainly controlled a combustion of crude oil or reforming of natural gas or coal gasification reaction. The controlled oxidation of crude oil gives the synthesis gas which is carbon monoxide and hydrogen and coal gasification also is the reaction of carbon with water to give CO and H<sub>2</sub>. And of course, the reforming of natural gas. Now, with this, we have discussed this to formation of synthesis gas. And then the, we will talk about this equilibrium in water-gas-shift reaction in bit more detail.

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### Water-Gas-Shift



- ❖ The significance of the equilibrium lies in
  - the exploitation of the reducing power of CO to produce H<sub>2</sub> from H<sub>2</sub>O under mild conditions
  - the removal of CO from the gas mixture for the Haber-Bosch process
  - H<sub>2</sub> enrichment of the synthesis gas for Fischer-Tropsch reactions



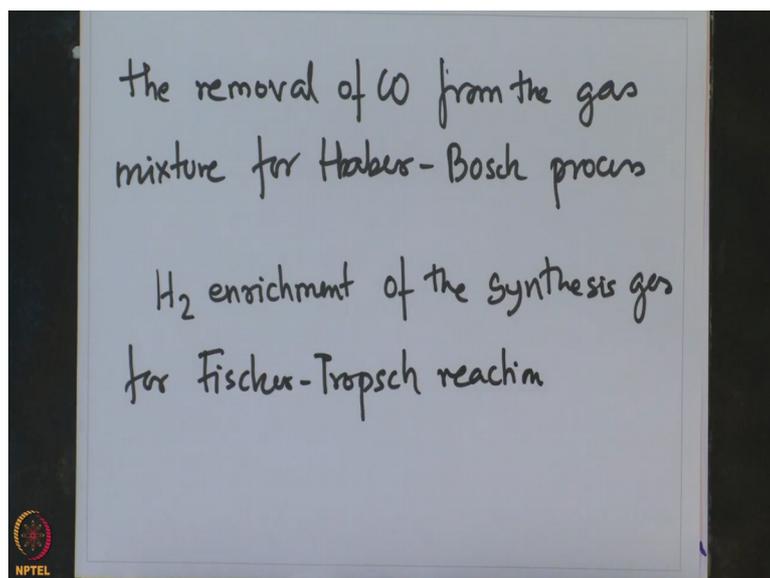
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The equilibrium in water-gas-shift reaction is the reaction of water with carbon monoxide in presence of heterogeneous catalyst of based on iron and copper that produces hydrogen and CO<sub>2</sub>. So, H<sub>2</sub>O + CO catalyst iron copper. These are heterogeneous catalyst at temperature > than 200 degree centigrade producing hydrogen + CO<sub>2</sub> delta H = - 42 kilojoule per mole. Now, the significance of this equilibrium lies in the fact that these are the, depending on where the equilibrium lies.

One can envision this reaction as carbon monoxide getting oxidised by stripping this oxygen from water and in turn producing carbon dioxide and hydrogen. So, significance of this reaction lies in exploitation of the reducing power of CO to produce hydrogen from water under mild condition. The significance lies in being able to produce H<sub>2</sub> from CO and H<sub>2</sub>O under mild condition, highlighting the reducing power of CO.

The removal of this process also has a significance because this allows removal of CO from the gas mixture of Haber-Bosch process which is used for making ammonia by reaction of hydrogen and nitrogen.

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So, also lies, the significance also lies in the removal from the mixture for Haber process. Hydrogen enrichment of the synthesis gas for Fischer-Tropsch reaction, synthesis gas for Fischer-Tropsch synthesis. So, this reaction is kind of very important because this using exploits the reducing power of CO, produces hydrogen under mild conditions and also removes CO from the gas mixture for the Haber-Bosch process and also leads to a hydrogen enrichment in the Fischer-Tropsch synthesis.

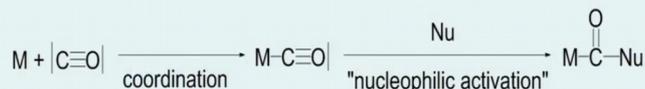
So, this is really a important reaction that exploits the reducing power of CO and itself CO gets oxidised to produce carbon dioxide and water gets reduced to hydrogen. So, this is an interesting reaction. Now current main challenges involves heterogeneous catalysis which involve high temperature is unfavourable for equilibrium for water-gas-shift reaction. And that sort of provides the impetus for carrying out the reaction under homogeneous conditions.

