Lecture - 09
Partial Oxidation Method for Hydrogen Production

Today we will learn the Partial Oxidation Method for Hydrogen Production.

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As the name suggest partial oxidation means sub stoichiometric amount of oxygen being reacting with the feedstock to produce the syngas. Now, the reason for this sub stoichiometric use of oxygen is that the complete oxidation can result into carbon dioxide and water and we will not be able to get the desired product which is hydrogen, and the delta H value suggests that this is an exothermic reaction.

So, the partial oxidation of hydrocarbon here in the reaction is mentioned for methane to produce syngas is an exothermic reaction and this can occur in the presence of oxidant, it can be oxygen or air. This is faster than the steam methane reforming because the operating conditions are very high temperatures and the reaction kinetics are favoured under those conditions. The H_2O by CO ratio which is obtained as 2, ideally it is 2 looking at the reaction; however, in real practice it lies somewhere around 1.6 to 1.8 which is less than SMR process.

In SMR partially the hydrogen is coming from steam which is not the case here in partial oxidation. Carbon dioxide is released which is higher in amount and the method can be utilized wherein the requirement of H_2 by CO ratio is lower. If the content required of hydrogen is lower in those processes it can be specifically used.

Now, the partial oxidation which is represented by PO_X can be either a non-catalytic process or it could be a catalytic one. In non-catalytic the reaction condition is such that the operating temperature is high 1200 to 1500 degree centigrade and the feedstock which is used can be any from gaseous to liquid to solid feedstock.

So, there is a fuel flexibility wherein any type of feed stock can be used. Generally in refineries where the bottom of the barrel fuels needs to be upgraded because they cannot be used because of the emission norms and they have high amounts of impurities like sulphur impurities or heavy metals or olefins as such they cannot be used as such.

So, they can be upgraded using this particular method. With the use of catalysis catalyst the operating temperature can be lowered down and this roughly lies in the range of 600 to 900 degree centigrade usually lower hydrocarbons are used for catalytic process.

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Non-Catalytic Partial Oxidation (POX)

- In the absence of catalyst, the temperature is higher
- Gaseous, liquid or solid hydrocarbons can be used
- No catalyst poisoning challenges
- Use of air or oxygen – reactivity of feed, application
- Pressure – 50-80 bar
- Temperature 1200-1500°C
- H_2/CO ratio depends on the feedstock composition and the quantity of the steam added
- Two processes - Texaco Syngas Generation Process (TSGP) and the Shell Gasification Process (SGP)
- Difference between the two is gas cooling process, waster heat recovery unit, design of the nozzle, removal of soot
- Upgrading bottom of barrel, low value fuels
- Can be used for FT fuel and methanol synthesis

$$C_nH_m + \left(\frac{n}{2}\right)O_2 \rightarrow nCO + \left(\frac{m}{2}\right)H_2 \; (exothermic)$$

$$C_nH_mS_x + \left(\frac{n}{2}\right)O_2 \rightarrow nCO + \left(\frac{m}{2} - x\right)H_2 + xH_2S \; (exothermic)$$

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2 \; (endothermic)$$

$$C_nH_m + nCO_2 \rightarrow 2nCO + \left(\frac{m}{2}\right)H_2 \; (endothermic)$$

$$C_nH_m \rightarrow (n - x)C + C_xH_y + \left\{\frac{(m - y)}{2}\right\}H_2 \; (endothermic)$$

$$C + \left(\frac{1}{2}\right)O_2 \rightarrow CO \; (exothermic)$$

$$C + H_2O \rightarrow CO + H_2 \; (endothermic)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \; (exothermic)$$

Starting with the non-catalytic partial oxidation, as name suggests that catalyst is not used as such the temperature required will be higher. Now, the fuel flexibility means natural gas which cannot be used using SMR process because there is a variety of hydrocarbons present

in the gaseous form or because the content of sulphur is higher or liquid fuels like heavy residual oils, or pet coke, coal all the feedstock can be upgraded; can be used for hydrogen production using non-catalytic partial oxidation, since there is no catalyst.

So, the catalyst deactivation problems are not there, we can use either air or oxygen as the oxidant; however, that use will depend upon what is the reactivity of feedstock which is used, if the feedstock which is used has a low reactivity oxygen that would be preferred, also it depends upon what is the induce application.

