Advanced Transition Metal Organometallic Chemistry
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Module - 11
Lecture - 53
Organometallic Catalysis Reactions: Fischer-Tropsch Synthesis

Welcome to this course on Advanced Transition Metal Organometallic Chemistry. Over the last few lectures we had been discussing industrial application of a important compound and this is that of carbon monoxide. And which popularly is known as C1 chemistry. Now, in this context we have discussed a reaction which is called water-gas-shift reaction. This reaction exploits the reductive power of carbon monoxide in terms of abstracting oxygen from water and then generating carbon dioxide and hydrogen.

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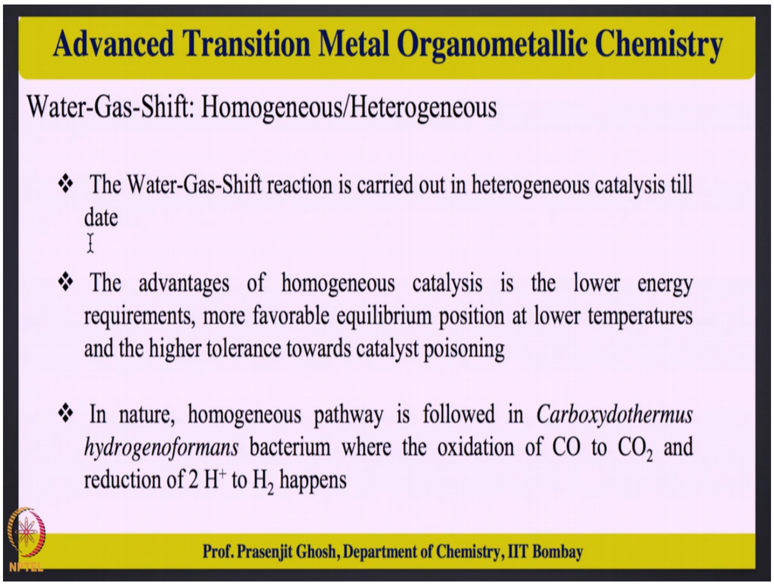

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Water-Gas-Shift: Homogeneous/Heterogeneous

- The Water-Gas-Shift reaction is carried out in heterogeneous catalysis till date
- The advantages of homogeneous catalysis is the lower energy requirements, more favorable equilibrium position at lower temperatures and the higher tolerance towards catalyst poisoning
- In nature, homogeneous pathway is followed in *Carboxydothermus hydrogenoformans* bacterium where the oxidation of CO to CO_2 and reduction of 2 H^+ to H_2 happens

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So, this is a reaction which is extremely important with, in industrial, from a industrial perspective. Particularly, not only with respect to removal of CO or conversion of CO, but also with respect to generation of hydrogen which is a important component for fuel. And these are done from a synthetic gas which is a mixture of carbon monoxide and hydrogen. Now, in the last lecture we have looked into water-gas-shift reaction in detail.

And what we had observed that this water-gas-shift reaction is mainly carried out using homogeneous catalysts because it requires extremely harsh reaction conditions. Now, one of the fallout of this reaction being carried out under heterogeneous catalysis condition is the fact that this equilibrium is shifted on the side which is not favourable for the generation of hydrogen.

And so, more advantageous homogeneous catalysis pathway is thus needed to bring about more control in this water-gas-shift chemistry. So, in this regard, what we had observed is that metal carbonyl complexes under basic conditions do carry out this water-gas-shift reaction to generate carbon dioxide and hydrogen from water and carbon monoxide. And in this context, we have looked at iron carbonyl hydride complexes that carry out this transformation under homogeneous catalytic condition.

In the last class we had observed that rhodium carbonyl complexes rhodium 3 and rhodium 1 also successfully carry out this water-gas-shift reaction under homogeneous conditions. So, this water-gas-shift reaction however till date is being carried out in heterogeneous condition. But one of the reason which goes against it or disadvantage of it is the requirement of very harsh conditions.

Now, it is important to note that in nature, the homogeneous pathway is followed by a bacteria which is called carboxydothermus hydrogenoformans bacteria which can carry out the oxidation of carbon monoxide to dioxide and reduction of 2 protons to hydrogen.

