Nano Structured Materials-Synthesis, Properties Self Assembly and Applications

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Module - 4
Lecture - 29
Photocatalysis – I

Welcome back to this course on nanostructured materials, synthesis, properties, self assembly and applications. Today, we are going to start the first lecture of module 4. And we are going to discuss the subject area of photocatalysis. And we have 3 lectures on photocatalysis A in this module. And today will be the first lecture of photocatalysis.

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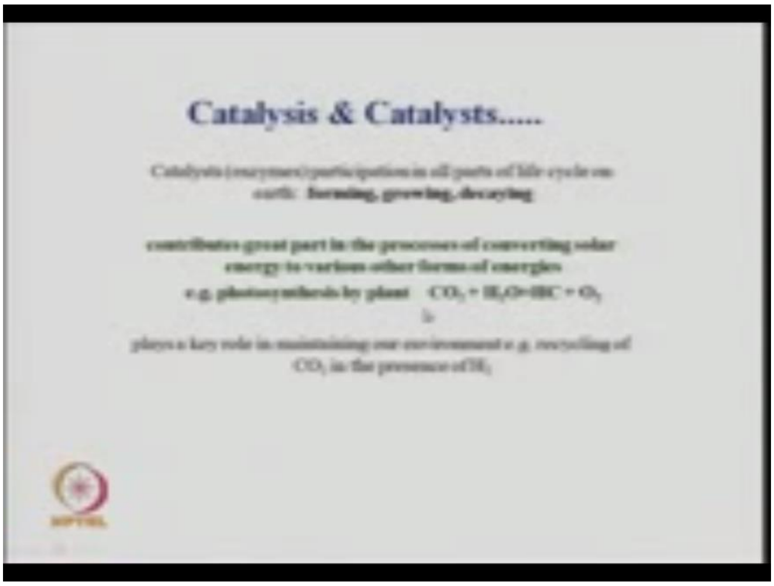

Catalysis & Catalysts.....

Catalysts (enzymes) participation in all parts of life cycle on earth: **forming, growing, decaying**

contributes great part in the processes of converting solar energy to various other forms of energies

e.g. photosynthesis by plant $CO_2 + H_2O = HC + O_2$

plays a key role in maintaining our environment e.g. recycling of CO_2 in the presence of H_2

So, before we go to photocatalysis, briefly we want to look at what is catalysis and what are catalyst? So, if you look around in all the leaving being an life processes around us lot of enzymes are participating and in all parts of the cycle of life. And these enzymes are nothing but catalyst and they are being used for the formation, the growth and the decay of these leaving organisms. And are part of the life cycle with of all leaving a creatures and flora and fauna on this a planet and elsewhere too. Now, the catalyst and catalysis contribute rate part in the processes of converting solar energy to various other forms of energies.

So, for example, all our food which is the plants and all the agricultural products are basically grown the hydrocarbons or the carbohydrates are made in the presence of solar radiation by photosynthesis by the plant. So, you convert carbon dioxide and water in the atmosphere to hydrocarbons which is food and oxygen is generated. So, this photosynthetic process involves several catalytic a cycles and is a very important reaction mechanism which people have understood over large number of years. Now, the catalyst also plays a important role in maintaining our an environment example recycling of carbon dioxide in the presence of hydrogen. So, the carbon dioxide emissions are converted to other forms of carbon hydrogen compound or carbon hydrogen oxygen based compounds by several catalyst and several are natural processes.

And now, there is tremendous interest in research and development of technologies which convert carbon dioxide produced in our atmosphere into carbohydrates through catalyst. So, this is these are some of the most important processes we are talking about we are talking about the life processes. We are talking about photosynthesis one of the most important process for maintaining life on the planet. And we are talking of reducing carbon dioxide in the environment and bring down to the pollution in the environment. So, in all these important global processes, catalyst play a very important role. If you look at the importance based on the chemical industry we can see the there is an annual sale of catalyst around 2 billion dollars.

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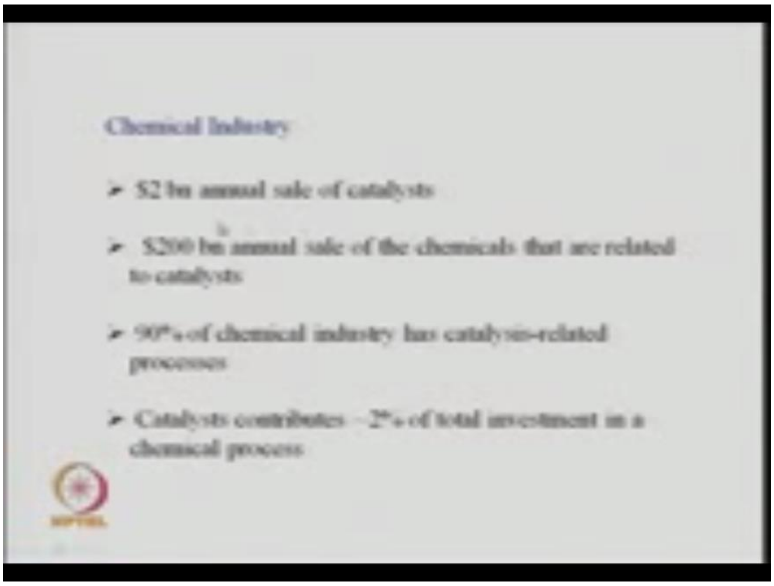

Chemical Industry

- $2 bn annual sale of catalysts
- $200 bn annual sale of the chemicals that are related to catalysts
- 90% of chemical industry has catalysis-related processes
- Catalysts contributes ~2% of total investment in a chemical process

And if you look at chemicals that are all related to catalyst not exactly catalyst then the sale go even 100 times more. So, it is 200 billion dollars is the annual market for chemicals that are related to catalyst 90 percent of chemical industry has processes which are catalytic which have catalyst during someway somewhere in the process. So, chemical industry uses a lot of catalysts in their technology. And overall 2 percent of the total investment in a chemical process in chemical plant is towards catalyst.