If the induce application desires high purity of hydrogen in that case oxygen could be used as an oxidant; however, if the induce application is where in certain amount of nitrogen is acceptable like for ammonia production then air can be used as an oxidant. In that case the outlet hydrogen stream will have nitrogen which can be used directly for fertilizer industry.
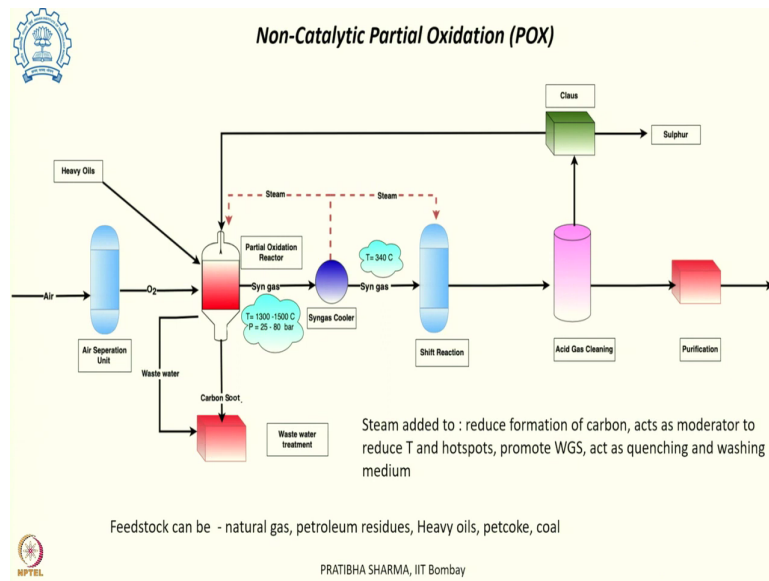
The operating conditions are 1200 to 1500 degree centigrade temperature, a higher pressure of 50 to 80 bar at max 280 bar. The H_2 by CO ratio which we will obtain from partial oxidation tepends upon, what is the composition of the feedstock which is used and also how much is the amount of steam which is added to the process.

There are two processes which are patented Texaco syngas generation process and shell gasification process; however, these are almost similar but the major difference lies in how the gas is being cooled in waste heat recovery unit, as well as the design of the nozzle and the removal of soot. This particular method could be best suited when the end products of the refinery or the low value fuels needs to be upgraded and the process H_2 by CO ratio since it is lower in this case. So, if this syngas can be used for Fischer drop fuel synthesis or for methanol synthesis. There are large number of reactions that can occur in non-catalytic partial oxidation.

The first one is hydrocarbon on partial oxidation giving syngas. So, the first reaction is a partial oxidation reaction, second one is also a partial oxidation reaction; however, if the fuel is contaminated with large quantities of sulphur, in that case under the reducing conditions it will form H_2S. Hydrocarbons they can also undergo reforming to produce syngas. So, the third reaction is the reforming reaction. Carbon dioxide which will be formed in the process can also react with the hydrocarbons to give syngas.

So, this is the dry reforming process and these higher hydrocarbons under the operating conditions can crack to give carbon, lower hydrocarbons and hydrogen. Besides these reactions the carbon which will be formed in the process can undergo partial oxidation to produce CO, it can undergo gasification to produce syngas and water gas shift reaction can take place in the non-catalytic partial oxidation process.

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To understand the entire process well, let us see the process flow. If oxygen is used as an oxidant in the process, it has to be produced using an air separation unit wherein the atmospheric air could be used to separate out oxygen from the rest of the elements. Now, this oxygen along with the feedstock and steam is used as the input for the partial oxidation reactor. If heavy residual oils are used they need to be preheated; they need to be atomized and then fed along with steam to the reactor along with oxygen.

Here in this special reactor where in the oxidation of the reactor feedstocks along with the oxidant takes place in the burner region followed by the rest of the reactions. So, that operating condition inside the partial oxidation reactor is high pressure and high temperature conditions which leads to metallurgical challenges and as such the vessel is a high pressure vessel which is a brick lined reactor.