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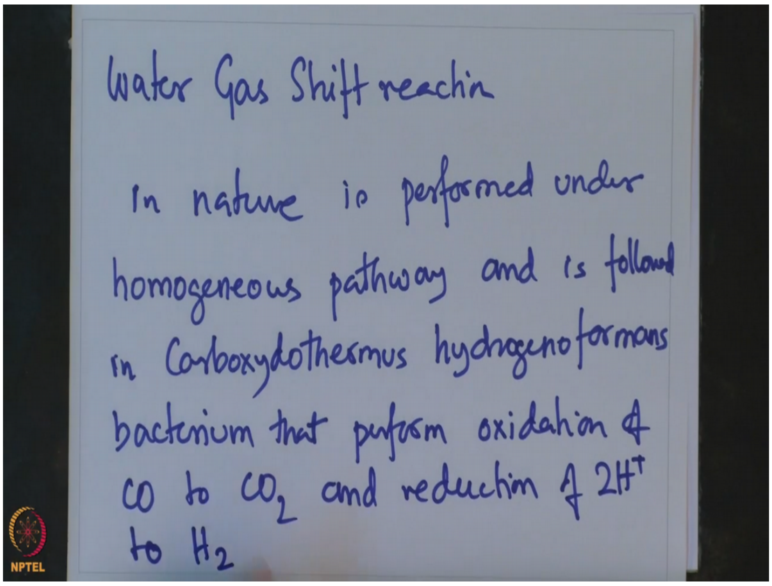

Water Gas Shift reaction

In nature is performed under homogeneous pathway and is followed in Carboxydothermus hydrogenoformans bacterium that perform oxidation of CO to CO_2 and reduction of $2H^+$ to H_2

So, this water-gas-shift reaction in nature is performed under homogeneous pathway and is followed in carboxydothermus hydrogenoformans bacterium that perform oxidation of CO to CO 2 and reduction of 2 H + to dihydrogen. So, what we see is that a more moderate homogeneous pathway is out there which nature uses in form of this bacterium that can carry out such reaction which at current point we require heterogeneous catalyst to perform the same conversion under very high drastic condition.

So, the immediate objective challenge in this area thus remains in achieving this water-gas-shift reaction under milder homogeneous catalytic conditions. So, with that, I would conclude our discussion on water-gas-shift reaction which involved oxidation of carbon monoxide to carbon dioxide and deduction of water to hydrogen. And then, look into another interesting reaction of C1 chemistry which is Fischer-Tropsch synthesis;

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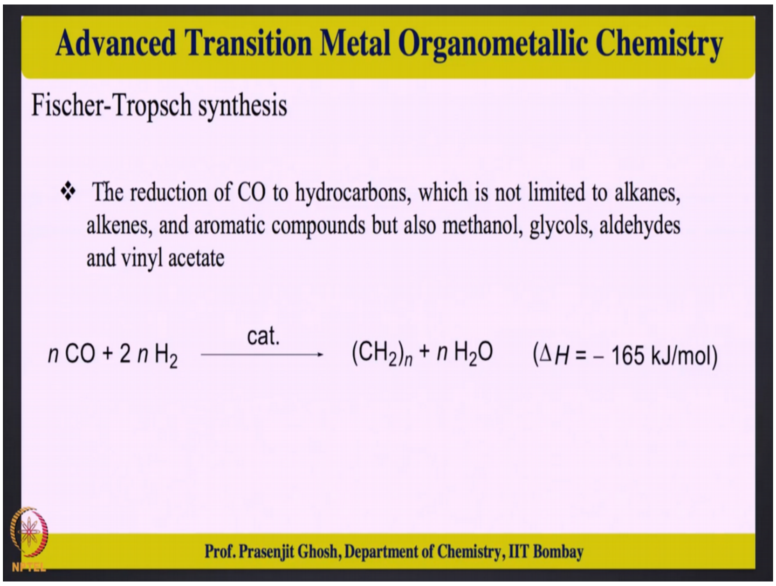

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Fischer-Tropsch synthesis

- The reduction of CO to hydrocarbons, which is not limited to alkanes, alkenes, and aromatic compounds but also methanol, glycols, aldehydes and vinyl acetate

$$n\,CO + 2n\,H_2 \xrightarrow{\text{cat.}} (CH_2)_n + n\,H_2O \quad (\Delta H = -165\ \text{kJ/mol})$$

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Which is about reduction of carbon monoxide to hydrocarbons and oxidation of hydrogen to water. So, these 2 reactions, this Fischer-Tropsch synthesis and water-gas-shift reactions are sort of complementary to each other in terms of exploring the redux domain in the sense that water-gas-shift reaction affects the oxidation of carbon monoxide to carbon dioxide while the Fischer-Tropsch synthesis affects the reduction of carbon monoxide to hydrogens. So, in the next portion of the reaction lecture, we are going to focus on Fischer-Tropsch synthesis.