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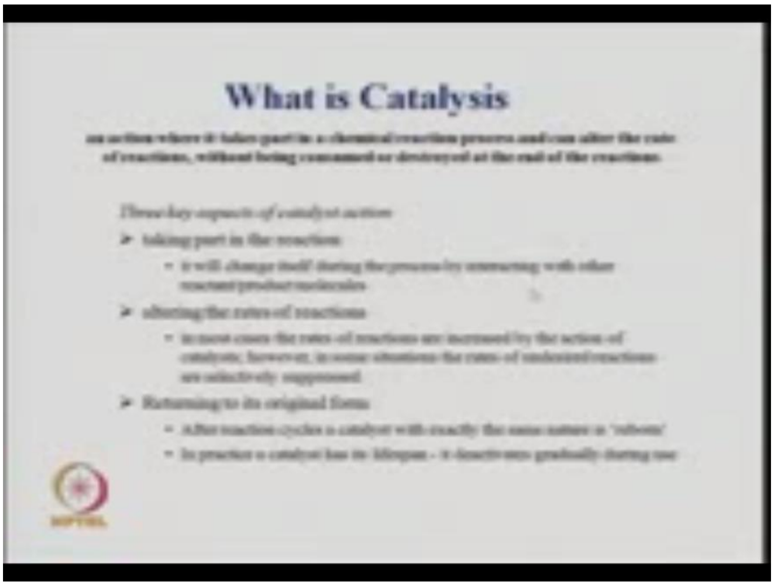

What is Catalysis

So, what is catalysis? This is brief introductory few points, which everybody at this level we taking this course probably has read somewhere or the other. But it is good to go over few of the key concepts of catalysis before we go to photocatalysis. So, what is catalysis? It is an action where part of in where this action takes part in a chemical reaction. And can alter the rate of the reaction without being consumed or destroyed at the end of the reaction. So, the catalyst is actually going to take part in the reaction but is not going to be used up at the end. And during this reaction the reactants are going to be converted into products there are 3 key aspects of the action of catalyst. It takes while it takes part in the reaction it will change itself during the process by interacting with the other reactant a product molecules.

And then it will be regenerate it at the end of the reaction it alters the rates of the reaction in most cases the rates of the reactions are increase. But in some cases the rate of some reaction which are not desirable can also we decreased. And here the catalyst are also called as catalytic poisons returning to it is a original form. So, its takes part in the reaction it alters the rate of reaction, and finally it has to return to its original form. So, after reaction the catalyst with the exactly the same nature is reborn or regenerate it an in actual practice. However after going through few 100 cycles or few thousand cycles which depends on each catalyst the activity of the catalyst goes down and. So, every catalyst has a live span and how good is your catalyst is, dependent on how long is this live span for how many cycles the catalyst can function without getting the tire orated. So, that is an important part of the, a catalyst and industrial catalyst has to be conical and hence should be to reused for a large number of cycles.

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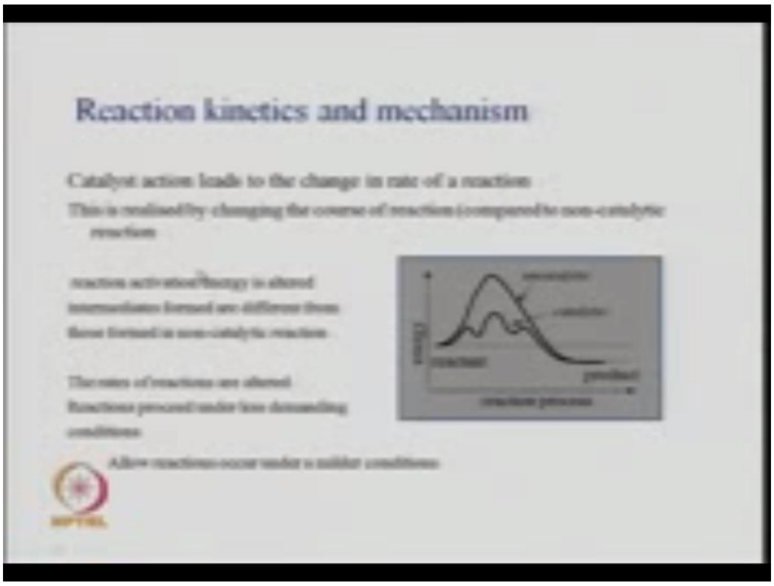

Reaction kinetics and mechanism

Catalyst action leads to the change in rate of a reaction

This is realised by changing the course of reaction (compared to non-catalytic reaction

Now the reaction kinetics and mechanism how does a catalyst actually change the rate of a reaction. And if you want to understand the change in the rate of a reaction compare to a process which is not using a catalyst. Then you can look at this plot, which is a very important plot in the subject of catalysis where you are looking at the change in the energy of the reactant and during the reaction process. So, the as the reaction is proceeding if you have no catalyst then the energy profile is given by this stock curves. So, as the reaction is progressing the energy is increasing goes over a maximum and then decreases and finally, you get the product. And so the energy of the product is lower than the energy of the reactant and this difference in energy between the reactant. And the product is the delta g of the change in free energy or change in enthalpy depending on what you are plotting on the y axis.

So, this delta g of reaction is given by the difference in a energy of reactant of product. But another important thing is how high is this maximum compare to what was the original energy of the reactant and this difference is called the activation energy. And so for the reactant to become a product it has to go through this maximum. So, it has to gain energy which is equivalent to this difference in a energy. And this difference in energy from this maximum to the energy of the reactant is called the activation energy or the activation barrier. And the reactant has to cross over the activation barrier to form the product. Now in a uncatalytic process where there is no catalyst involved this is the profile if you add a catalyst then the profile gets changed.

And you may have a maximum which is much lower in energy than the maximum in the uncatalytic process. So, what has happened is the activation energy of the catalytic process has been reduced by the catalyst. And this is the key concept of the kinetics in the presence of the catalyst the activation energy is decreased when the catalyst is present. Or you may know that there is no change in the free energy of the reaction, because that is given by the difference in the reactant and product energy and. This difference remains constant whether you use a catalyst or you do not use a catalyst a. So, this maximum in the catalytic process is much lower than the maximum in the uncatalytic process which means the activation barrier is reduced.

Now, you can see several maxima’s here. So, you may have one 2 3 activated complexes and this, the situation of the molecule at this energy. If you can find out what is a structure of the molecule at this stage. Then that is called the activated complex and the structure of the activated complex you can think about it or the transition state or in between 2 such small maximums you see there is a valley is the minimum. And there is another minimum here and these are called intermediates. So, in catalytic process you not only lower the activated the activation energy. But you may also end of with a intermediate states and the intermediates can be isolated. They may be stable for a short amount of time and can be isolated or scene spectroscopically their signatures can be seen spectroscopically. So, overall the reaction activation energy is altered intermediate formed are different from those noncatalytic reaction.

