# Hydrogen Energy: Production, Storage, Transportation and Safety
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## Lecture - 14
## Hydrogen Production by Methane Decomposition

Today we will learn Hydrogen Production by Methane Decomposition. In the earlier lectures we have seen mostly the oxidative processes, wherein oxidant acts as a reactant. This process of methane decomposition is a non-oxidative process. So, here in when the hydrocarbon are subjected to high temperatures they decompose. Now how much amount of energy which will be required for the decomposition that depends upon, which type of hydrocarbon it is.

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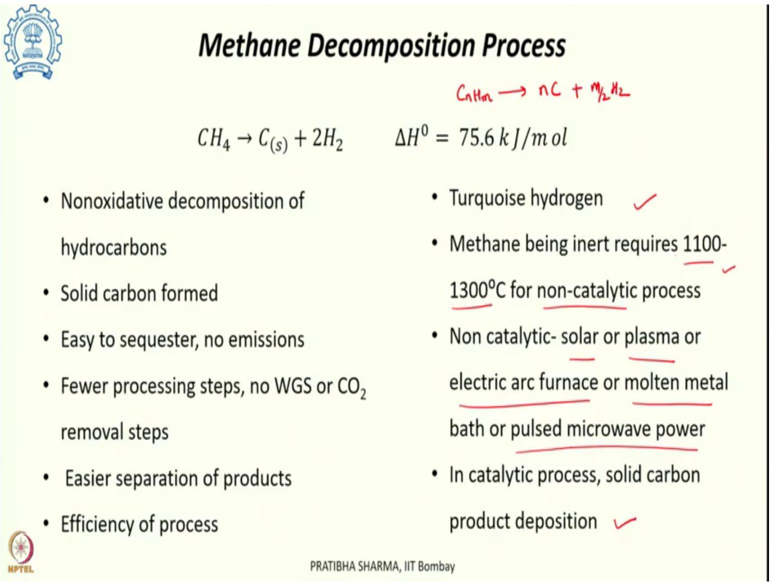

**Methane Decomposition Process**

$C_nH_m \longrightarrow nC + \frac{m}{2}H_2$

$CH_4 \rightarrow C_{(s)} + 2H_2 \qquad \Delta H^0 = 75.6\ kJ/mol$

- Nonoxidative decomposition of hydrocarbons
- Solid carbon formed
- Easy to sequester, no emissions
- Fewer processing steps, no WGS or $CO_2$ removal steps
- Easier separation of products
- Efficiency of process

- Turquoise hydrogen ✓
- Methane being inert requires 1100-1300°C for non-catalytic process ✓
- Non catalytic- solar or plasma or electric arc furnace or molten metal bath or pulsed microwave power
- In catalytic process, solid carbon product deposition ✓

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Like for example, we can write general equation for hydrogen decomposition as that any hydrocarbon will decompose to form solid carbon and hydrogen. The amount of energy that will be required for the reaction depends upon whether it is a saturated hydrocarbon or an unsaturated hydrocarbon. It is highest for saturated hydrocarbons; alkanes it is less for unsaturated hydrocarbon. In fact, it is exothermic for aromatics like acetylene or for benzene. So, the reactions are exothermic.

Now let us look at the methane decomposition process. Methane decomposes to give solid carbon and hydrogen. If we see the ΔH value, this is an endothermic reaction with delta H of

75.6 kilojoule per mole. If we look at the numbers as compared to SMR we can see that this is less endothermic and that endothermicity is because in methane it is a stable compound, it is inert, it is symmetric, there is lack of polarity and its electronic structure. There is no functional group as such this is stable and it requires energy for its decomposition.

And if we see the product which is formed is a solid carbon and this can also have a value and it can be used for various other applications. Since the product is solid carbon it is very easy to separate as compared to the products that we got in case of other processes like the reforming, those were gases whether carbon monoxide or carbon dioxide and we have to separate them and bulky separation processes were required and then to sequester them was complicated compared to the methane decomposition process.

Other than that, we are not getting any CO or $CO_2$ emissions in the process. So, the method is relatively simpler. The number of steps involved are less because we do not require a water gas shift or carbon dioxide removal step in the process. Since the products i.e., one product is gaseous product, another product is a solid product it is easier to separate. If we look at the efficiency of the process although it is less efficient typically if we compare it is 58% efficiency and this is similar to if we consider steam methane reforming with carbon capture use and sequestration.

The hydrogen which is produced using this method is called turquoise hydrogen. So, that is the color code which is assigned to the hydrogen produced using methane decomposition method. Now since this is inert, so it requires higher temperature for decomposition. Now if the process is a non-catalytic process then the required temperatures range from 1100 to 1300 degree centigrade for the decomposition of methane.

However, this required heat to take it to that temperature can be provided by means of either solar heating or through plasma in an electric arc furnace or using a molten metal in a molten metal bath or using pulsed microwave power. If the temperature is to be reduced at which this decomposition reaction occurs, in that case the catalyst is to be used.

So, the solid carbon in that case which is obtained that has a tendency towards depositing onto the catalyst. So, that is the basic challenge that we have already seen in the earlier methods also, that in any catalytic process the challenges of deactivation is always there.