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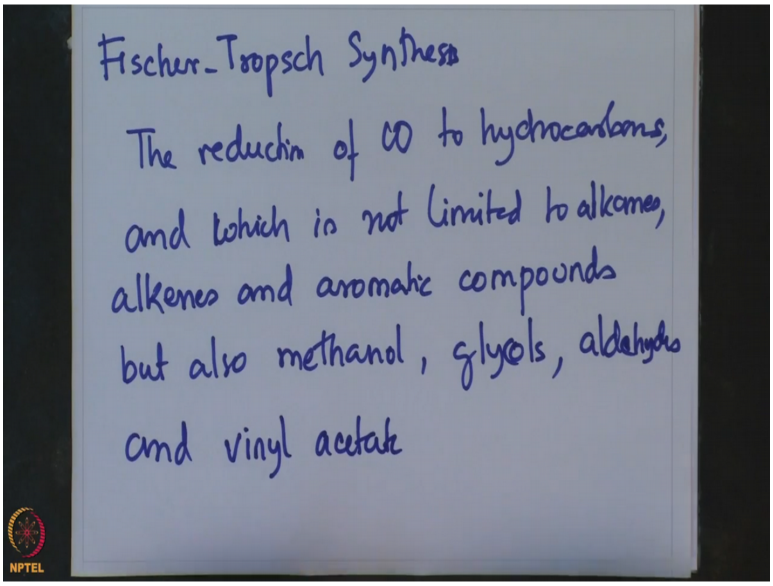

Fischer-Tropsch Synthesis

The reduction of CO to hydrocarbons, and which is not limited to alkanes, alkenes and aromatic compounds but also methanol, glycols, aldehydes and vinyl acetate

So, this is a reduction of carbon monoxide to hydrocarbons and in the process of doing that, the products or the array of products which this Fischer-Tropsch synthesis offer is a kind of a huge and the products are not just limited to alkanes alkenes or aromatic compounds but also leads to the formation of methanol, glycols, aldehyde and vinyl acetates. And which is not limited to alkanes, alkenes and aromatic compounds but also gives rise to methanol, glycol, aldehydes and vinyl acetates. So, this is illustrated by this equation which summarises the chemistry in Fischer-Tropsch synthesis in just 1 line.

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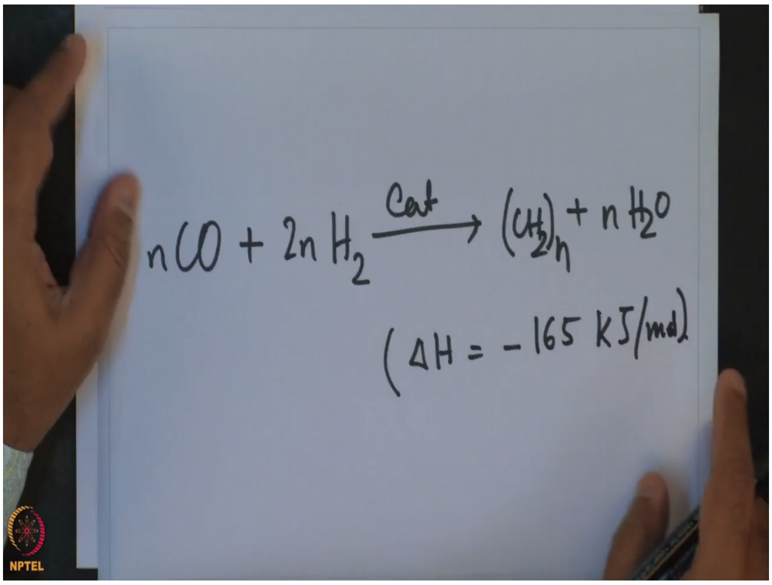

$$nCO + 2nH_2 \xrightarrow{Cat} (CH_2)_n + nH_2O$$

$$(\Delta H = -165\ kJ/mol)$$

And that is given by + 2 n H 2 in presence of a catalyst giving hydrocarbon CH 2 n + n H 2 O. And delta H for this reaction is – 165 kilojoule per mole.

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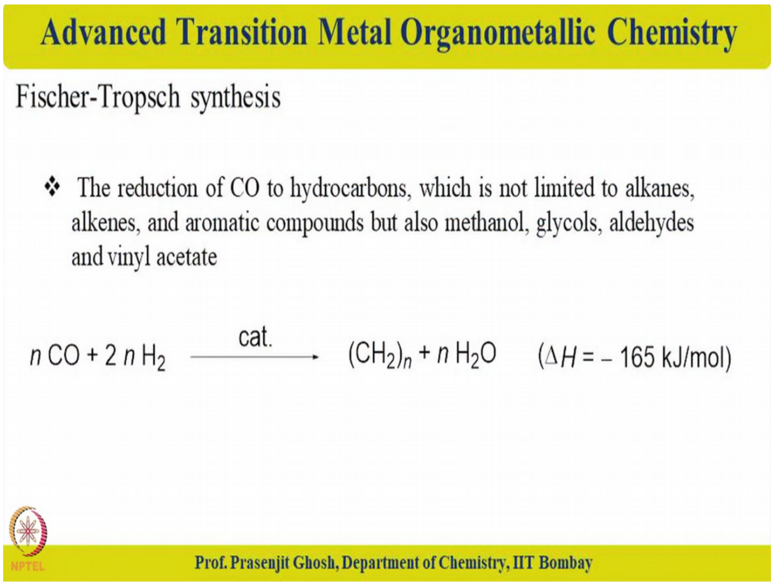