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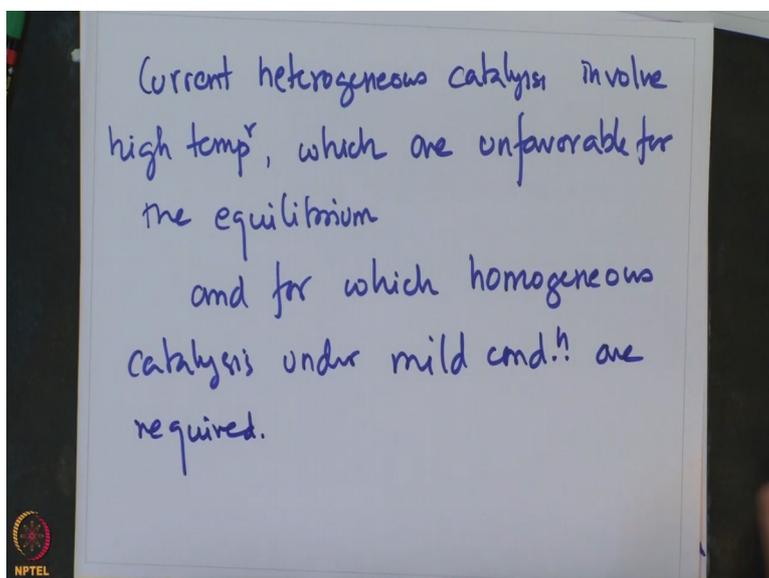
### Water-Gas-Shift: Homogeneous medium

- ❖ As the current heterogeneous catalysis involve high reaction temperatures which is unfavorable for the position of equilibrium for the water-gas-shift reaction, homogeneous developmental studies are underway
- ❖ The main target is the nucleophilic activation of CO which is done by the coordination of CO to a TM followed by the addition of nucleophile to the C atom



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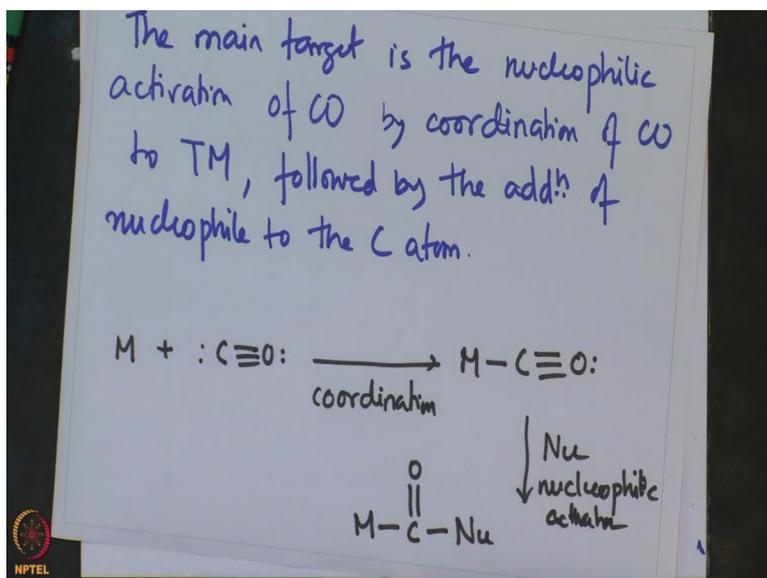
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So, current heterogeneous catalysts involve high temperature which are unfavourable for the position of equilibrium, for the equilibrium. And this is the reason why homogeneous catalyst which can do this reaction under more milder conditions are required. And for which homogeneous catalysis under mild conditions are required. Now, in this homogeneous conditions for mild conditions required.