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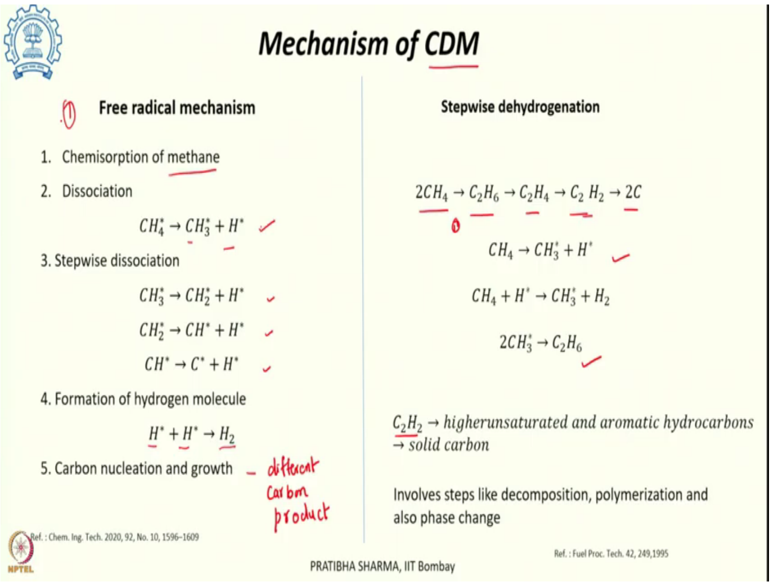

### Mechanism of CDM

① **Free radical mechanism**

1. Chemisorption of methane
2. Dissociation

$$CH_4^* \rightarrow CH_3^* + H^*$$

3. Stepwise dissociation

$$CH_3^* \rightarrow CH_2^* + H^*$$

$$CH_2^* \rightarrow CH^* + H^*$$

$$CH^* \rightarrow C^* + H^*$$

4. Formation of hydrogen molecule

$$H^* + H^* \rightarrow H_2$$

5. Carbon nucleation and growth – different carbon product

Ref. : Chem. Ing. Tech. 2020, 92, No. 10, 1596–1609

**Stepwise dehydrogenation**

$$2CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2\,H_2 \rightarrow 2C$$

$$CH_4 \rightarrow CH_3^* + H^*$$

$$CH_4 + H^* \rightarrow CH_3^* + H_2$$

$$2CH_3^* \rightarrow C_2H_6$$

$C_2H_2 \rightarrow$ *higherunsaturated and aromatic hydrocarbons* $\rightarrow$ *solid carbon*

Involves steps like decomposition, polymerization and also phase change

Ref. : Fuel Proc. Tech. 42, 249,1995

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Now, if we look at the mechanism of the decomposition reaction catalytic decomposition reaction, it is also in short written as CDM. So, there are two different mechanisms which are being proposed.

One is a free radical mechanism. So, the steps that are involved in the process are the methane which is reactant. On the surface of catalyst it gets chemisorbed and thereafter it undergoes a series of steps primarily a dissociation step wherein it dissociates to free radical methyl radical and H and thereafter in different steps it further undergoes dissociation producing $CH_2$ radical, CH radical and C.

Now, these H hydrogen radicals they combine to form hydrogen molecule and that gets released or desorbed from the surface. Thereafter the carbon which is formed in the process that undergoes nucleation and growth and resulting into different forms of carbons, different carbon products are obtained in the process and that all depends upon which type of catalyst we have used how much is the conversion, how is what is the activity. So, that carbon product is finally formed.

There is another mechanism which is being proposed for the catalytic decomposition of methane. Herein the methane undergoes a sequence of steps to finally, form solid carbon. In the first step it is converting into ethane and then this process of conversion the first step of conversion of methane to ethane that also involves several steps involving a dissociation of methane forming radicals and that reaction with methane to finally, form the ethane.

Thereafter, it undergoes other steps wherein when it forms an acetylene and finally, forms carbon that itself is a sequence of steps, where highly unsaturated and aromatic hydrocarbons result from acetylene and finally, leading to the formation of solid carbon. So, all these processes in the second method they involve a series of decomposition reactions, polymerization reactions and also phase change from gas to liquid to solid.

The mechanism 1 however, have received more acceptance compared to the mechanism 2.

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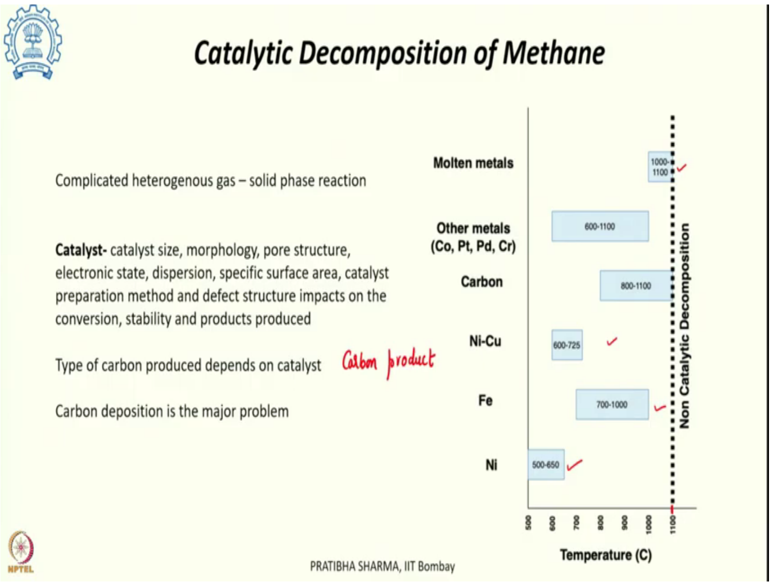

## Catalytic Decomposition of Methane

Complicated heterogenous gas – solid phase reaction

**Catalyst-** catalyst size, morphology, pore structure, electronic state, dispersion, specific surface area, catalyst preparation method and defect structure impacts on the conversion, stability and products produced

Type of carbon produced depends on catalyst Carbon product

Carbon deposition is the major problem

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Now, if the catalytic decomposition of methane if we see this is a complicated heterogeneous gas solid phase reaction and depending upon what is the catalyst being used, there are different in different temperatures these catalyst provides reasonable activity. For example, if nickel is used as a catalyst the region in which its activity is less than 600 degree centigrade, wherein it has a very high activity, but it deactivates very fast.