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Fischer-Tropsch synthesis

- The reduction of CO to hydrocarbons, which is not limited to alkanes, alkenes, and aromatic compounds but also methanol, glycols, aldehydes and vinyl acetate

$$n\,\mathrm{CO} + 2\,n\,\mathrm{H_2} \xrightarrow{\text{cat.}} (\mathrm{CH_2})_n + n\,\mathrm{H_2O} \qquad (\Delta H = -165\ \text{kJ/mol})$$

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This Fischer-Tropsch synthesis by and large is performed using heterogeneous catalyst. And one of the main limitations of Fischer-Tropsch synthesis is the specificity of the product mixture is extremely low. And that means that a large number of products are obtained.

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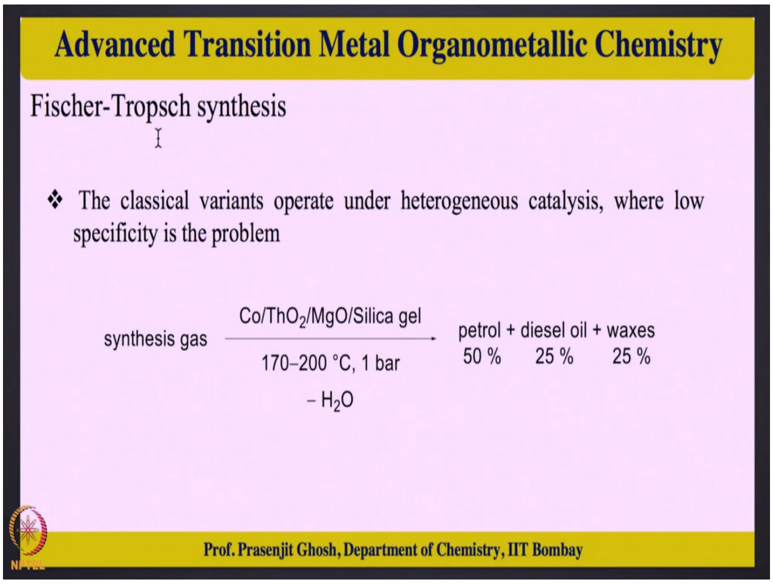

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Fischer-Tropsch synthesis

- The classical variants operate under heterogeneous catalysis, where low specificity is the problem

$$\text{synthesis gas} \xrightarrow[\substack{170\text{–}200\ ^\circ\text{C, 1 bar}\\ -\,\mathrm{H_2O}}]{\mathrm{Co/ThO_2/MgO/Silica\ gel}} \underset{50\ \%}{\text{petrol}} + \underset{25\ \%}{\text{diesel oil}} + \underset{25\ \%}{\text{waxes}}$$

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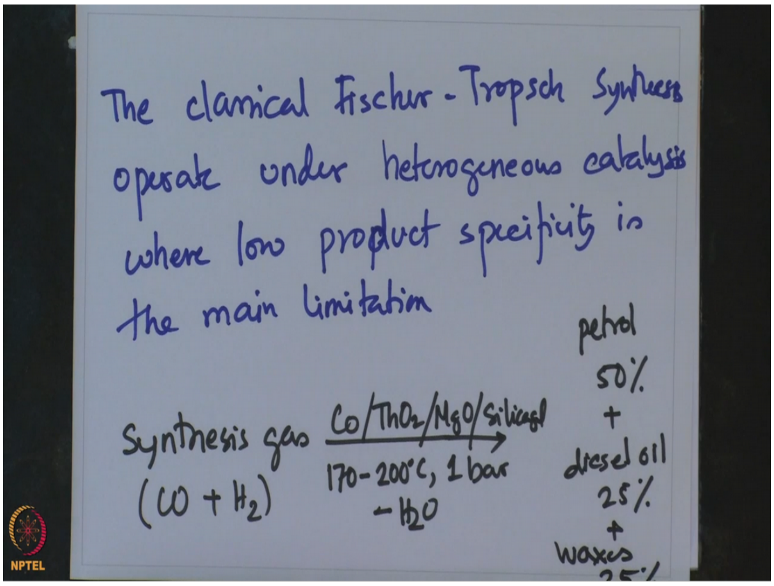