Now, one would think that how would homogeneous catalyst be able to carry out this reaction under mild condition. And the main rational to that is that the main, the homogeneous catalysis the nucleophilic activation of CO may be performed by coordination of CO to the transition metal followed by addition of the nucleophile. So, this is an important strategy

which sort of would be used for carrying out this oxidation of CO 2 carbon dioxide. (Refer Slide Time: 11:45)



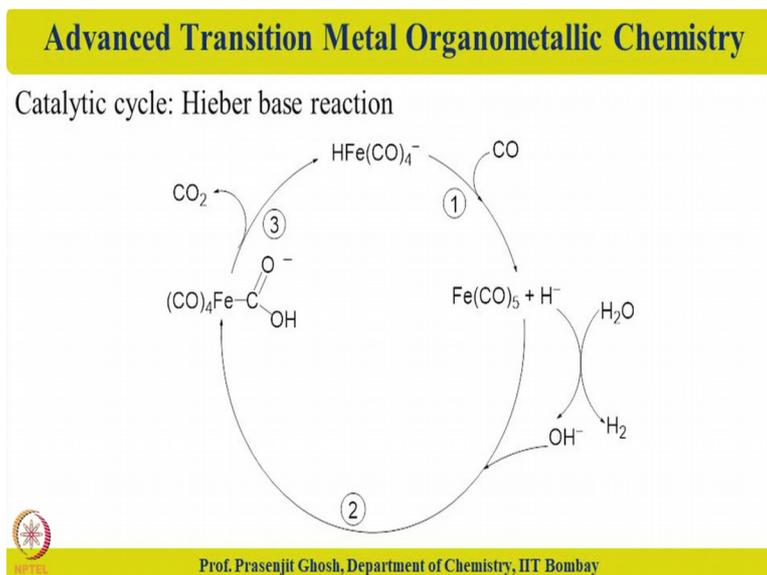
So, the strategy the main objective, main target in this front is the nucleophilic activation of CO by coordination of CO to transition metal followed by addition of nucleophile to the carbon atom. And this is simply represented by the schematic representation where metal + carbon dioxide monoxide forms the activation through coordination to give M CO. And then, the nucleophile acts on the carbon which this state is called nucleophilic activation to give M CO Nu.

So, homogeneous catalysis thus provides a very systematic approach of activating this carbon monoxide molecule by coordination of the carbon monoxide to the metal centre followed by the nucleophilic attack occurring at the carbon. Now, activation of substrate by coordination to transition metal is not new in homogeneous catalysis but on the other hand it is a very common step in homogeneous catalysis.

And we have observed this in many catalytic reactions, particularly with respect to olefin activation reactions where olefins get activated primarily by coordination to transition metal. So, similar strategy can be put in place for the CO activation, followed by nucleophilic attack on the carbon of the activated CO resulting in M CO nucleophile. And this is the strategy that is sort for achieving a milder conditions using homogeneous catalysis for this water-gas-shift reaction in which CO can react with water to produce hydrogen and carbon dioxide.

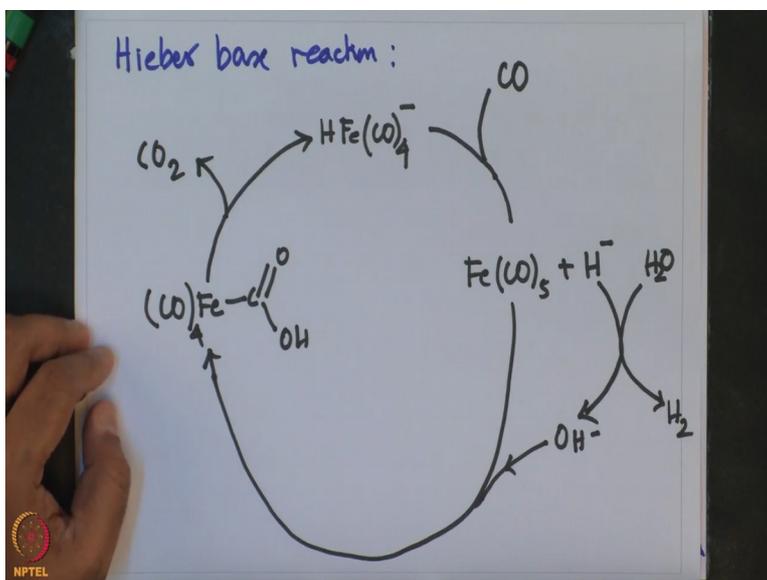
So, this; and this activation of CO by coordination can be so effective that even weak nucleophiles like water can undergo reaction.

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So, and this is explained by, the reaction is explained in Hieber's base reaction given by 2 catalytic cycles.