So, the thermal stability of nickel is poor. Other catalyst like iron it can operate in a temperature range of 700 to 1000 degree centigrade. There are bimetallic catalyst which can be used, then carbon itself can be used as a catalyst. However, they work at a higher temperature 800 to 1100 degree centigrade.

So, the non catalytic decomposition as we mentioned the temperature required is 1100 degree centigrade. So, without any catalyst and then we can use different molten metal's or salt; however, they operate at a higher temperature for the decomposition. Now when this is a catalytic method, there are lot many factors of the catalysts they are responsible for the conversion or the stability of providing the required yield.

So, like the catalyst size, its morphology, its pore structure like pore volume, electronic state, how is well it is dispersed over the support? What is the specific surface area available where in the reactants can adsorb to form the products? What is the method of catalyst preparation? Whether it is wet impregnation, whether it is fusing, whether it is co-precipitation all that impacts also the defect structure of the catalyst that impacts how much will be the conversion of reactants?

What will be the thermal stability of the catalyst? and the selectivity towards the product here the product produced, the yield of hydrogen which is obtained in the process and which type of carbon which will be produced in the process also depends upon the catalyst. It is important here because the carbon which is produced the carbon product which is obtained that itself can be used. So, the byproduct which is a byproduct in the process can be used for various applications.

This method of methane decomposition that was actually well known for from in fact, very long it was about in 1900s this method was started and the method of decomposition was called thermal black process, where carbon black was produced for various applications.

However, thereafter more efficient processes they took over and this method was not being used. Recently this method has also regained an interest because of the convenience lesser number of steps, the easy separation of the product and hydrogen. So, this method has again gained an interest. But, with the catalytic decomposition the major problem still remains that of carbon deposition.

Among the different catalyst that can be used for the decomposition reaction of methane the most widely studied ones are nickel, cobalt and iron. Now these transition metal catalysts when they are used they have a very good activity. They have moderate sort of operating conditions. So, not very high temperatures are required.

At the same time they give certain valuable carbon products which can be used for other applications. Transition metals they have a partially filled 3D orbital and that promotes the methane decomposition. Electron transfer takes place from the CH bond and thereby a better conversion can be achieved with the transition metals. Nickel this is the most active one, but it deactivates very fast and its deactivation like it can be used only below 600 degrees centigrade.

So, it is not thermally stable compared to nickel, cobalt has a lower activity, but it has a better thermal stability and the cost is however high, it has a toxicity. So, then iron is the next catalyst which is studied and that has a higher resistance towards coke deposition and it has a better thermal stability as well. It can be used in a temperature range of 700 to 1000 degree centigrade.

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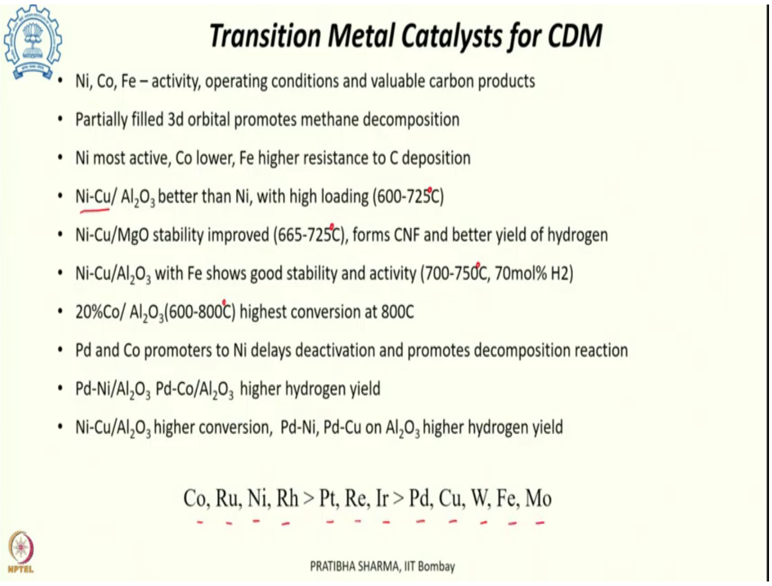

### Transition Metal Catalysts for CDM

- Ni, Co, Fe – activity, operating conditions and valuable carbon products
- Partially filled 3d orbital promotes methane decomposition
- Ni most active, Co lower, Fe higher resistance to C deposition
- Ni-Cu/ $Al_2O_3$ better than Ni, with high loading (600-725°C)
- Ni-Cu/MgO stability improved (665-725°C), forms CNF and better yield of hydrogen
- Ni-Cu/$Al_2O_3$ with Fe shows good stability and activity (700-750°C, 70mol% H2)
- 20%Co/ $Al_2O_3$(600-800°C) highest conversion at 800C
- Pd and Co promoters to Ni delays deactivation and promotes decomposition reaction
- Pd-Ni/$Al_2O_3$ Pd-Co/$Al_2O_3$ higher hydrogen yield
- Ni-Cu/$Al_2O_3$ higher conversion, Pd-Ni, Pd-Cu on $Al_2O_3$ higher hydrogen yield

Co, Ru, Ni, Rh > Pt, Re, Ir > Pd, Cu, W, Fe, Mo

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So, the problem with nickel which is that it is not very stable. Bimetallic catalyst can be used along with nickel like copper can be used on an alumina support that shows better stability compared to the nickel. However, the loading required is higher and it operates better in 600 to 725 degrees centigrade range. When nickel copper on magnesium oxide is used. It has a better stability in the range of 665 to 725 degrees centigrade and it forms carbon nano fibers and also provides a better yield of hydrogen.