The classical Fischer-Tropsch Synthesis operate under heterogeneous catalysis where low product specificity is the main limitation

$$\underset{(CO + H_2)}{\text{Synthesis gas}} \xrightarrow[170-200^\circ C,\ 1\ \text{bar},\ -H_2O]{Co/ThO_2/MgO/\text{Silica gel}} \text{petrol } 50\% + \text{diesel oil } 25\% + \text{waxes } 25\%$$

So, the classical variant Fischer-Tropsch synthesis operate under heterogeneous catalysis where low specificity of product catalysis, where low product specificity is the main limitation. And this is given as synthesis gas. Now, synthesis gas is mainly a mixture of carbon monoxide and hydrogen in presence of cobalt, thorium oxide, magnesium oxide, silica gel; 170 to 200 degree centigrade 1 bar – water giving petrol 50% + diesel oil 25% + waxes 25%.

So, what we see is that, this conversion which is really a important from industrial point of view of being able to reduce carbon monoxide with hydrogen to produce hydrocarbons indeed is feasible concept, though in concept is feasible using heterogeneous catalysis which employ drastic condition. However, the limitation of Fischer-Tropsch synthesis is the fact that it has very low product specificity and a large number of different compounds are obtained.

And that sort of can be get it into petrol about 50%, diesel oil 25%, waxes another 25%. Now, the process had been refined to some extent to increase the selectivity and a process in South Africa produces some improved results in terms of this mixture of compound being obtained.

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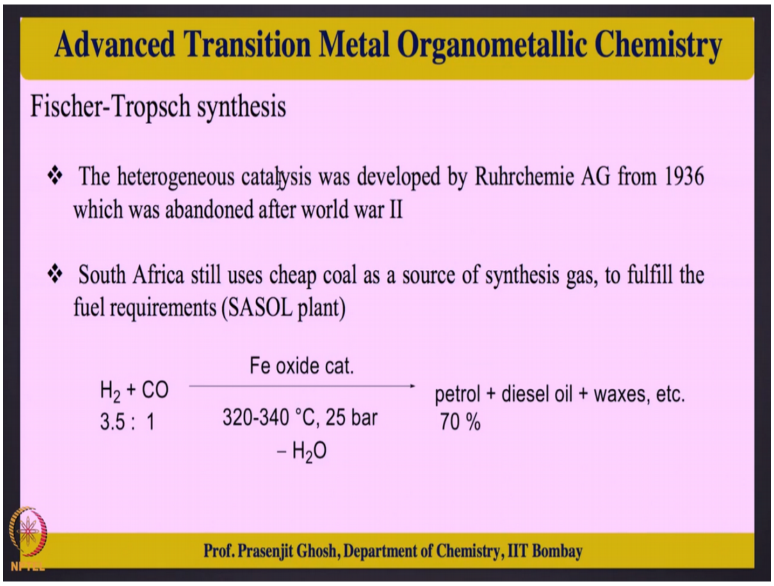

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Fischer-Tropsch synthesis

- The heterogeneous catalysis was developed by Ruhrchemie AG from 1936 which was abandoned after world war II
- South Africa still uses cheap coal as a source of synthesis gas, to fulfill the fuel requirements (SASOL plant)

$$\underset{3.5\ :\ 1}{H_2 + CO} \xrightarrow[\text{320-340 °C, 25 bar}\ -H_2O]{\text{Fe oxide cat.}} \underset{70\ \%}{\text{petrol + diesel oil + waxes, etc.}}$$

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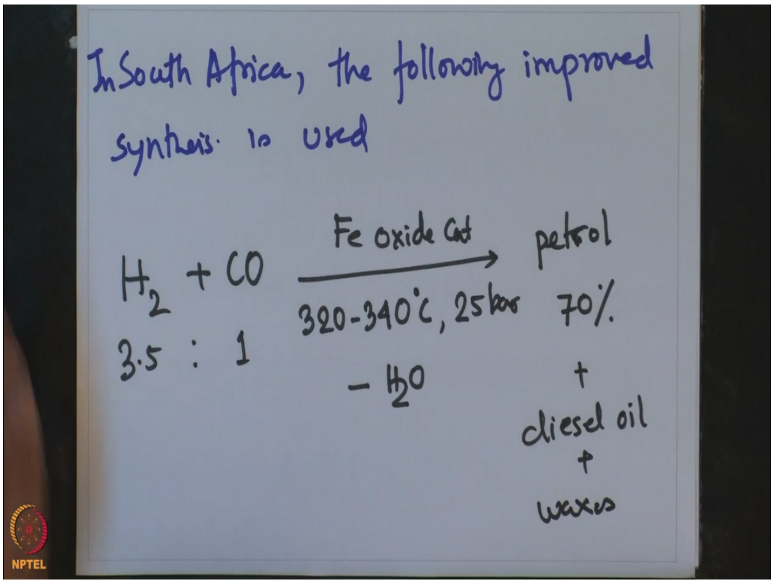

