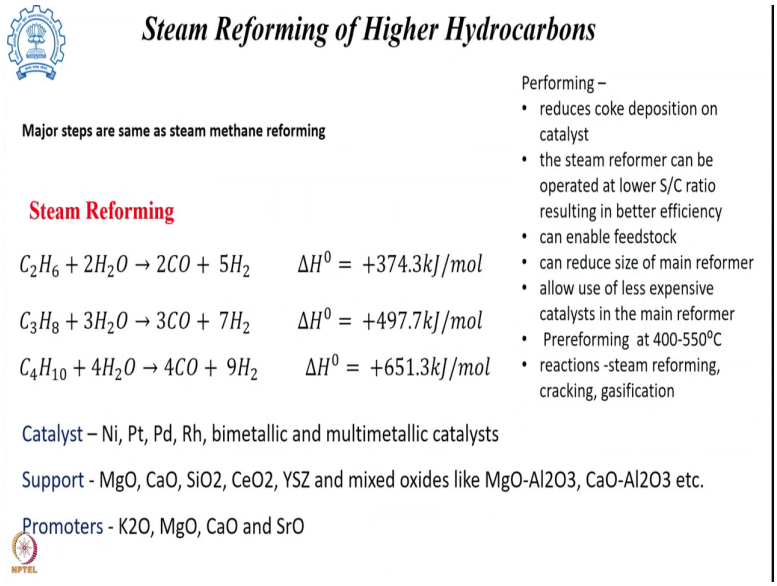
Hydrogen Energy: Production, Storage, Transportation and Safety

Prof. Pratibha Sharma
Department of Energy Science and Engineering
Indian Institute of Technology, Bombay

Lecture - 06
Steam Reforming of Higher Hydrocarbons

In the last class, we have seen the steam methane reforming process wherein methane is used as the feedstock.

(Refer Slide Time: 00:29)



However, in today's class we will see Steam Reforming of Higher Hydrocarbons. Now, these can be gaseous hydrocarbons, liquid hydrocarbons. When it comes to higher hydrocarbons, the steps still remain the same as that of steam methane reforming. It involves of initial feedstock pretreatment followed by steam reforming process, then water gas shift and finally the purification step.

However, higher hydrocarbons as compared to methane, are more reactive so inclusion of a pre-reformer becomes necessary. And there are several advantages of using a pre-reformer when doing the steam reforming of higher hydrocarbons. When we have a pre-reformer prior to the primary reformer, it reduces the higher hydrocarbons into the lower hydrocarbons, and that reduces the coke deposition onto the catalyst which can lead to deactivation.

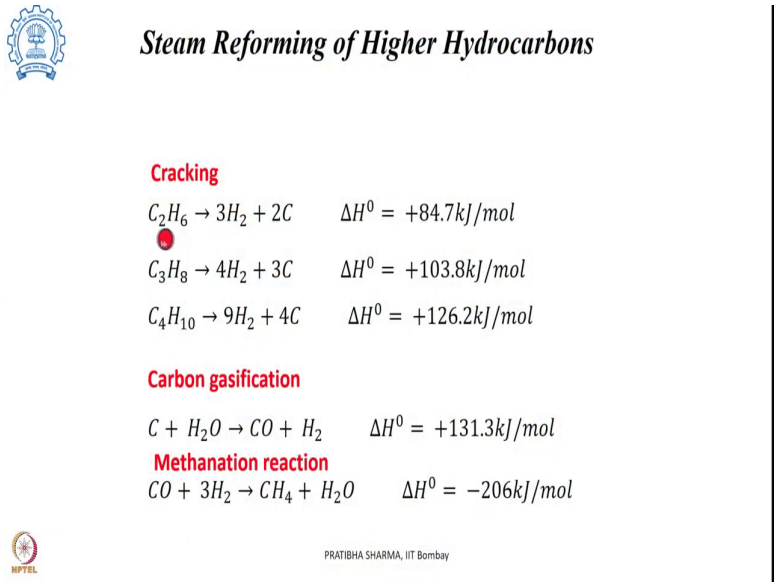
At the same time the steam requirement in the primary reformer also reduces when a pre-reformer is being introduced. It can also enable a variety of feedstock that can be used for the reforming process. By the use of a pre-reformer prior to the primary reformer, since the higher hydrocarbons are being reduced at the same time the temperature of the process can be reduced as such the less expensive catalyst can be used in the main reformer.

In pre reformers usually the reactions are similar to the primary reformer and the reaction conditions are 400 to 550 degree centigrade of temperature. And same catalyst nickel and alumina is being used most of the time. And, there are different reactions that take place in the reforming process like steam gasification at the same time steam reforming, cracking reaction.

Now, when it comes to the higher hydrocarbons like LPG is available and it could be a source of producing hydrogen and preferred feedstock bas such if we see, there are different elements which are present inside either it can be methane, propane or butane. And, their steam reforming can give syn gas, but the important point to note here is the delta H value it increases as the C increases. Now, this means that the process gets more and more endothermic as the carbon content in the feedstock increases.

Now, for this particular reforming process there are several catalysts which have been looked at including nickel, platinum, palladium, rhodium, bimetallic catalyst and several multi metallic catalyst on supports like magnesium oxide, calcium oxide, silica, cerium oxide, atria stabilized, zirconium. There are several mixed oxide that has also been looked at like magnesium oxide alumina, calcium oxide alumina. Different promoters which have been used for the reforming reaction K_2O, MgO, calcium oxide, stromsyn oxide.