Similarly, nickel-copper along with iron on an alumina support has a good stability in the range of 700 to 750 degrees centigrade and it can even give yields of 70 mol% of hydrogen, cobalt on alumina can be used in the range of 600 to 800 degrees centigrade and it has the highest conversion found at 800 degrees centigrade.

Other metals like palladium on nickel or palladium on cobalt have also been used and they provide a higher yield. Palladium also acts as a promoter. So, palladium and cobalt they can be used as a promoter in case of nickel and that delays the deactivation process and also enhances the conversion. So, promotes the decomposition reaction as well.

Now if we look at the order of activity of the various metals, then we can see that cobalt, ruthenium, nickel, rhodium have the activity higher than the platinum, rhenium, uranium, iridium and that is even higher than palladium, copper, tungsten, iron and molybdenum.

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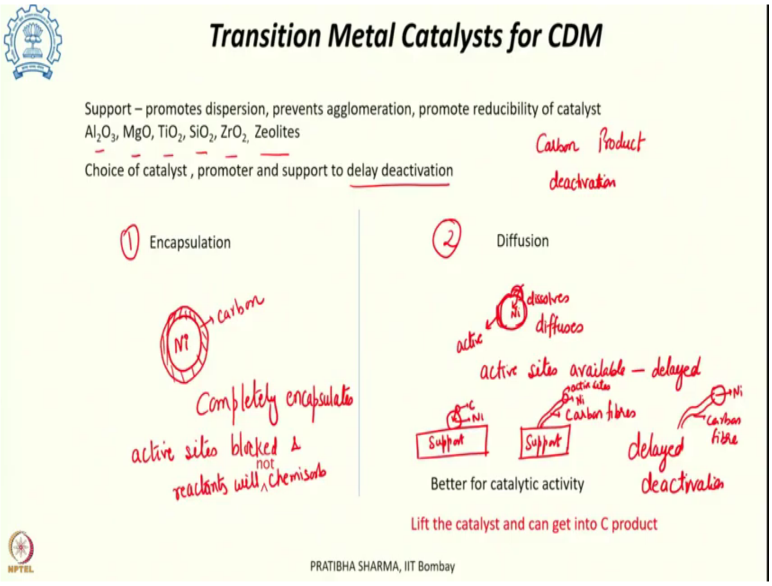

## Transition Metal Catalysts for CDM

Support – promotes dispersion, prevents agglomeration, promote reducibility of catalyst

$Al_2O_3$, MgO, $TiO_2$, $SiO_2$, $ZrO_2$, Zeolites

Choice of catalyst , promoter and support to delay deactivation

Carbon Product deactivation

① Encapsulation

Completely encapsulate

active sites blocked & reactants will not chemisorb

② Diffusion

active sites available – delayed

delayed deactivation

Better for catalytic activity

Lift the catalyst and can get into C product

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Now, catalyst definitely plays an important role, but support also is equally important because that provides a good dispersion, and better dispersion will prevent agglomeration. It will even promote reducibility of the catalyst because many of the catalyst like nickel is used in nickel oxide form and it has to be reduced to metallic nickel before it reacts. So, that is the active site of the catalyst.

So, the support can promote the reducibility of the catalyst. Now various support materials have been seen act very promising like alumina, magnesium oxide, $TiO_2$, $SiO_2$ , $ZrO_2$ and the zeolites. Unlike the other reforming methods in the catalytic decomposition of methane the deactivation is inevitable. The reason is the product is the carbon and that carbon which is obtained as the product it deposits onto the surface of the catalyst and that finally, deactivates.

So, deactivation is a must process in the decomposition of methane. However, the requirement is an appropriate choice of catalyst, promoter and support can delay this deactivation. So, that is what is required. Now this deactivation can occur through different routes. One method could be where the catalyst let us say it is nickel because of the carbon formation that carbon forms uniformly all across the surface of the catalyst.

So, it completely covers the catalyst. It completely encapsulates the catalyst this is what is not desirable. So, in that case the active sites of the catalyst are blocked. So, active sites are blocked by the carbon formation and that will not allow the reactants to chemisorb on to the surface. Another method of deactivation could be wherein on the catalyst the carbon which is deposited first dissolves into the catalyst and diffuses inside. Here in much of the surface area is still left out wherein there is no carbon deposit.

So, this still remains active where the carbon deposition has not occurred. So, if there is free surface or active sites available even after carbon deposition which diffuses inside, then the catalyst deactivation gets delayed. In some of the cases what happens is on the support when there is a catalyst sitting the carbon which is formed onto the surface that starts to get into the catalyst and at times after sometime that lifts up the catalyst forming some sort of structures.

So, the catalyst here got lifted from the support. At this condition also it has surface which is having active sites and still it can promote the decomposition of methane. So, compared to the two different deactivation methods which is encapsulation and diffusion, in the second method where the carbon diffuses inside the nickel and lifts it up from the support forming different carbon structures like carbon fibers. The catalyst still have certain active sites present on the surface which can still allow the decomposition reaction to take place.

So, in case when the diffusion is the method of carbon deposition on the catalyst then there is a delayed deactivation of the catalyst which results and this is better in terms of catalytic activity. At times the problem is that this carbon which gets deposited on the surface like the carbon fibers, this get removed from the substrate.

So, it forms the product and that metal which is present at the top, let us say this is the carbon fiber and the metal which is nickel here which is present at the tip of the carbon fiber that also enters into the product, bulk product that is carbon and this if the metal is used is toxic like cobalt then that can lead to the toxicity of the carbon product and that can affect the downstream applications where it is being used.