Once these reactions occur inside the partial oxidation reactor, syngas is formed and depending upon the feedstock there would be several particulate matter soot will be formed in the reactor using steam that can be scrubbed off and that can be collected. So, the waste water

along with the soot could be recycled and treated water can be again fed back to the partial oxidation reactor and the soot can again be fed back to the partial oxidation reactor.

After the syngas is being produced by the process at a high temperature this needs to be cooled down before it enters into the shift reactor. So, this temperature difference can be used for generating steam after it has been cooled in a syngas cooler. The temperature of the syngas is about 340 degree centigrade and this can be fed to carbon dioxide shift reactor, wherein with the help of steam the carbon monoxide will react with steam to produce carbon dioxide and if the feedstock is rich in sulphur impurities then we will under the reducing conditions have H 2 S. So, both the acid gases needs to be cleaned.

H_2S and carbon dioxide needs to be removed either in two step method or it could be in one step method. Earlier, plants used to have two step method wherein H_2S was removed prior to the shift reactor as sulphur impurities can poison the shift catalyst and thereafter the carbon dioxide was removed in the later part.

However in the modern plants an integrated acid gas removal is done where both the acid gases are removed in one step, first H_2S is removed using various solvents methanol is most widely used solvent. So, cold methanol is used to first separate out H_2S, the sulphur could be obtained and could be fed to the Claus plant and finally, an elemental sulphur could be obtained that could be used for various applications.

Carbon dioxide is again removed using the solvent removal method and that carbon dioxide which is obtained can go for carbon capture use and sequestration. Small amount of other impurities which are left out in the hydrogen outlet stream can further undergo purification step to get pure hydrogen.
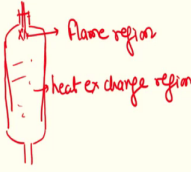
Now, in the entire process, steam is added and that plays multiple roles. So, steam is added to not only reduce the carbon formation in the water gas shift process, but it also after cooling has substantial amount of steam in the syngas that can undergo water gas shift reaction.

It also acts as a moderator since the operating conditions are very high temperature in the partial oxidation reactor, there can be hotspots and uncontrolled reaction leading to very high temperatures and that can be moderated with the help of steam. It is also being used for quenching the soot which is formed and cleaned on the other particulate matter. So, this is how the entire process is.

Now, as we have mentioned that the reactor which is being used for non-catalytic partial oxidation reactor is a brick lined reactor, wherein there is a burner region to which the oxidants is being fed. So, that is the flame region where in partial oxidation reaction occurs and thereafter is the heat exchange region. In this process since there is no indirect heat exchange involved, by indirect heat exchange we mean in SMR we had externally heated reformer tubes which were heated by means of burners.

Here in within the same reactor the combustion of the oxidation of the reactants produces the desired reaction temperature. So, there is no indirect heat exchange here involved, in the process the heat recovery is poor and the heat losses are more as such the thermal efficiency of the process is lower since the reaction conditions are very high temperature conditions.

So, the kinetics of the reactions are faster, the convergence are better. So, the methane conversion achieved in the process are high. Compared to SMR since number of heat exchangers are less as such the design becomes compact, simple and the reactor is less expensive. If we see the efficiency of the process this is somewhat between 60 to 75 percent; however, the hydrogen which is being produced in the process is lower in content.

Energy efficiency 15.9 to 19.3 mega joule per normal meter cube and this is an important process in the refineries.

Catalytic Partial Oxidation (CPOX)

Partial Oxidation $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ $\Delta H^0 = -38 kJ/mol$

Dry reforming: $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ $\Delta H_{298} = 247\ kJ/mol$

Water gas shift: $CO + H_2O \leftrightarrow H_2 + CO_2$ $\Delta H_{298} = -41\ kJ/mol$

Boudouard equilibrium: $CO_2 + C \leftrightarrow 2CO$ $\Delta H_{298} = 171\ kJ/mol$

Combustion: $CH_4 + O_2 \rightarrow 2H_2O + CO_2$ $\Delta H_{298} = -803\ kJ/mol$

Combustion: $2CO + O_2 \rightarrow 2CO_2$ $\Delta H_{298} = -294\ kJ/mol$

Combustion: $2H_2 + O_2 \rightarrow 2H_2O$ $\Delta H_{298} = -286\ kJ/mol$

Equilibrium decided by these equations and hence methane conversion, product selectivity and yield