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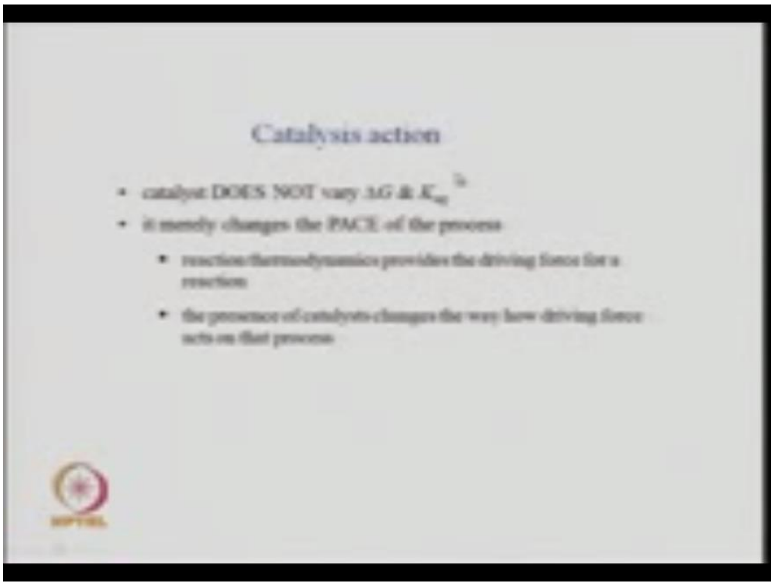

Catalysis action

- catalyst DOES NOT vary ΔG & K_{eq}
- it merely changes the PACE of the process
    - reaction thermodynamics provides the driving force for a reaction
    - the presence of catalysts changes the way how driving force acts on that process

And the reactions proceed under less demanding conditions. So, you can do reactions much more easily presence of the catalyst we may as already mentioned the catalyst does not vary the change in free energy. And the equilibrium constant is related to we change in free energy and since the free energy does not change whether you are doing catalytic reaction or a noncatalytic reaction. Hence the equilibrium constant is also does not change in the presence of catalyst, what the catalyst does is merely change the phase of the process of the rate of the reaction. And the 2 points which one has to remember in catalysis the thermodynamics provides the driving force for a reaction. And the presence of the catalyst changes the way how the driving force acts on that process. So, the driving force is the delta G and the rate of the reaction using a lower activation energy is the change that catalyst provide to how the driving force will act on that process.

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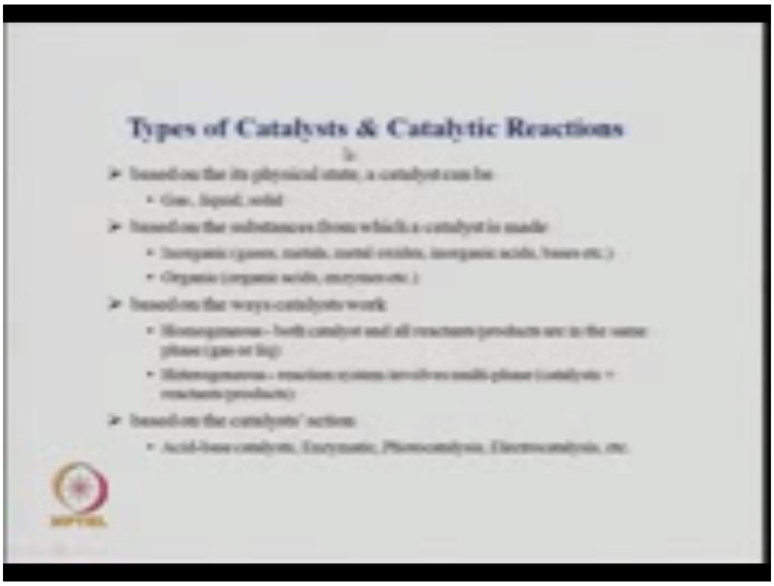

Types of Catalysts & Catalytic Reactions

Now, there are different types of catalyst and catalytic reactions if based on its physical state whether it is a gas liquid. Or solid you can have different type of catalyst then based on the nature of the substances whether it is organic compounds or inorganic compound. You have a inorganic catalyst; you have organic catalyst all the enzymes in our body are organic. So, they act as organic catalyst, but their can we saw from inorganic metal item containing enzymes also there are enzymes where you have some inorganic part also in enzymes. Now, depending how the catalyst works whether it works in solution in with another ion or in solvent where it is miscible then you call it a homogeneous catalyst. Similarly, in the gas phase if everything is the gas the catalyst is gas and the reactants are gases that is also homogeneous catalytic process.

Whereas, heterogeneous process involves more than one phase you have a catalyst which may be is solid. And you may have reactants or products which are in solution or which are liquids. So, when you have 2 or more types of phases then it is called a heterogeneous catalysis. So, you have homogeneous catalysis and heterogeneous catalysis. Then depending on the type of action of the catalyst whether it is a acid based. So, acid catalysts you put some acid and it catalysis is a reaction or you put a base you can catalyze the reaction or you have enzymes. So, that is enzymes catalysis so you have acid catalysis based catalysis enzymes catalysis. Then if you use light which is going to be the major discussion in our next part of the lectures. So, you can call it photocatalysis, because you all using light when this light can be in the ultraviolent region or in the visible region.

Or in any other region but mostly the reactions that we are interested in are in the visible or ultraviolent because we want to use the solar radiation. And so you photocatalysis is a type of catalyst which depends on the presence of light during the catalytic process. So, then you can do electro catalysis that means in the presence of a electric potential. Or when you pass a current then you can do a then you can alter the rates of a reactions and that is called electro catalysis. So, these are the different types of cat catalytic actions based on the type of whether it is a enzymatic reaction or it is a photocatalytic reaction or a electro catalytic reaction. You can have different types of names for this catalytic processes.