So, the transition metals we have seen they have very good activity compared to them the carbon based catalyst which is another category of catalyst that can be used for catalytic decomposition of methane. They have a lower activity and since they have a lower activity, so they operate at a higher temperature.

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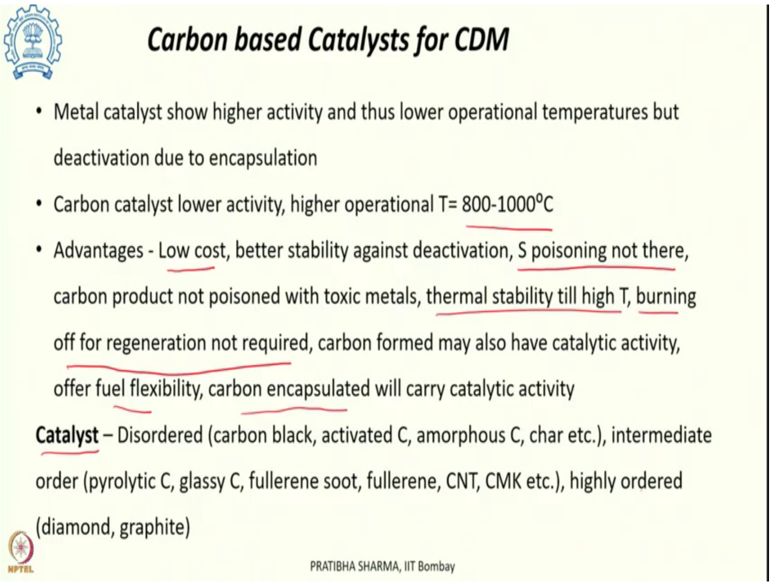

### Carbon based Catalysts for CDM

- Metal catalyst show higher activity and thus lower operational temperatures but deactivation due to encapsulation
- Carbon catalyst lower activity, higher operational T= 800-1000$^{o}$C
- Advantages - Low cost, better stability against deactivation, S poisoning not there, carbon product not poisoned with toxic metals, thermal stability till high T, burning off for regeneration not required, carbon formed may also have catalytic activity, offer fuel flexibility, carbon encapsulated will carry catalytic activity

**Catalyst** – Disordered (carbon black, activated C, amorphous C, char etc.), intermediate order (pyrolytic C, glassy C, fullerene soot, fullerene, CNT, CMK etc.), highly ordered (diamond, graphite)

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So, the carbon catalyst they operate at higher temperature in the range of 800 to 1000 degree centigrade, but they have a large number of advantages also. The cost of these carbon catalyst is lower; they have a better stability towards deactivation. Unlike the metal catalyst sulfur poisoning or if there are certain impurities present in the feedstock.

That poisoning is not there or it is resistant towards the Sulphur poisoning. The carbon product as we have seen in the transition metals. When it comes into the carbon product then if the transition metal is toxic, then the product get poisoned with that toxic metal. If we use carbon based catalyst that problem is not there. They have a higher thermal stability and they can be used at higher temperature.

We will see that the regeneration of the catalyst after some time. So, the burning of the catalyst or the carbon which is deposited to regenerate the catalyst is not required when it is carbon based catalyst. At the same time the carbon product which is formed in the process that also has a catalytic activity. We can use a variety of fuel in the case because the deactivation is comparatively lower. It has a better stability.

Carbon if it is encapsulated like it happens in case of transition metals we have seen just now. If it is encapsulated in the carbon product still it will carry that catalytic activity. So, there are many advantages of using carbon based catalyst.

The catalyst which are there include the disordered carbon, carbon black, activated carbon, amorphous carbon, char, acetylene black and then there are carbon structures which are intermediate having intermediate order, pyrolytic carbon, glassy carbon, fullerene soot, fullerene, CNT, CMK etc. and then comes the class of highly ordered carbon which is graphite and diamond.

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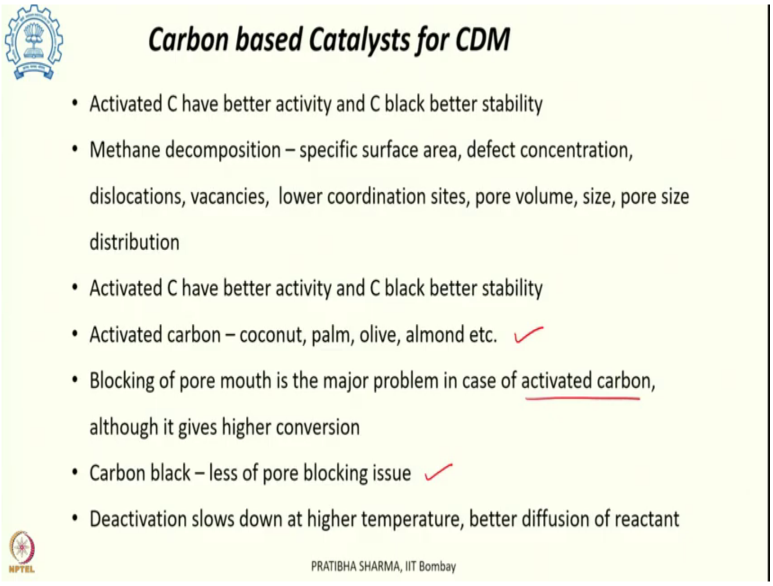

## Carbon based Catalysts for CDM

- Activated C have better activity and C black better stability
- Methane decomposition – specific surface area, defect concentration, dislocations, vacancies, lower coordination sites, pore volume, size, pore size distribution
- Activated C have better activity and C black better stability
- Activated carbon – coconut, palm, olive, almond etc. ✓
- Blocking of pore mouth is the major problem in case of activated carbon, although it gives higher conversion
- Carbon black – less of pore blocking issue ✓
- Deactivation slows down at higher temperature, better diffusion of reactant

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It has been observed that the disordered carbon has a better activity compared to the ordered structures. So, disordered have the highest activity compared to carbon structures having intermediate order and the highly ordered ones they have the lowest activity. Among the most studied carbon based catalyst activated carbon and carbon black they are showing activity and stability.