- Catalyst lower down the temperature from 1200-1500⁰C to 900⁰C
- Increases selectivity of product
- Mostly reported for methane but can have C2+
- Syngas selectivity and higher methane conversion above 750⁰C
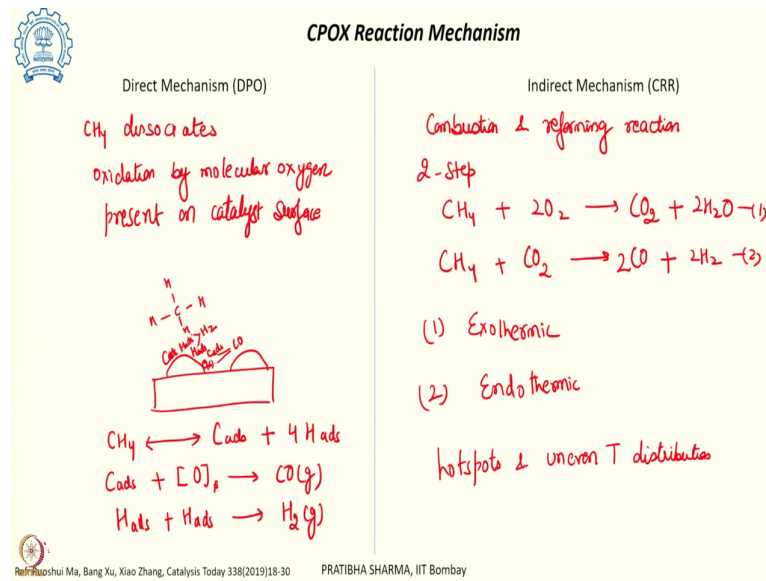
PRATIBHA SHARMA, IIT Bombay

If you look at the catalytic partial oxidation then with the use of catalyst we can lower down the operating temperature from 1200-1500 degree centigrade to 900 degree centigrade and with the use of catalyst the selectivity towards the product which is hydrogen in our case improves.

Most of the reports are on catalytic partial oxidation of methane; however, C2 plus or higher hydrocarbons can also be used, but they may have problems associated with the catalyst deactivation. It is found that the selectivity towards syngas formation and a higher methane conversion could be achieved at temperatures above 750 degree centigrade.

Along with the major reaction which is the partial oxidation of methane to give syngas, there are a large number of competing reactions that can also occur in the process like the dry reforming of methane to produce syngas, water gas shift of the carbon monoxide to produce hydrogen and carbon dioxide. The Boudouard reaction wherein carbon which is being formed reacts with carbon dioxide to give CO, combustion of methane can occur giving carbon dioxide and water, combustion of CO to give carbon dioxide, combustion for hydrogen to produce water.

Now, which of these reactions will occur at the equilibrium state will be decided by the equations and hence that will also decide how much percentage of methane conversion occurs, what is the product selectivity, what is the yield of hydrogen which could be obtained in the process.

CPOX Reaction Mechanism

Direct Mechanism (DPO)

CH$_4$ dissociates
oxidation by molecular oxygen
present on catalyst surface

CH$_4 \longleftrightarrow$ C$_{ads}$ + 4H$_{ads}$
C$_{ads}$ + [O]$_s \longrightarrow$ CO(g)
H$_{ads}$ + H$_{ads} \longrightarrow$ H$_2$(g)

Indirect Mechanism (CRR)

Combustion & reforming reaction
2-step
CH$_4$ + 2O$_2 \longrightarrow$ CO$_2$ + 2H$_2$O —(1)
CH$_4$ + CO$_2 \longrightarrow$ 2CO + 2H$_2$ —(2)

(1) Exothermic

(2) Endothermic

hotspots & uneven T distribution

Ref: Ruoshui Ma, Bang Xu, Xiao Zhang, Catalysis Today 338(2019)18-30   PRATIBHA SHARMA, IIT Bombay

If we try to explain the catalytic partial oxidation mechanism. It is a very fast reaction with a very small residence time, it is very difficult to exactly identify the mechanism, but there are two postulates. One is a direct mechanism occurs where in the methane it dissociates on the surface of catalyst. So, we have a support having catalyst. So, the methane it dissociates on the catalyst carbon getting adsorbed, hydrogen also getting absorbed and then oxidation occurs by molecular oxygen which is present on the catalyst surface.