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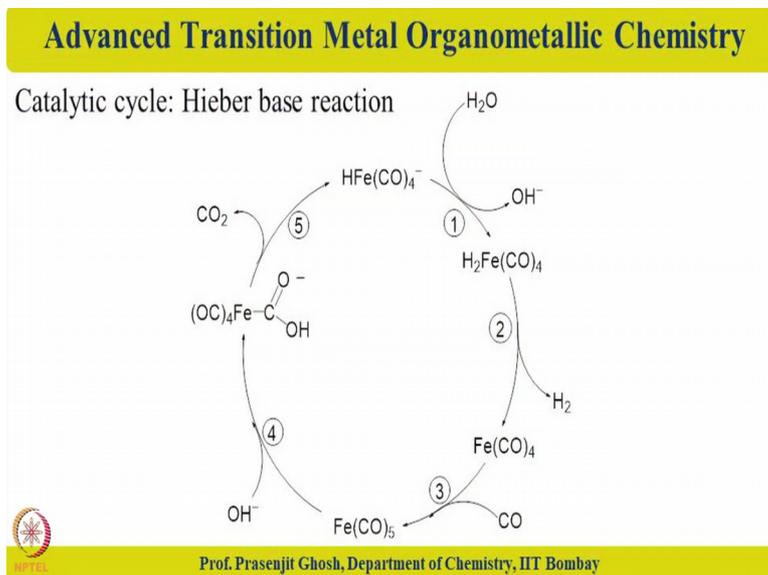
Hieber base reaction which is given by 2 catalytic cycles where even water can be used weak nucleophile can water can be used to attract the carbon monoxide coordinated metal oxide. So, the reaction starts with a metallate. For example,  $\text{HFeCO}_4^-$  – first obviously is the reaction with CO giving  $\text{FeCO}_5 + \text{H}^-$ . Now this carbon monoxide gets coordinated to iron giving a  $\text{CO}_5$  and the hydride leaves this  $\text{H}^-$ , then reacts with water to give dihydrogen  $\text{H}_2$ .

And this water gets deprotonated by  $\text{H}^-$  to get  $\text{OH}^-$ . It is a beautiful chemistry in the offing. And this  $\text{OH}^-$  then attacks this CO coordinated to transition metal a wonderful example in which by using a metallate anion water is activated by deprotonation of water with the iron hydride generating  $\text{H}_2$  and  $\text{OH}^-$ . Now, this  $\text{OH}^-$  attacks the coordinated carbonyl to give  $\text{Fe}(\text{CO})_4$ .

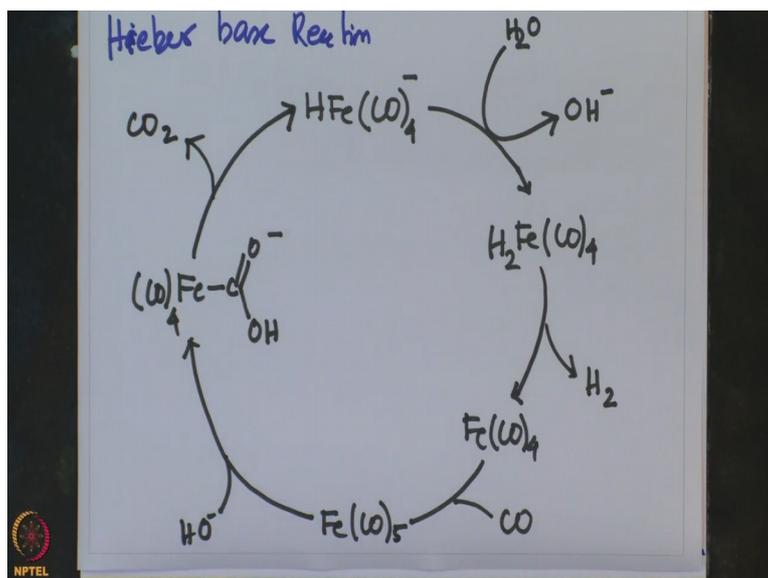
And  $\text{Fe}(\text{CO})_4$  would then decarboxylate to give  $\text{CO}_2$  and along with the regeneration of  $\text{Fe}(\text{HCO})_4^-$ . So, wonderful chemistry in which this catalytic cycle is based on. And this adopts the principle that the CO gets activated by coordination to iron. And then the nucleophile which is  $\text{OH}^-$  generated from this metallate anion consisting of hydride. This metallate anion then attacks to convert into an acid.