If we compare the two then activated carbon has a better activity and carbon black has a better stability. When it comes to use of these disordered catalysts carbon catalyst then for methane decomposition the specific surface area, defect concentration, what are the dislocations, vacancies, the lower coordination sites, pore volume, the size of the catalyst, their pore size distribution all impacts the methane decomposition process.

Activated carbon from which source they are arising. They are being prepared which raw material whether it is coconut shell or palm or olive or almond that affects the final product which is formed. The major problem that is observed when it is activated carbon although they have a better activity that could be seen is the pore blocking and this reduces the area which is available for the methane decomposition.

So, the external surface area if it is higher then it will allow more of active site for the decomposition. Now if pores also available the inside pore volume can also be used for decomposition of methane. However, if the mouth of the pore itself gets blocked then the activity of that material reduces and that is the major problem that has been seen in case of activated carbon.

Although it could have given a higher conversion, but because of this problem compared to the theoretical conversion the achieved conversions are typically lower. In case of carbon black this issue is relatively less and the block blocking of the pores is comparatively lower. Now this deactivation which takes place with these materials however is found to reduce at a higher temperature.

The reason is if the pores are partially blocked then the reactant diffuses in a better way at a higher temperature and that could lead to decomposition of the reactant. Now the, which product is obtained? Carbon product is obtained that also is important because that can be used for various applications and some of the exotic form of carbon they find their applications in various energy storage devices or various catalytic processes.

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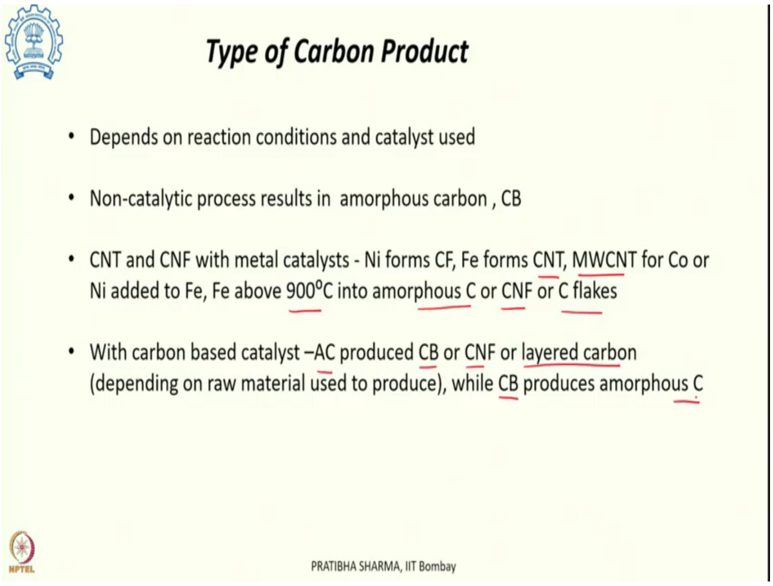

## Type of Carbon Product

- Depends on reaction conditions and catalyst used
- Non-catalytic process results in amorphous carbon , CB
- CNT and CNF with metal catalysts - Ni forms CF, Fe forms CNT, MWCNT for Co or Ni added to Fe, Fe above 900$^{o}$C into amorphous C or CNF or C flakes
- With carbon based catalyst –AC produced CB or CNF or layered carbon (depending on raw material used to produce), while CB produces amorphous C

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Now, which type of carbon will be obtained that depends upon what are the reaction conditions and also which catalyst is being used like non-catalytic processes they mostly result into amorphous carbon or carbon black. If it is nickel then it is carbon fibers. If iron then carbon nanotubes, with cobalt or nickel being added to iron it is multi walled carbon nanotubes.

However, with iron when it is above 900 degree centigrade then it forms either amorphous carbon, carbon nano fibers or carbon flakes. With carbon based catalyst like activated carbon if it is used as a catalyst it produces carbon black or carbon nano fiber or layered carbon and that depends upon what is the source from which we have got the activated carbon. The raw material used to produce activated carbon.

If it is carbon black used as a catalyst it produces amorphous carbon. So, depending on what catalyst is being used? The type of carbon product may vary. Since the catalyst deactivation as we know it is inevitable. In SMR if we talk about the catalyst life of say 5 years of continuous operation, here the life of catalyst is very small. It is even less than 10 hours. So, it is few hours of activity, because carbon is the major product which is obtained.