In South Africa, the following improved synthesis is used

$$\underset{3.5\ :\ 1}{H_2 + CO} \xrightarrow[\text{320-340°C, 25 bar}\ -H_2O]{\text{Fe oxide Cat}} \text{petrol } 70\% + \text{diesel oil} + \text{waxes}$$

So, in South Africa, the following improved synthesis is used. And this is given as, by the reaction, hydrogen + carbon monoxide 3.5:1 giving iron oxide catalyst 320 to 340 degree centigrade 25 bar – water giving petrol at a higher portion of 70% + diesel oil + waxes. So, one sees that upon changing the catalyst to some iron oxide based heterogeneous catalyst, one can improve upon this product selectivity. However, that is not too much given the fact that, only the petrol component increased from 50% to 75% under this improved method.

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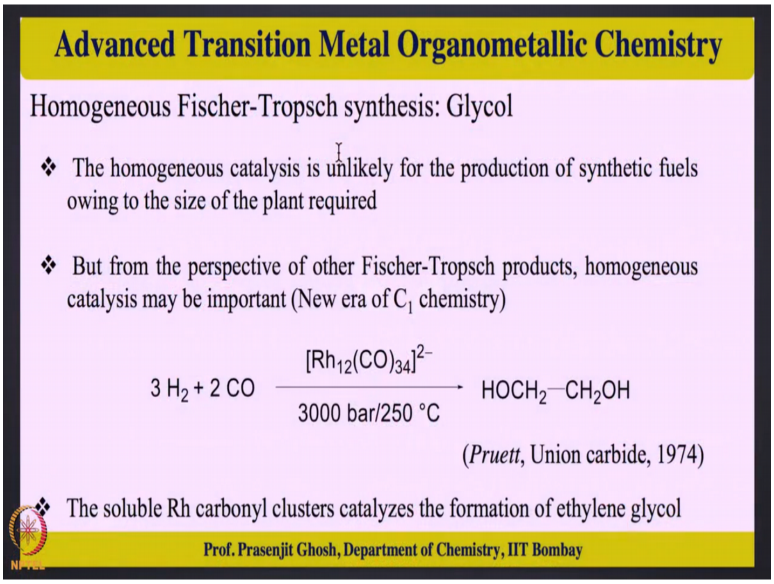

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Homogeneous Fischer-Tropsch synthesis: Glycol

- The homogeneous catalysis is unlikely for the production of synthetic fuels owing to the size of the plant required
- But from the perspective of other Fischer-Tropsch products, homogeneous catalysis may be important (New era of C_1 chemistry)

$$3\,H_2 + 2\,CO \xrightarrow[3000\ \text{bar}/250\ ^\circ\text{C}]{[Rh_{12}(CO)_{34}]^{2-}} HOCH_2{-}CH_2OH$$

(*Pruett*, Union carbide, 1974)

- The soluble Rh carbonyl clusters catalyzes the formation of ethylene glycol

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So, one of these reason, of course selectivity, there is a the need for developing homogeneous Fischer-Tropsch synthesis. And here is a report with a rhodium catalyst which can carry out this Fischer-Tropsch synthesis producing glycol under homogeneous catalysis condition. Now, this is also industrially relevant method which has been developed by union carbide. So, the homogeneous counterpart of Fischer-Tropsch synthesis;

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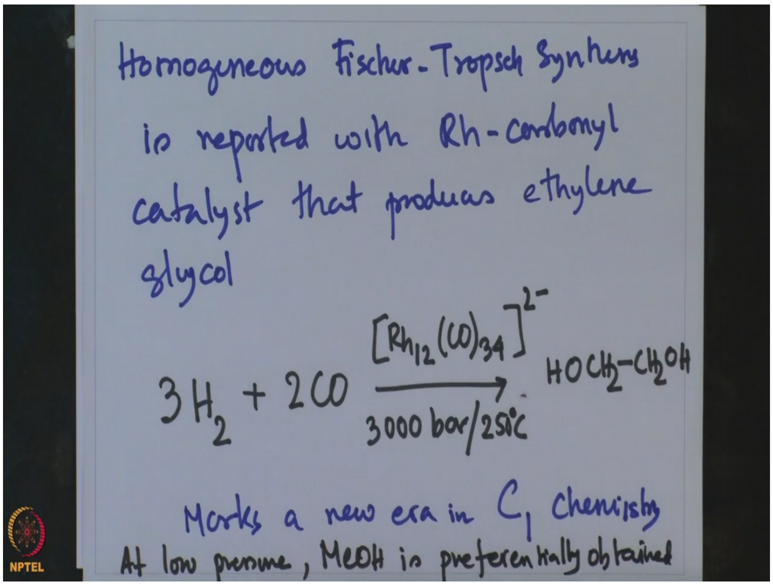