So, the oxygen which is on the catalyst surface reacts with the adsorbed carbon on the surface to give CO and the hydrogen adsorbed, they combine to form hydrogen molecule. So, as such it is expected that methane on the surface of the catalyst gets adsorbed, dissociated into carbon and hydrogen both of which gets adsorbed. This adsorbed carbon combines with the surface oxygen to produce CO and the adsorbed hydrogen combines with another adsorbed hydrogen to give hydrogen molecule. This is a direct method of catalytic partial oxidation.

The indirect method which is known as combustion and reforming reaction. This is a two step method, initially methane undergoes combustion reaction to produce carbon dioxide and water, methane undergoes reforming to produce syngas in the process. And first one being an exothermic process, second one being endothermic process, it can lead to hotspots or uneven temperature distribution inside the reactor.

So, these are two reaction mechanisms which are proposed for catalytic partial oxidation.

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Noble Metal Catalysts

- Good conversion and high reactivity
- Pt/Al_2O_3 , shows good activity but sintering is a problem, Ce/Zr used as promoter to reduce deactivation, cost major challenge, high loading
- Rh on CeO_2/Al_2O_3, lower levels of loading, but the method of synthesis changes the characteristics
- Ru although comparatively less expensive but not stable and deactivate due to irreversible oxidation, however alumina support was found to be better.
- Cost is the major bottleneck when use in industrial scale hydrogen production is to be considered
- reducing cost by combining with other metals

PRATIBHA SHARMA, IIT Bombay

Again when it comes to catalytic partial oxidation catalyst has the major role. Catalyst have already studied in great detail about the characteristics which catalysts should have. What are the requirements in terms of catalyst support and promoters? In catalytic partial oxidation we can have either noble metals or non-noble metals called catalysts or various other options.

The noble metals are good in the sense that they provide good conversion and they have higher reactivity. They have higher selectivity towards the product, platinum on alumina support was used in catalytic partial oxidation and it is known to have a good activity, but the major problem associated was that of sintering.

So, at higher temperature sintering was observed; however, this could be improved if cerium zirconium could be used as a promoter and that can reduce the problem of catalyst deactivation, but the major challenge remains is the cost here and with all the noble metals the cost is the major issue towards commercialization of overuse in the industrial scale processes. If with platinum like for example, the cost is although remains volatile and it is approximately 30000 times that of the nickel.
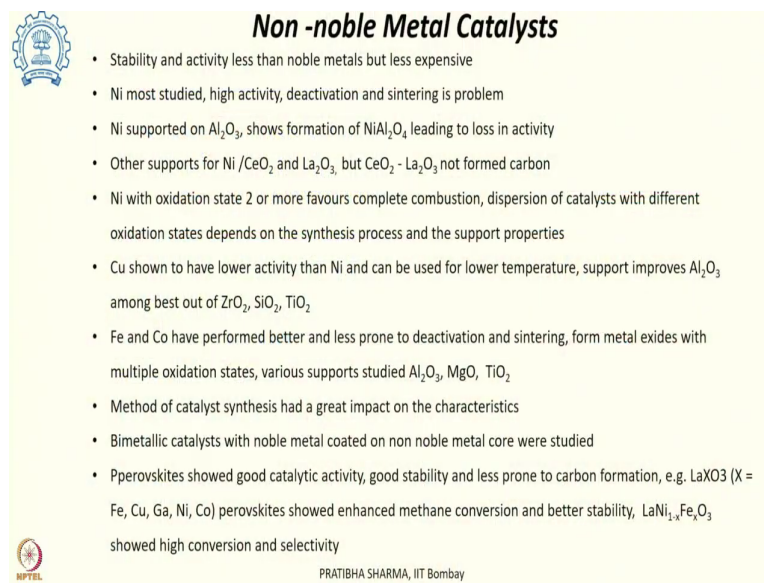
So, that is the major obstacle; however, higher loading is also required higher than 1 percent about 1.5 percent loading is required that again is a disadvantage. Rhodium on cerium oxide alumina is a good catalyst wherein the loading percentage of rhodium compared to platinum is lower.