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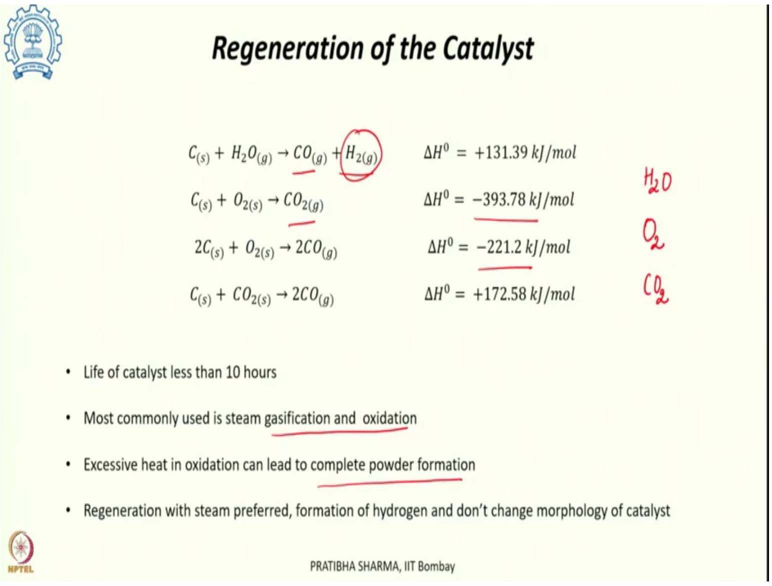

## Regeneration of the Catalyst

$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$ $\Delta H^0 = +131.39\ kJ/mol$ $H_2O$

$C_{(s)} + O_{2(s)} \rightarrow CO_{2(g)}$ $\Delta H^0 = -393.78\ kJ/mol$ $O_2$

$2C_{(s)} + O_{2(s)} \rightarrow 2CO_{(g)}$ $\Delta H^0 = -221.2\ kJ/mol$

$C_{(s)} + CO_{2(s)} \rightarrow 2CO_{(g)}$ $\Delta H^0 = +172.58\ kJ/mol$ $CO_2$

- Life of catalyst less than 10 hours
- Most commonly used is steam gasification and oxidation
- Excessive heat in oxidation can lead to complete powder formation
- Regeneration with steam preferred, formation of hydrogen and don't change morphology of catalyst

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So, if it is the activity is lost then it can be regained or regenerated by means of various processes like carbon in the presence of steam can undergo gasification or it can undergo partial or complete oxidation or it can be in presence of carbon dioxide can convert into CO. So, in this process the catalyst can get regenerated and the surface carbon converts into CO or $CO_2$ with steam it also results in an additional product which is hydrogen.

So, the most commonly used method for regeneration is gasification as well as oxidation, but when it is oxidation we can see that this is an exothermic reaction and if it is excessive heat is being produced it can lead to sintering of the catalyst and at times it can be a complete powder formation. So, regeneration with steam in that case is preferred. At the same time if it is with steam we can get additional hydrogen as a product and the surface morphology of the catalyst also remains unchanged with the use of steam.

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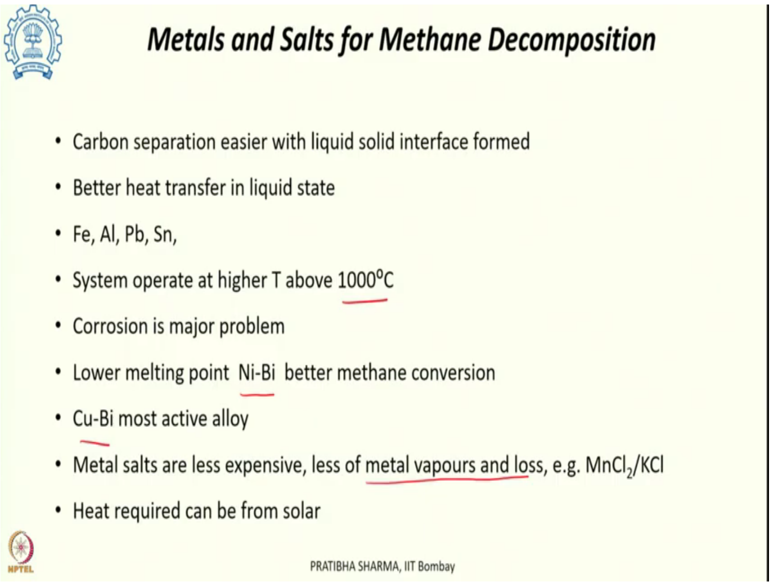

## Metals and Salts for Methane Decomposition

- Carbon separation easier with liquid solid interface formed
- Better heat transfer in liquid state
- Fe, Al, Pb, Sn,
- System operate at higher T above 1000°C
- Corrosion is major problem
- Lower melting point Ni-Bi better methane conversion
- Cu-Bi most active alloy
- Metal salts are less expensive, less of metal vapours and loss, e.g. $MnCl_2/KCl$
- Heat required can be from solar

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If metals or salts are used in molten state that can also decompose methane producing hydrogen and carbon product. This is easier to separate carbon in this particular method where in either molten metal or molten salts across that methane is being bubbled producing hydrogen and solid carbon.

Now, since these are in different states one is in liquid state the molten metal. Carbon obtained is in solid state and hydrogen in the gaseous state. It is easier to separate carbon and hydrogen, the products in this method. Because the molten metals are in the liquid state there is better heat transfer which can be achieved the different metals which can be used includes iron, aluminum, antimony, lead.

But, these systems they operate at a higher temperature above 1000 degree centigrade and there are corrosion related challenges in the process. Now since the temperature are higher, low melting point materials are considered like nickel and bismuth, copper and bismuth. They have a good activity at the same time can be operational at a lower temperature compared to molten metals, metal salts they are less expensive.

At the same time the problem associated with the loss of metals is reduced, when metal salts are used like $MnCl_2$ or KCl and the heat which is required to take it to higher temperatures can be provided by means of solar heating. On the process there are effect of different parameters. So, if we have seen that the methane decomposition reaction is an endothermic process. So, it is preferred at a higher temperature.

But, at higher temperature deactivation will be higher and will also result into sintering. It is preferred at a lower pressure. Gas hourly space velocities if these are higher, then that will reduce the residence time and thus the hydrogen produced will also reduce, which will also increase into the catalyst deactivation because there is very less time for the carbon product to diffuse inside the catalyst. So, it will basically encapsulate the catalyst leading to deactivation.