Homogeneous Fischer-Tropsch Synthesis is reported with Rh-carbonyl catalyst that produces ethylene glycol

$$3H_2 + 2CO \xrightarrow[3000\ \text{bar}/250^\circ\text{C}]{[Rh_{12}(CO)_{34}]^{2-}} HOCH_2{-}CH_2OH$$

Marks a new era in C_1 Chemistry

At low pressure, MeOH is preferentially obtained

Is reported with a rhodium carbonyl catalyst that produces ethylene glycol. And this is given by the following reaction. + 2 CO rhodium 12 CO 34 to – 3000 bar and 25 degree centigrade produces H 2 O CH 2 CH 2 O H. And this ethylene glycol is obtained under homogeneous catalysis condition at with a very high temperature of 250 degree centigrade and a very high pressure of about 3000 bars.

Now, even though the conditions are harsh, these homogeneous catalysts sort of marks new era in C1 chemistry. So, this homogeneous catalysis using rhodium carbon cluster marks a new era in C1 chemistry. It must also be noted that, at a lower pressure, not as high as that of 3000 bar, instead of, at lower pressure instead of ethylene glycol, methanol is obtained for this reaction. So, at low pressure, methanol is preferentially obtained instead of this ethylene glycol.

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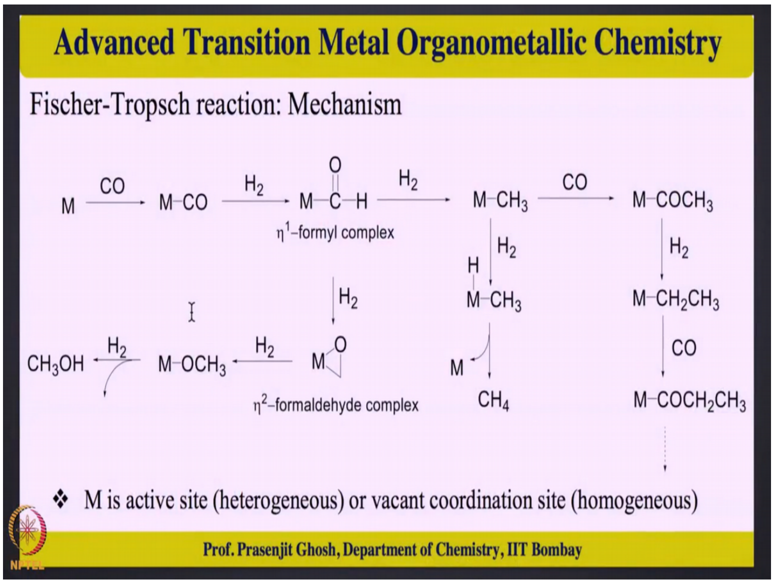

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Fischer-Tropsch reaction: Mechanism

- ❖ M is active site (heterogeneous) or vacant coordination site (homogeneous)

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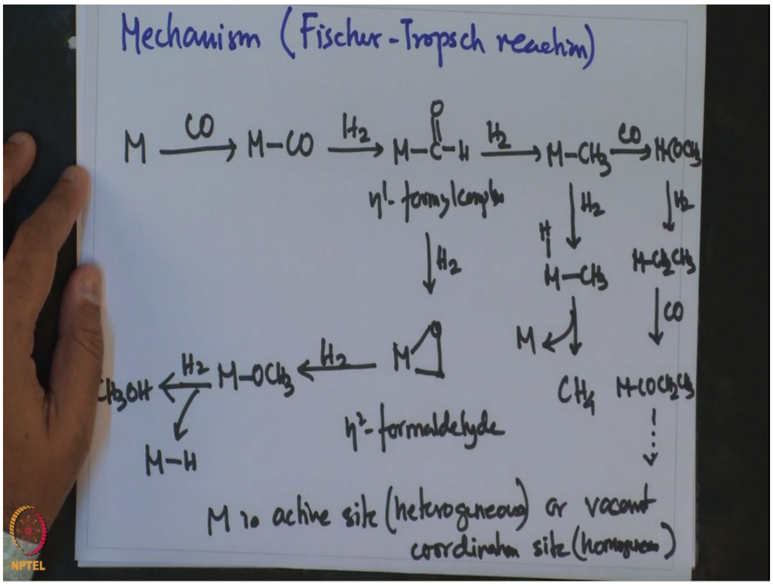