It is found that how the catalyst is being synthesized that has a effect on the entire process. Like if the catalyst is synthesized using some of the techniques which are low temperature methods wet impregnation in that case work well under the lowered operating conditions; however, at higher operating conditions they are prone to more sintering.

Ruthenium, it is comparatively less expensive among the noble metal catalyst, but it is not stable and it gets deactivated. The reason found is different oxidation state. So, there is transition between the different oxidation state sometimes it is irreversible, as such the activity it is not recovered in the process, but this was found to improve when alumina support was used for the ruthenium catalyst.

So, with all the noble metals the major bottleneck lies in the cost and reducing the cost could be another possible option and that these can be combined with other metals which are less expensive, or can noble metal, non-noble metals can be used.

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Non -noble Metal Catalysts
- Stability and activity less than noble metals but less expensive
- Ni most studied, high activity, deactivation and sintering is problem
- Ni supported on Al_2O_3, shows formation of $NiAl_2O_4$ leading to loss in activity
- Other supports for Ni /CeO_2 and La_2O_3, but CeO_2 - La_2O_3 not formed carbon
- Ni with oxidation state 2 or more favours complete combustion, dispersion of catalysts with different oxidation states depends on the synthesis process and the support properties
- Cu shown to have lower activity than Ni and can be used for lower temperature, support improves Al_2O_3 among best out of ZrO_2, SiO_2, TiO_2
- Fe and Co have performed better and less prone to deactivation and sintering, form metal exides with multiple oxidation states, various supports studied Al_2O_3, MgO, TiO_2
- Method of catalyst synthesis had a great impact on the characteristics
- Bimetallic catalysts with noble metal coated on non noble metal core were studied
- Pperovskites showed good catalytic activity, good stability and less prone to carbon formation, e.g. LaXO3 (X = Fe, Cu, Ga, Ni, Co) perovskites showed enhanced methane conversion and better stability, $LaNi_{1-x}Fe_xO_3$ showed high conversion and selectivity

PRATIBHA SHARMA, IIT Bombay

Non-noble metals definitely have a lower activity, have a lower conversion compared to the noble metals, but the advantage they enjoy is that they are less expensive. Among the non-noble metals nickel is the most widely studied one and it has a high activity as well as better conversion, but the problem that nickel catalysts face is the sintering and deactivation with the nickel when it is supported on alumina, then it reacts with the support.

So, nickel on alumina is used for the SMR catalyst as well, but nickel interacts with the alumina to form $NiAl_2O_4$ and it loses its activity. There are other supports which are also studied like nickel on ceria or La_2O_3 and among the two separately if we are using them as support; however, combined one being used as a support CiO_2 and La_2O_3. It is less prone to carbon formation. Nickel i exist in various oxidation state and any oxidation state higher than 2 or equal to 2 favour complete combustion, rather than the partial combustion.

So, here in the dispersion, how it is dispersed, the different active oxidation states, how it is being synthesized, what are the support properties all these affect the activity of the catalyst. Copper having a lower less expensive, but it shows catalytic activity lower than nickel and also it can be used for only lower temperature because of the lower poor thermal stability at higher temperature; however, that can be addressed if it is supported on alumina catalyst other than that the other supports which were studied are zirconia, silica and titania.