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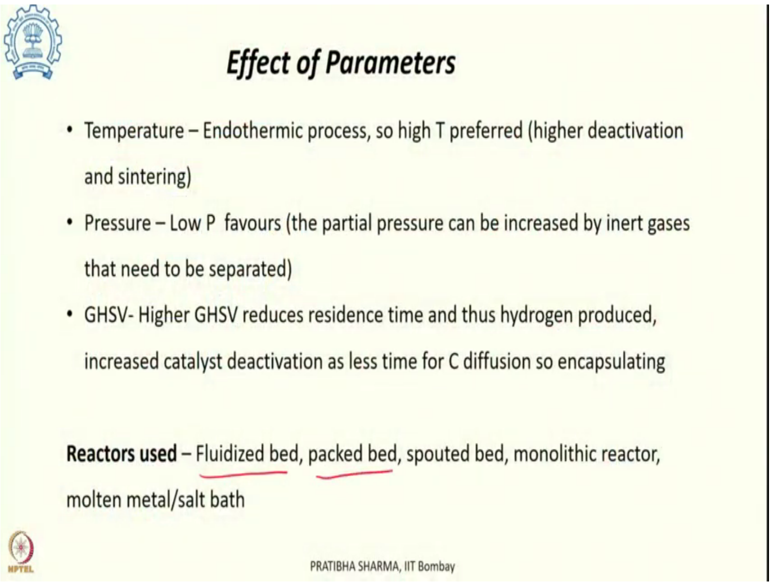

## Effect of Parameters

- Temperature – Endothermic process, so high T preferred (higher deactivation and sintering)
- Pressure – Low P favours (the partial pressure can be increased by inert gases that need to be separated)
- GHSV- Higher GHSV reduces residence time and thus hydrogen produced, increased catalyst deactivation as less time for C diffusion so encapsulating

**Reactors used** – Fluidized bed, packed bed, spouted bed, monolithic reactor, molten metal/salt bath

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Now, various types of reactors they are used fluidized bed, packed bed, spouted bed, monolithic reactor, molten metal or salt bath are used for CDM process. Primarily fluidized bed is being used because this allows easy flow of gases, uniform flow, uniform temperature, reactants and the catalyst can be easily supplied and taken away from the bed.

Packed bed has its own disadvantage, because the blocking of the pores is more severe in case of packed bed.

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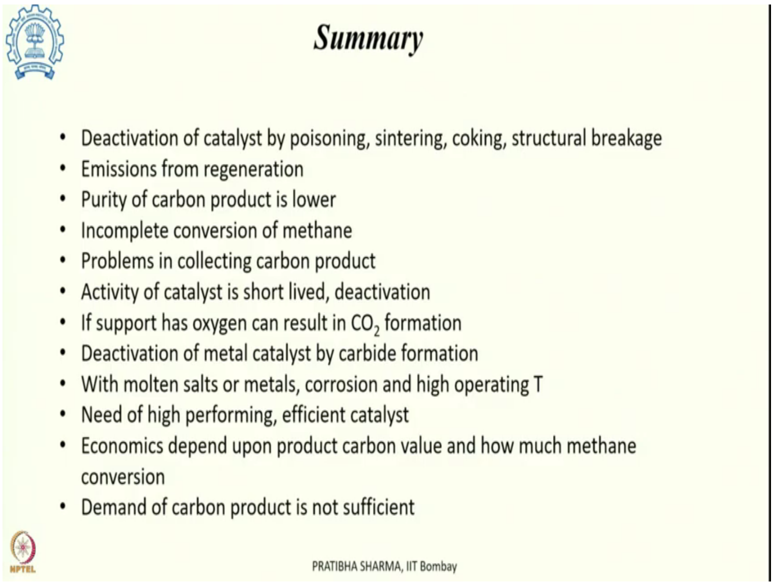

## Summary

- Deactivation of catalyst by poisoning, sintering, coking, structural breakage
- Emissions from regeneration
- Purity of carbon product is lower
- Incomplete conversion of methane
- Problems in collecting carbon product
- Activity of catalyst is short lived, deactivation
- If support has oxygen can result in $CO_2$ formation
- Deactivation of metal catalyst by carbide formation
- With molten salts or metals, corrosion and high operating T
- Need of high performing, efficient catalyst
- Economics depend upon product carbon value and how much methane conversion
- Demand of carbon product is not sufficient

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So, this method is of hydrogen production is not new, but still it is not being used on a industrial scale for hydrogen production. There are several challenges associated. To summarize those challenges the major problem is of catalyst deactivation which could be either because of poisoning, sintering, coking or breaking up of the catalyst.

At the same time the advantage of the process was that the method do not releases emissions. But, when we regenerate the catalyst when we burn off the catalyst CO or $CO_2$ is again released. So, the advantage is lost in the process. The purity of carbon product which is obtained is also lower. Incomplete conversion of methane also results. There are problems associated with collecting carbon separating it from the catalyst. At the same time because the activity of the catalyst is very short lived.

So, deactivation and then regeneration is essentially required. If the support it is having certain amount of oxygen then there will be $CO_2$ emissions during the conversion process and if it is $CO_2$ emission as well as when we are burning off the catalyst then the hydrogen product stream gets diluted with these emissions and then purification is required. In case of molten salts or metals corrosion as well as high operating temperature is the challenge.

And the requirement is that new catalyst which are highly efficient. They have reduced sintering and deactivation are required. When it comes into economics of the process that depends upon the conversion of methane at the same time what is the value of the carbon product which is obtained in the process. Currently if we see the demand of the product which is not very high, but it is expected that demand may grow and with the better catalyst this method could be commercialized. So, that is about the decomposition of methane process.

Thank you.