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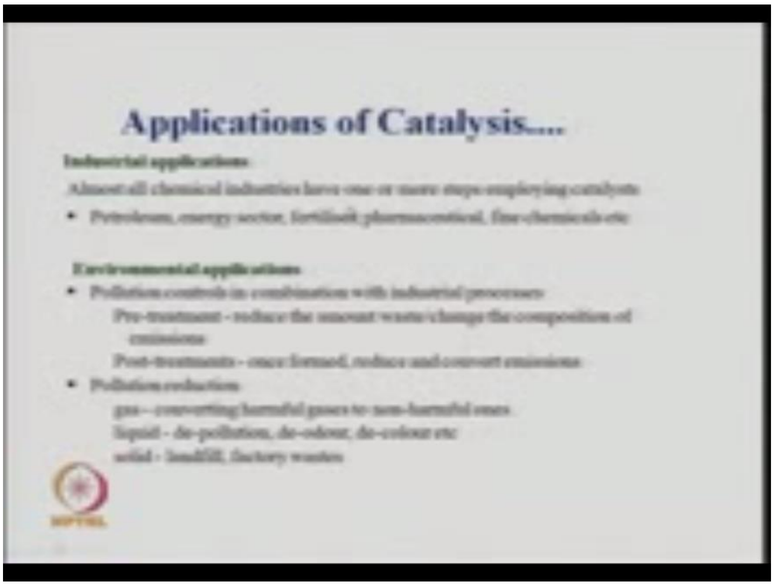

Applications of Catalysis....

Industrial applications

Almost all chemical industries have one or more steps employing catalysts

- Petroleum, energy sector, fertilizer, pharmaceutical, fine chemicals etc

Environmental applications

- Pollution controls in combination with industrial processes
  Pre-treatment - reduce the amount waste/change the composition of emissions
  Post-treatments - once formed, reduce and convert emissions
- Pollution reduction
  gas – converting harmful gases to non-harmful ones
  liquid - de-pollution, de-odour, de-colour etc
  solid - landfill, factory wastes

Now, there are many, many applications of catalysis as we discussed in the initial slides nearly 90 percent of the industrial processes which may chemicals involve catalyst. And so there are lots of applications of catalysis. Example in all chemical industries, we have some steps which involve catalyst like in the petroleum sector when you want to break down the petroleum which is obtained from the oil the after drilling the oil. Then you want to break down the petroleum that you got into different fractions of hydrocarbons. You may need cat catalyst these are called cracking catalyst, because they are cracking the hydrocarbons of some long chain hydrocarbons into smaller chain hydrocarbons and to separate them.

So, in the petroleum industry in the energy sector in the fertilizer sector pharmaceutical sector and fine chemicals in all these industrial chemical industry a plants you will need catalyst in some process of the other. Then in environmental applications where you want to reduce pollution you can do several processes like pretreatment using catalyst, which reduce the amount of waste or change the composition of the emission such that the emission is less toxic by using a catalyst in the process during the exhaust. If you can change gas like carbon monoxide to a less toxic gas like carbon dioxide that can be done using some catalyst. Similarly, you can if you can change the carbon dioxide into some hydrocarbons that or sub sugars that would be even better for the environment.

So, you can do pretreatment then you can also do post treatment once the toxic thing is formed then can you treat it so reduce and convert emitted toxic substances. So, that is post treatment so the again continue on pollution reduction you can convert harmful gases to nonharmful gases like an send carbon monoxide. You can make it carbon dioxide or carbon dioxide can be changed to hydrocarbons or sugars. And that is what is being done in converting harmful gasses to nonharmful ones.

Then liquid can be depolluted by changing the toxic liquid in a non toxic liquid then you can change the order of the liquid. For example, the liquid is not very toxic but it has a bad odor. So, then you can use a catalyst to deodor will liquid if the liquid has some color you can remove that color that is decolorization using catalyst. Then this was how you handle liquid pollutants then solid pollutants in landfills and factory wastes you can use catalyst to reduce the toxicity of the solid waste. So, you have applications of catalysis in large amount in industries chemical industries and also in significant amount in environmental applications in remediation of pollution.

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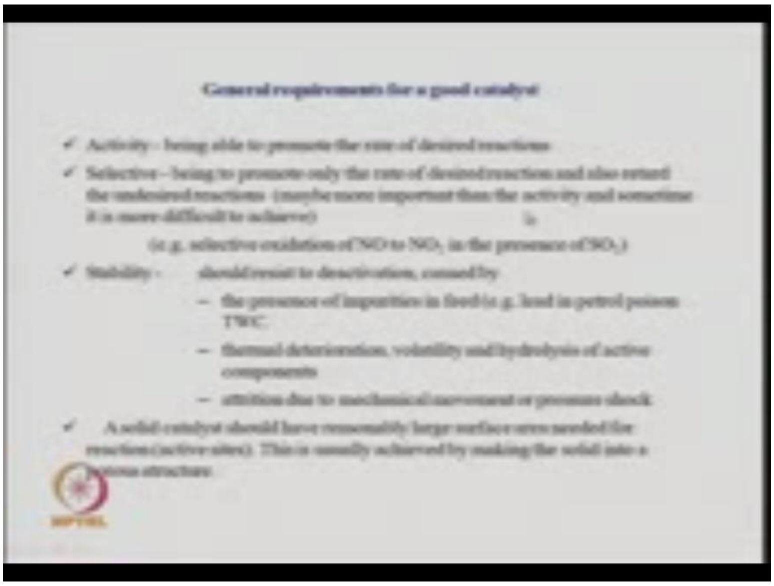

General requirements for a good catalyst

- ✓ Activity - being able to promote the rate of desired reactions
- ✓ Selective – being to promote only the rate of desired reaction and also retard the undesired reactions (maybe more important than the activity and sometime it is more difficult to achieve)

  (e.g. selective oxidation of NO to NO_2 in the presence of SO_2)
- ✓ Stability - should resist to deactivation, caused by
  - the presence of impurities in feed (e.g. lead in petrol poisons TWC
  - thermal deterioration, volatility and hydrolysis of active components
  - attrition due to mechanical movement or pressure shock
- ✓ A solid catalyst should have reasonably large surface area needed for reaction (active sites). This is usually achieved by making the solid into a porous structure

For good catalyst what are the key requirements one is activity. So it should be able to enhance the rate of the reaction which you desire. And the second is selectivity the catalyst should be able to actively promote one particular reaction which you desire it can if it promotes 2 or 3 reaction. Then you will have 2 or 3 by product, but if you want only one product selectively then the catalyst should be promoting only that particular process not any other process. So, it has to be very selective and this is some times more important than the activity and sometimes it is more difficult to achieve.