And then subsequently the acid decarboxylates giving out carbon dioxide along with this generation of iron hydride tetra carbonyl anion. So, this is a wonderful example for this Hieber base catalytic cycle. There is another similar Hieber base catalytic cycle which has been proposed. And we are going to sort of look at this catalytic pathway as well.

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Hieber base reaction, this reaction also starts with this iron hydride tetra carbonyl anion. The reaction of water giving  $\text{OH}^-$ . So, this  $\text{OH}^-$  and then as a result  $\text{H}^+$  is generated. So, this water sort of gets deprotonated by this iron hydride tetra carbonyl anion resulting in iron dihydrogen tetra carbonyl complex. So, this is an elegant chemistry in place can be same for both of the catalytic cycles.

So, here what we see that this iron hydride tetra carbonyl anion deprotonating water to generate  $\text{OH}^-$  along with formation of a dihydrogen dihydride iron tetra carbonyl compound which even loses this dihydrogen molecule by reductive elimination to give iron tetra carbonyl. And that now reacts with carbon monoxide to form the Fe carbonyl coordinated  $\text{Fe}(\text{CO})_5$ .

So, once this  $\text{Fe}(\text{CO})_5$  so formed reacts with  $\text{OH}^-$  which has been released in the first step. And this  $\text{OH}^-$  then attacks to the carbonyl moiety bound coordinate to iron as was the suggested scheme of activation. So,  $\text{OH}^-$  then attacks one of the coordinate carbonyls to give  $\text{Fe}(\text{CO})_4\text{OH}$ . And then, that similar to what we had discussed earlier, decarboxylates giving  $\text{CO}_2$  and  $\text{HFe}(\text{CO})_4^-$ .

So, what one sees that this is a wonderful chemistry in which the reaction of carbon monoxide with water leads to the formation of carbon dioxide and hydrogen; carbon dioxide and hydrogen as have been desired under mild condition using a homogeneous catalytic pathway. So, this is a wonderful demonstration of the fact that how people on going from

heterogeneous catalytic pathway which also used this conversion of  $\text{H}_2\text{O} + \text{CO}$  giving  $\text{H}_2 + \text{CO}_2$ .

But it requires temperature at over 200 degree centigrade very harsh condition. Such a condition can be reduced by proper choice of catalyst, homogeneous catalyst in which in this case is hydride iron tetra carbonyl. And then, it just simply converts this hydroxide water to hydroxide nucleophile along with regeneration of  $\text{H}_2$  and formation of carbon dioxide in a catalytic fashion and bring down the difficulty in performing this reaction.

So, this is a 2 wonderful examples of homogeneous catalysis that have been used to carry out water-gas-shift reaction. So, metal carbonyls in general catalyze homogeneous reactions in basic medium. So, one can see the reason for medium to be basic because you know, one has to deprotonate this water and generate this OH nucleophile.

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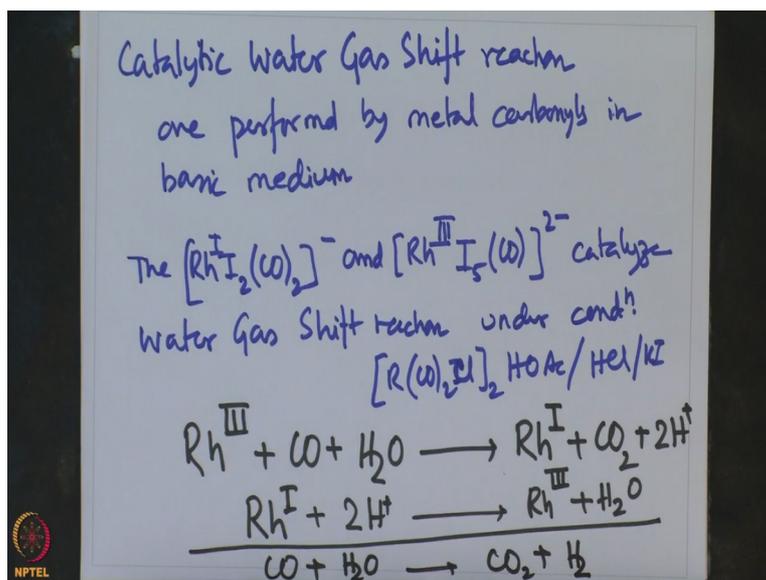
Catalytic Water-Gas-Shift