Mechanism (Fischer-Tropsch reaction)

M is active site (heterogeneous) or vacant coordination site (homogeneous)

So, the mechanism Fischer-Tropsch reaction is given as follows: M reacting with carbon monoxide giving M CO; that reacting with hydrogen giving M CO H; that reacting with hydrogen giving M CH 3; that reacting with CO giving M O M CO CH 3. So, this is a sequence and M CHO is nothing but a eta 1 formyl complex that reacts with hydrogen giving M O this, this is eta 2 formaldehyde complex.

And that reacts with hydrogen giving M O CH 3 further reaction with hydrogen giving CH 3 OH and resulting in metal M hydride. So, this gives methanol and metal hydride. Similarly, the reaction of M CH 3 with hydrogen giving a metal hydride methyl which eliminates the metal productive elimination to give methane. And then, the reaction of M CO CH 3 with hydrogen gives M CH 2 CH 3; that with carbon monoxide giving M CO CH 2 CH 3.

And that keeps on going. So, this M, M is classified as, is active site of a heterogeneous catalysis or vacant coordination site of homogeneous catalysis. So, the mechanism involves first the activation of carbon monoxide by coordination to the metal carbonyl. Then reaction with hydrogen to give the metal formyl complex. The reaction of metal formyl complex with hydrogen gives the methyl metal methyl complex.

And the first further insertion of CO gives the methyl CO CH 3. Now, this methyl formyl complex then reacts with hydrogen to give M CH 2 O which is nothing but eta 2 formaldehyde complex. And that formaldehyde complex upon reaction with M CO CH 3 gives the, upon reaction with hydrogen gives metal methoxy complex. Now, metal methoxy complex reacts further with hydrogen to give metal hydride and methanol.

And this over here, this metal methyl complex upon reaction with hydrogen undergoes oxidative addition to give a metal hydride methyl complex which then reductively eliminates to give methane. And similarly, the carbon monoxide inserts to give methol CO CH 3 that reacts with hydrogen to give metal CH 2 CH 3 ethyle, that react with carbon monoxide to give metal CO CH 2 CH 3.

And that can again reacts with hydrogen and generate a wide variety of product. So, what we see is that this mechanism of Fischer-Tropsch synthesis produces a lot many of the products ranging from alcohols to alkanes to even ketones and so forth. So, this is a nice demonstration of this C1 chemistry where the reduction of carbon monoxide can be achieved at a very high conditions, homogeneous as well as heterogeneous to produce hydrocarbons or alcohols or esters, so on and so forth.

So, with this I would like to draw a conclusion on today's discussion on Fischer-Tropsch synthesis. To begin with, what we had observed that this Fischer-Tropsch synthesis is an important reaction, particularly with respect to the reduction of carbon monoxide to hydrocarbons.

But one of the major limitation is that this reaction though feasible under heterogeneous conditions but has a extremely low product selectivity leading to the formation of petrol, diesel and waxes in about 50% petrol and 25% each of diesel and waxes with catalyst comprising of copper, sodium, magnesium oxide, thorium oxide, silica gel and so on and so forth.

Now, upon improvement of the heterogeneous catalysis conditions, one can use iron oxide and can increase the petrol component from 50% to 70%. However, the heterogeneous conditions still has issues with product selectivity. In that respect, we had observed that a rhodium carbonyl compound catalyst marks the new era in C1 chemistry as it represents the first homogeneous catalysis of this Fischer-Tropsch synthesis that exclusively give ethylene glycol.

And we have we have also looked into the catalytic pathway or the mechanism by which the Fischer-Tropsch synthesis might react with carbon monoxide and hydrogen giving products like alkyl, alkane, ketone and alcohol. And this mechanistic pathway sort of initiates with carbon active carbon CO monoxide activation by coordination to metal, followed by reduction with hydrogen and so forth in several mechanistic pathways leading to formation of this mixture of product.

So, with this I would like to conclude our today’s discussion on Fischer-Tropsch synthesis. And we are going to be discussing more dealing particularly looking at the mechanism under heterogeneous conditions for forming higher order alkanes in Fischer-Tropsch synthesis. And subsequently we are going to take up other organometallic catalytic applications when we take up this topic in the next lecture.

I sincerely thank you for your patient hearing of this lecture. And we are going to be discussing a bit more of Fischer-Tropsch synthesis before we take up other examples of organometallic catalysis when we meet in the next lecture. Till then, goodbye and thank you.