So, selectivity of a catalyst is highly desirable and sometime it is quite difficult to get a catalyst which is very good catalyst in terms of its activity, but may be not so good in terms of its selectivity. So, an example of selective of suggestion of nitric oxide to nitrogen dioxide is in the presence of sulphur dioxide so sulphur dioxide acts can be computing gas. So, if you want catalyst to only oxidize nitric oxide to nitrogen dioxide, but not oxidize sulphur dioxide. Then you need a very selective catalyst to act on nitric oxide then the catalyst itself should be stable, because you want to use the catalyst for several hundreds or thousands of cycles.

So, the catalyst it should be highly stable is should resist deactivation which is cause by impurities example lead in petrol can poison. So, let in in several our gasoline or petrol as we call we have this impurities. And this impurities can act as a poison or catalytic it will cause a deterioration of the catalyst. The or there can be thermal deterioration there can be volatility and hydrolysis of active components, which are part of the catalyst. Other thing is specially if it is a solid catalyst you can have what is called attrition when due to mechanical movement or pressure shock. This solid catalyst can become different morphology can be obtained due to the mechanical movement or pressure shock.

And that will change the change in the morphology or the surface will change the stability of the catalyst and it may also change the activity of the catalyst, because catalyst are highly sensitive to their morphology the surfaces and since the active sites are present mostly in the surfaces and the edges. And the defects on the surface hence any change in the type of surface or morphology will significantly affect the ability of the catalyst to act as it would in its optimal morphology. So, final thing, but most important thing a solid catalyst should have a very large surface area.

Because in solid catalyst most of the reaction is at the surfaces as mentioned earlier and the active sites are all on the surfaces. So, if the surface area is very high you have a high proportion of active sites and enhance the catalyst can act much better. So, the activity will be very high when the surface area of the catalyst is very high. And typically you use very fine particles as catalyst the reason is you want to high surface area in addition. You can enhance the surface area by making a solid into a porous structure. So, if you have a porous structure the surface area again will be very high and you will have high activity of the catalyst.

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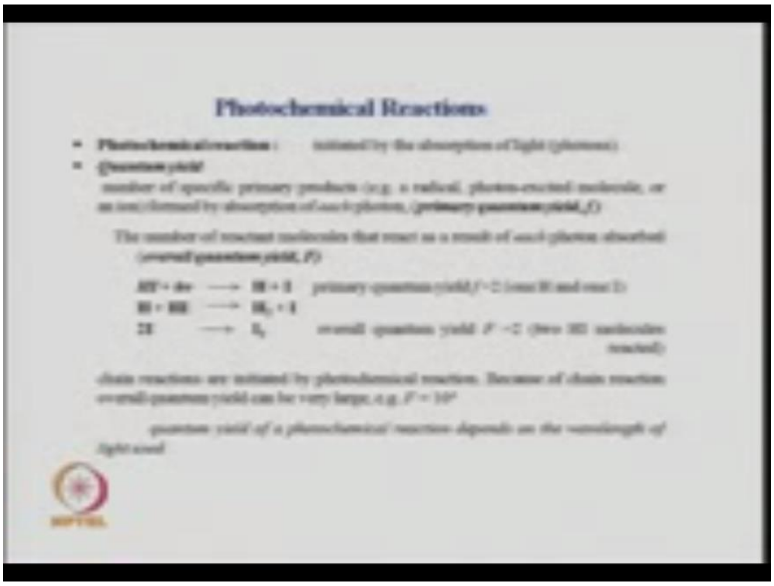

Photochemical Reactions

So, this was about generally about all about catalyst now let us come to photochemical reactions, because you have to merge the photochemical property and the catalytic properties to get a good photo catalyst. So, what are photochemical reactions typically any reaction which is initiated by the absorption of light or photons. And then you can define what is called the quantum yield in all photochemical process in all photo catalytic reaction. You may have to give a number, which is the quantum yield so what is the quantum yield. So, the number of specific primary products example a radical of photon excited molecule or anion.

So, when light is absorbed or photons are absorbed by the photo catalyst then you may generate a radical so radical is highly reactive. Because it has a unpaired electrons you may have a photon excited molecule a molecule have in the excited state or an ion photo excited ion. And these primary product these are called primary product can be found by absorption of each photon. So, how many such primary products are obtained by the absorption of one photon is called the primary quantum yield given by the small f. Now, the number of reactant molecules that reacts as the result of the photon absorb gives the overall quantum yield gives the capital F.

So, you have 2 quantities one is the number of primary products are that is how many radicals and how many photo excited molecules. Or how many photo excited ions are found from the absorption of one photons is given by the primary quantum yield. However, the number of reactant molecules that react here it is the number of excited molecules or radical generated here it is number of reactant molecules that will react as a result of one photon that is called overall quantum yield or capital F. So, this you can understand by looking at the following reactions. So, this is the reaction of hydrogen iodide in the presence of light to a form hydrogen and iodine atoms.

So, what has happened in this step is you have taken assume one photon of light with energy H new. So light you are using a frequency new and small h is a planks constant so one photon when it falls on hydrogen iodide creates 1 H and 1 I and. So, since there are 2 such particles the primary quantum yield small f is 2. Then this hydrogen iodide, which is the reactant in the overall process and this H again reacts with hydrogen iodide to give you H 2 plus I. So, overall in the process you use to H I’s only one photon was used in this overall process but 2 H I reacted. So, again the overall quantum yield capital F is 2 because 2 H I molecules reacted with the absorption of only 1 photon. So I hope this is clear that you have primary quantum yield is the number of radicals are photonic exacted molecules which are being created when one photon is absorbed.

And if you look of at how many reactant molecules reacted based on one photon. Then that is called the overall quantum yield and is given by capital F. Now, you can have a very large capital F it can be 10000 or even more in certain kind of photochemical reactions. And these are chain reactions and these are known and several chain reactions are known. And many of them are actually a photochemical reaction that means they are initiated by the by the absorption of a photon. And it can gives rise to several reactions as a chain and ultimately you can get several molecules of reactant react.