- ❖ The metal carbonyls in general catalyze the Water-Gas-Shift reaction in basic medium
- ❖ The species  $[\text{Rh}^{\text{I}}_2(\text{CO})_2]^-$  and  $[\text{Rh}^{\text{III}}\text{I}_5(\text{CO})]^{2-}$  are also able to catalyze the Water-Gas-Shift reaction which is present in  $[\text{Rh}(\text{CO})_2\text{Cl}]_2/\text{HOAc}/\text{HCl}/\text{KI}$  system

$$\begin{array}{l} \text{Rh}^{\text{III}} + \text{CO} + \text{H}_2\text{O} \longrightarrow \text{Rh}^{\text{I}} + \text{CO}_2 + 2\text{H}^+ \\ \text{Rh}^{\text{I}} + 2\text{H}^+ \longrightarrow \text{Rh}^{\text{III}} + \text{H}_2 \\ \hline \text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2 \end{array}$$

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So, catalytic water-gas-shift reaction are performed by metal carbonyls in basic medium. There are apart from iron species the rhodium species of the type rhodium ido carbon CO carbon carbonyls also able to catalyse water-gas-shift reaction and the equation is given as below. The rhodium I 2 CO whole 2 – and this is + 1 oxygen state and rhodium 3 I 5 CO 2 – catalyse water-gas-shift reaction which is present under conditions of R rhodium dicarbonyl chloride dimer HO acetic acid HCL and KI.

The reaction is given as follows. Rhodium 3 + CO + H 2 O giving rhodium 1 + CO 2 + 2 H +. And rhodium 1 + 2 H + giving rhodium 3 + H 2. So, the overall net reaction can be written as CO + H 2 O giving CO 2 + H 2. So, with this, I would like to conclude this today's discussion on water-gas-shift reaction. And what we have discussed in today's reaction is that this water-gas-shift reaction which is very important, particularly with respect to utilisation of carbon monoxide.

And this can be achieved by reaction of carbon monoxide with water and this produces carbon dioxide and hydrogen. And this reaction is affected by transition metals with catalysts like iron and these reactions are carried out under heterogenous conditions that they require very high temperature of above 200 degree centigrade which sort of shifts the equilibria of water-gas-shift reaction in unfavourable way.

And because of which more milder approach consisting of homogeneous catalysis are required. And from the strategy that has been used for carrying out this reaction under homogeneous catalytic condition is the utilisation of the fact that, this carbon monoxide can

be activated by coordination to transition metal followed by nucleophilic attack at the carbon on the transition metal.

Now, substrate activation by coordination to transition metal is not a new concept in homogeneous catalysis. And most of the catalytic reactions do proceed by getting activated through coordination to transition metal. Indeed, the metal carbonyls under basic conditions like iron carbonyl tetracarbonyl hydride anion in presence of water do carry out this water-gas-shift reaction under catalytic fashion in which it uses water and carbon monoxide and produces carbon dioxide and hydrogen.

Not only; and there has been 2 catalytic cycles that have been proposed for this transformation. The iron apart, rhodium carbonyls also catalyse this water-gas-shift reaction and the, in a 2 step process, the first step involves the reaction of rhodium 3 with carbon monoxide and water giving rhodium 1 and carbon dioxide and twice  $H^+$ . And the subsequent step involve rhodium 1 with  $H^+$  giving rhodium 3 and  $H_2$ .

So, overall, this rhodium 1 and rhodium 1 cancels out. And rhodium 3 and rhodium 3 cancels out. The net reaction which comes out of it is that  $CO + H_2$  giving  $CO_2 + H_2$ . So, this is exactly what is expected of the product for water-gas-shift reaction. And that can be achieved in a homogeneous catalytic fashion under mild condition. So, with this, I would like to conclude today's discussion on water-gas-shift reaction and then take up this topic in bit more detail in the subsequent lecture in where we will also look at the other aspect of the C1 chemistry which involves reduction of carbon monoxide to hydrocarbons as a part of Fischer-Tropsch synthesis.

So, I once again thank you for patiently listening to me in this lecture and I look forward to take up this Fischer-Tropsch synthesis in bit more detail and also continue on the water-gas-shift reaction. Some aspect of it still remains to be discussed in the next lecture. Till then, goodbye and thank you.