(Refer Slide Time: 04:02)

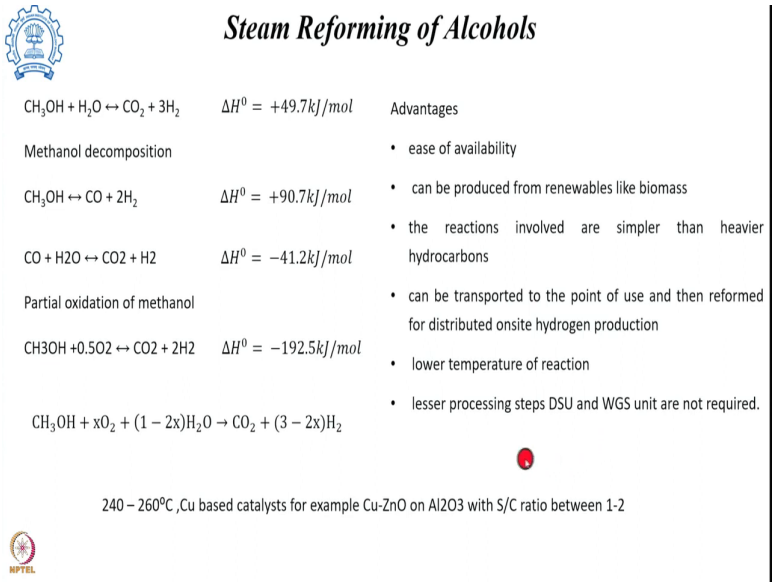


Other than the reforming process that occurs in the primary reformer there are several other processes can occur like the cracking. So, these hydrocarbons ethane or propane or butane they can crack to give carbon and hydrogen. Carbon gasification can also occur in the reactor at the same time methanation can also occur; wherein, the carbon monoxide which is formed can again react with hydrogen giving methane.

Not only the gaseous hydrocarbons liquid hydrocarbons can also undergo steam reforming to produce hydrogen; for example, methanol. There are several advantages to use methanol for hydrogen production, because it is easily available it can be produced from renewables like biomass. The reactions which are involved in the alcohol based steam reforming reactions.

These are comparatively simpler than the heavier hydrocarbons. These can be transported from the point of use, they can be taken to the point of use, then they can be reformed, they can be distributed for onsite hydrogen production. And the temperatures which are involved in the reaction are lower.

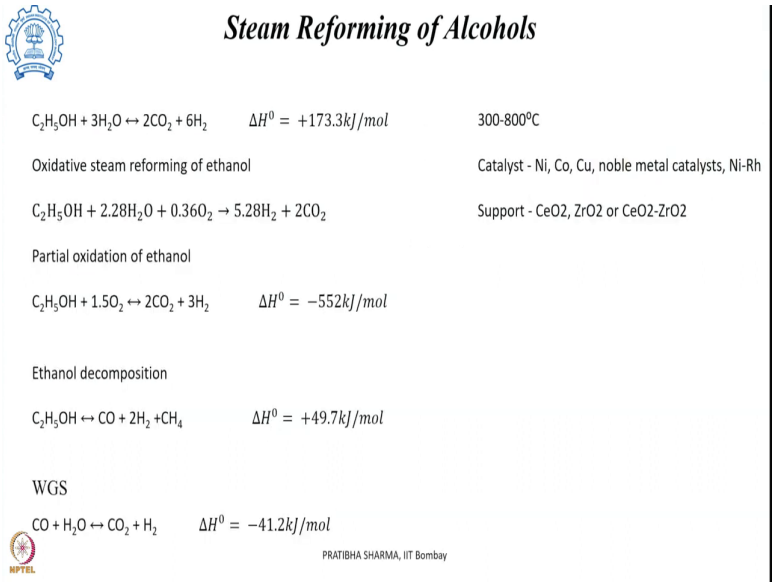
(Refer Slide Time: 05:12)



And a processing steps also reduced because desulphurization unit and water gas shift unit is not required in the reforming of alcohols. So, if we look at the methane reforming then methane reacts with steam to give carbon dioxide and hydrogen and we can see that the delta H value is 49.7 kilo joule again it is an endothermic reaction; however, the primary method for getting syn gas is decomposition of methanol followed by a water gas shift reaction partial oxidation.

Now, this is an endothermic reaction so as such a small split stream of oxygen can help in reducing the required heat input. So, in presence of small amount of oxygen, the reforming can take place that is the oxidative steam reforming and that can result into the formation of hydrogen. Now, the conditions of operation are quite mild 240 to 260 degree centigrade and this reaction can occur on copper based catalyst like copper zinc oxide on alumina support. And the steam to carbon ratio used for the process is about 1 to 2.

(Refer Slide Time: 06:31)



Ethanol can also be used for deforming and producing hydrogen. So, ethanol on undergoing steam reformation can produce hydrogen and again this is an endothermic reaction; however, the heat of reaction as we can see the value is higher than that for methanol. It can also undergo oxidative steam reforming where in a small amount of oxygen is used to reduce the required heat energy.

The required heat of reaction would be lower in that case and as such it can undergo the oxidative steam reforming to produce hydrogen. Partial oxidation also can produce hydrogen and we can see this is an exothermic process and ethanol can decompose to give hydrogen, carbon monoxide and methane. Finally, it can undergo water gas shift reaction producing more hydrogen.

So, the reaction conditions are the reaction takes place at 300 to 800 degree centigrade in the presence of catalyst like nickel, cobalt, copper and other noble metals, bimetallic catalyst like nickel and on rhodium has been found to be the best catalyst on supports like cerium oxide, zirconium oxide or cerium oxide and zirconium oxide combination. So, this is what we have seen about the steam reforming of higher hydrocarbons along with the steam reforming of methane.

Thank you.