And so if 10000 molecules of some molecule a react to give products after absorbing only one photon then you are overall quantum yield will be several thousand because you use only one photon. And the reactants kept reacting and exciting one molecule or the other without absorption of any further photon. So, the overall quantum yield will be very high now the quantum yield of a photochemical reaction depends on the wavelength of lights. So, if you use a light of a particular wavelength you may have some quantum yield if you change the wavelength of light then you will you will have some other quantum yield. So, that is another thing which you can study for the same reaction use light of different wavelengths. And for that then you have to use different kinds of light sources.

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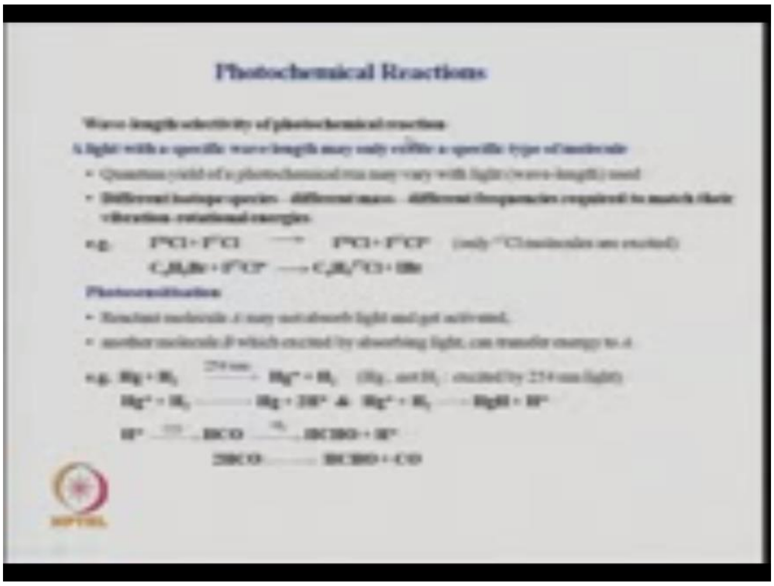

Photochemical Reactions

So, if you are using a laser then you have to you use a laser of different wavelengths now continue on photochemical reactions. The wavelength selectivity of a photochemical reaction we just discuss that a light of a particular wavelength can may only excite a specific type of molecule. And hence the quantum yield of a photochemical reaction may vary with the wavelength of the light which we are using thus another important thing is. If you have isotopes so different isotopes species since they have a different mass. Hence different frequencies are required to match their vibrational rotational energies. The vibrational rotational energy depend on the mass of the constituent atoms. And so if you have isotopes you may have the same molecules say H 2 0, but if you have H 2 O and D 2 O. They are similar molecule.

But they are masses change, because we have replaced hydrogen with its isotope which is deuterium and so this reaction shows that that if you have iodine chloride which is having iodine in with the mass of 36. And you also have iodine chloride where the iodine isotope 37 is present. So, you can have this kind of molecules which are specifically made with only iodine 36 atoms and another molecule made by only iodine 37. So, this is isotopic iodine chloride if you react them in the presence of light. Then it may happen that only one of the chlorine is excited. So, in iodine chloride having the atomic number the mass number of 36 is not getting excited, because this chlorine is not getting excited.

Because this chlorine is not getting excited or not absorbing the photon, only this chlorine which is 37 chlorine. So, ICL will get excited by that photon since 37 chlorine is getting excited. And so you can write with the star showing this is the photo excited molecule. And then this photo excited molecule can do further reaction. For example, in this case it is bromobenzene and this 37 ICL excited molecule reacts with bromobenzene and hence the chlorine which is substituted in the bromine position. So, from bromobenzene you can get chlorobenzene and if you find the mass of this chlorine group which you can do by several techniques then you will find that this chlorine has a mass of 37.

And that allowed people to understand these mechanisms that since only chlorine 37 is present in chlorobenzene. Then it should be possible only for the 37 iodine chloride to be photo excited and hence this mechanism was arrive that. Now, similarly, there is another process where the molecule which is being excited is not actually the molecule which you want to react. But that excited molecule can then transfer its energy to the molecule of interest this then is called photosensitization. So, the molecule A which you want to react that is the reactant may not be absorbing the light. And so it will not get photo excited, but the molecule B which is in close approximate with a can be excited by the light which you are shining on the material.

So, if B can get excited by the light which we are using and goes to an excited state then it can transfer its energy to A and then a gets activated. So, this called photosensitization and here B will be call the photosensitizer, because that is the molecule which is getting excited and sensitizing A. So, if you look at a reaction of mercury be hydrogen using 254 nanometer light. So, this kind of monochromatic which means you are using light of only one wavelength normally you can get in lasers where you can have very monochromatic beam. Otherwise you will have to use certain kind of filter etcetera, where sometimes it is not. So, monochromatic, but if you have this 254 nanometer light and you do this reaction.

Then only mercury gets excited the hydrogen does not get excited, but this excited mercury then reacts with hydrogen's. And then you get the splitting of hydrogen molecule. So, mercury here is acting as the photosensitizer this hydrogen once produced can then react with carbon monoxide to form sugars. And then those sugars like can be reduce with the hydrogen's gas to form formally high. So, these are this a reaction where you can understand what is a photosensitizer. So, typically what is photocatalysis process is that you have a catalyst. And it activates or it increases the rate of a reaction in the presence of photons in the presence of light.

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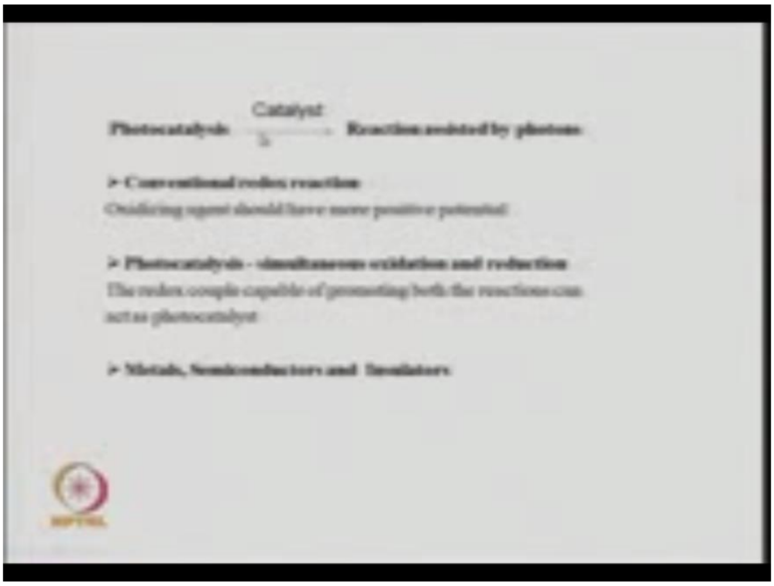