Iron and cobalt also perform better, but at the same time they are less prone to deactivation and sintering and they form metal oxides with multiple oxidation states. Fe_2O_3, Fe_3O_4, FeO are found to be like some of the oxidation state that perform better compared to the other oxidation state, and these can be on the various support like alumina magnesium oxide or TiO_2.
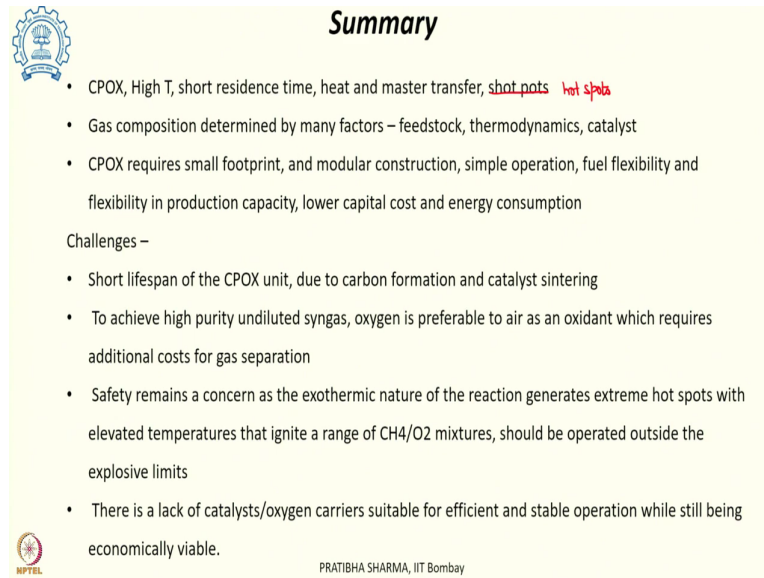
Now, in summarizing the non-noble part it is the method by which catalyst is being synthesized and that has an impact on the activity of the catalyst, how it is going to interact with the support, and how is the thermal stability, is it prone to deactivation or sintering or not. So, all these are dependent on how it is being synthesized, what is the size, what is the shape of the catalyst, what is the surface area. So, there are many factors which influence the conversion selectivity as well as the activity.

The option could be to reduce the cost at the same time to improve the activity use of bimetallic catalyst. So, we can combine noble and non-noble metals in such a way that noble metals are coated on to non-noble metal which is used in the core.

So, a core of non-noble metal and a shell of noble metal wherein we can reduce the use of noble metal, we can decrease the cost at the same time we can have the benefit of using noble metal. Other catalyst like perovskites, they also show good activity and stability and they are less prone to carbon formation. So, like the ABO_3, in a position La, on B position iron,

copper, nickel, cobalt. They have good catalytic activity and they show good conversion at the same time selectivity.

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Summary

- CPOX, High T, short residence time, heat and master transfer, shot pots *hot spots*
- Gas composition determined by many factors – feedstock, thermodynamics, catalyst
- CPOX requires small footprint, and modular construction, simple operation, fuel flexibility and flexibility in production capacity, lower capital cost and energy consumption

Challenges –

- Short lifespan of the CPOX unit, due to carbon formation and catalyst sintering
- To achieve high purity undiluted syngas, oxygen is preferable to air as an oxidant which requires additional costs for gas separation
- Safety remains a concern as the exothermic nature of the reaction generates extreme hot spots with elevated temperatures that ignite a range of CH4/O2 mixtures, should be operated outside the explosive limits
- There is a lack of catalysts/oxygen carriers suitable for efficient and stable operation while still being economically viable.

PRATIBHA SHARMA, IIT Bombay

To summarize this part, we have seen both the catalytic and non-catalytic partial oxidation. The biggest advantage of non-catalytic partial oxidation is the fuel flexibility i.e., any fuel can be used with the catalytic oxidation; however, the operating temperature gets lower down compared to the non-catalytic partial oxidation, the residence time is small, when it comes to partial oxidation the heat transfer and mass transfer could be a problem and there could be hotspot which could be formed in the reactor.

The gas composition which is obtained after the partial oxidation depends upon factors like what is the feedstock composition, thermodynamics is going to play important role in determining what is the gas output and the catalyst which is used. So, the catalytic partial oxidation, this is compared to SMR requires a smaller footprint, it can be in a modular construction, it is simple to operate, we can use other fuels as well other than methane and it can provide because it is a modular operation. So, it provides a flexibility in production capacity.

The capital cost requirement is lower and the energy consumption is lower because it is an exothermic process; however, there are challenges with the partial oxidation process like the lifespan of the partial oxidation is lower and these are the obvious regions, when you are using catalyst they are prone to carbon formation and sintering.

If we want to use; if we want to use air as an oxidant then the outlet gas stream will be diluted with nitrogen else we need to use oxygen and then we will require air separation unit that will add to the cost of production.

Since this is a oxidation method and it is an exothermic reaction the gases can react explosively and we have to operate outside these explosive limits. So, extreme hotspots highly elevated temperatures needs to be avoided, and the catalyst and oxygen carriers. So, still they are at the cost of the thermal stability the conversion and selectivity. So, appropriate catalyst support needs which is also at the time economically viable is required for efficient and stable operation of partial oxidation.

Thank you.