Photocatalysis $\xrightarrow[h\nu]{\text{Catalyst}}$ Reaction assisted by photons

- **Conventional redox reaction**

Oxidizing agent should have more positive potential

- **Photocatalysis - simultaneous oxidation and reduction**

The redox couple capable of promoting both the reactions can act as photocatalyst

- **Metals, Semiconductors and Insulators**

So that is photo catalysis in any conventional redox reaction the oxidizing agent should have more positive potential. So, in photocatalysis how it is different from any any oxidation or reduction reaction is that simultaneously. You are doing both oxidation and reduction and the redox couple should be capable or promoting both the reactions and then only it can act as a photocatalyst. So, there are several types of photocatalyst one can discuss but as we will see that semiconductors with reasonable band gap are some of the best photocatalyst that you can get. Because in metals we have no band gap the conduction band and the valance band are overlapping in the insulator band gap is very high. So, ideally in semi in the semiconductors you have a reasonable band gap and that is important for doing photocatalysis.

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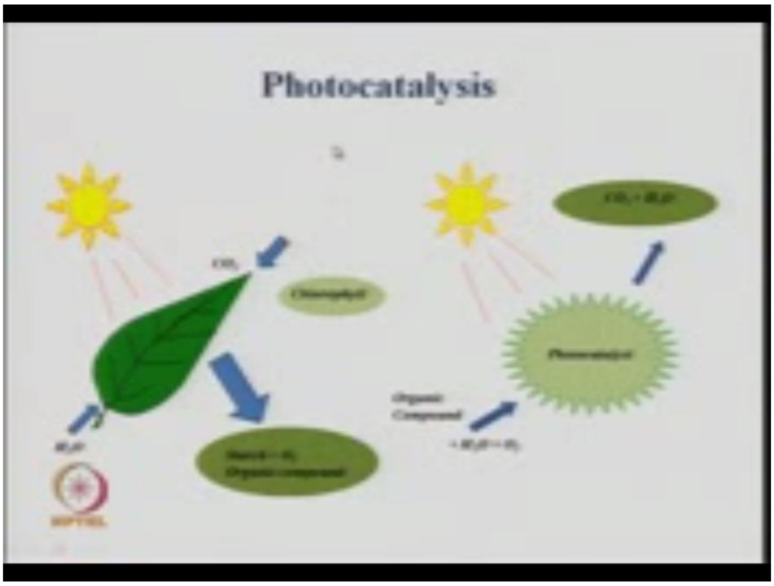

Photocatalysis

So, what is photocatalysis in a schematic view is you have in this is the process of photosynthesis where photocatalysis is taking place. So, you have this green leaf which has this chlorophyll which absorb this solar radiation which act as a there are act as a antenna. And then picks up the solar the photons from the solar energy and in the presence of carbon dioxide then water it can gives rise to starch and oxygens you can get a carbohydrate. And oxygen in the presence of carbon dioxide and water and light and this light harvesting is done by chlorophyll which is present in the plant in the leaf. This, the other thing is what lab made photocatalyst does this is a natural process photocatalyst can take solar radiations.

And if you have an organic compound it will it can change the organic compound into carbon dioxide and water. So, in the presence of an organic compound say a hydrate or hydrocarbon in the presence of water and oxygen a photocatalyst can change it to carbon dioxide and water. So, this is a little the opposite of what we are doing in photosynthesis where we are making starch. And oxygen using carbon dioxide and water here we are taking an organic compound. And like a carbohydrate can be taken or a hydrocarbon in the presence of water and oxygen you are producing carbon dioxide and water. So, that is what the photocatalyst.

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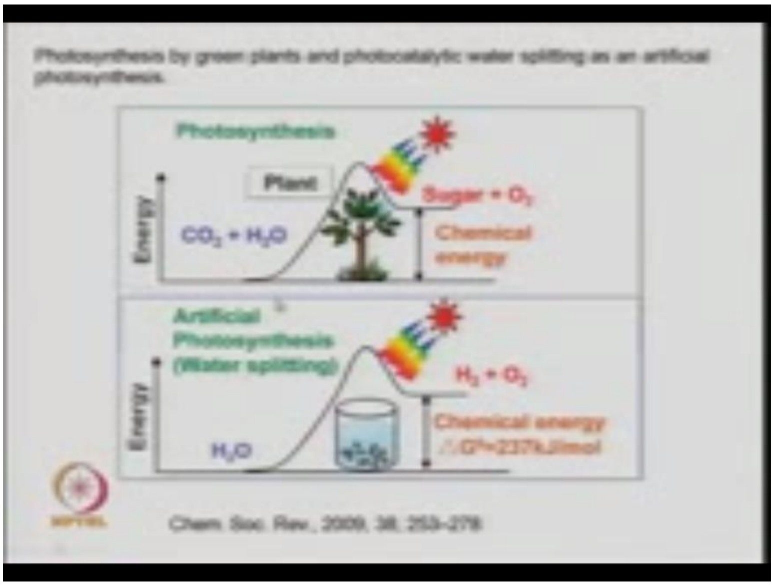

Photosynthesis by green plants and photocatalytic water splitting as an artificial photosynthesis.

Chem. Soc. Rev., 2009, 38, 253-278

So this is another compose comparison that if you have photosynthesis an artificial photosynthesis where a photocatalyst is being used. So, the comparison is in a naturally what is photosynthesis is in the presence of solar radiation with the plants are using carbon dioxide and water to produce sugar and oxygen. And this much chemical energy is being used, because the energy the delta g is not negative the delta G is the difference of this and this energy and that is positive. So the energy of the final products is higher than the energy other lower the reactance.

And so you have to give this amount of chemical energy which the plant has and generate. And it uses it to make sugar in the artificially in the lab when we try to do the same thing the same photosynthesis that we call it as water splitting reaction. Because the starting material here what we take is water and the product instead of sugar what we get is hydrogen and oxygen. So, because in water splitting your reactant is only water in the presence of the catalyst is water can be broken apart or splitted in the presence of solar radiation. And the photocatalyst to hydrogen and oxygen and again you have to give energy of the order of 237 kilo joule per mol. So, this is also a reaction which needs energy.

So, you can see some similarity between photosynthesis and water splitting and hence water splitting reaction is called artificial photosynthesis. And there is lot of research in this area to mimic the reactions in a green plant. So, this can be called a leaf mimic if you can find good photocatalyst which can break water into hydrogen and oxygen in the presence of sunlight at a decent rate of reaction. So, that is important to make it efficient photocatalyst you must have a reasonable rate of reaction.

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Design of photocatalytic materials
: controlling factors

- Band gap
- Carrier transport
- Crystallinity
- Surface Area
- Chemical stability

So, design a photocatalytic materials how you designed what will be a good photocatalyst. So, there are certain characteristics of these materials and one is the band gap. And I said that you cannot use a material which has a very high band gap. Because then you will need light very high energy, but you want to use light which is easily available. And which is the light which is easily available is the solar radiation and solar radiation has got distribution of frequencies. But most of the frequencies that you that you get are lying in the visible and the ultraviolet which you want to use. And so the band gap of the material that you want use the semiconductor material should be in that region of visible.

And ultraviolet then carrier transport, because you will have electrons and holes and these have to be transported to different electrodes to generate some current based on photocatalysis. Hence carrier transport is important the carrier transport and band gap both are affected by the crystallinity of the sample. So, how much crystalline it does is it, because an amorphous solid or a poorly crystalline solid will have a slightly different band gap. And hence that will affect the photocatalytic process then surface area we already discussed very high surface area means very high number of active sites. And so their reaction rate will be very high and it will be a good catalyst. Then the stability of the catalyst is important, because you want to use and reuse this catalyst several times. So, these are some of the controlling factors which you think about when you are trying to design photocatalytic materials.

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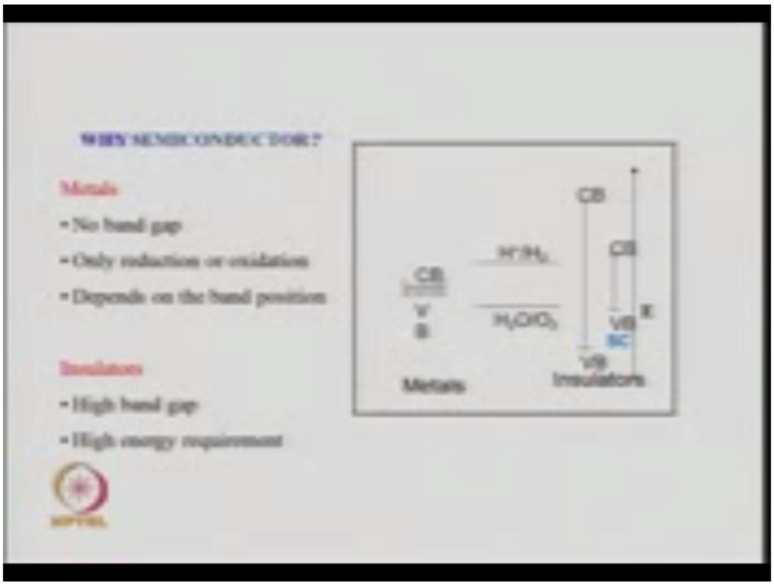

WHY SEMICONDUCTOR?

Metals
- No band gap
- Only reduction or oxidation
- Depends on the band position

Insulators
- High band gap
- High energy requirement

So, why semiconductor, because as I said in metals there is no band gap you can only do reduction oxidation in insulators; you have very high ban gap high energy requirement. And this you will not be able to do with the visible radiation or near u v radiation. Now, typically you can see that a semiconductor has this band gap the conduction band and valence band. And this is the energy difference of what you do need for water splitting. And if you have a very high band gap which is in insulators or no band gap like in metals. And that does not help this water splitting reaction, but a reasonable band gap like present in several semiconductors can help this splitting of water due to similar type of band gaps.

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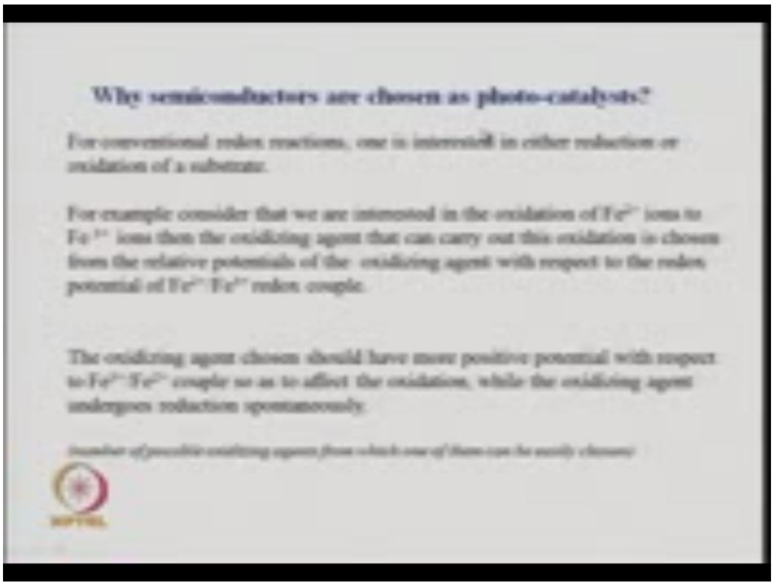

Why semiconductors are chosen as photo-catalysts?

For conventional redox reactions, one is interested in either reduction or oxidation of a substrate.

For example consider that we are interested in the oxidation of Fe^{2+} ions to Fe^{3+} ions then the oxidizing agent that can carry out this oxidation is chosen from the relative potentials of the oxidizing agent with respect to the redox potential of Fe^{2+}/Fe^{3+} redox couple.

The oxidizing agent chosen should have more positive potential with respect to Fe^{3+}/Fe^{2+} couple so as to affect the oxidation, while the oxidizing agent undergoes reduction spontaneously.

(number of possible oxidizing agents from which one of them can be easily chosen)

So again why semiconductors are chosen as photocatalyst? Because for conventional redox reactions one is I interest in either reduction or oxidation. And whereas in a photocatalyst you have to do both reduction and oxidation the, if you consider the oxidation of iron 2 iron 3 plus F e 2 to F e 3. Then you can use an oxidizing agent to carry out this oxidation that is given by the, which will be good oxidizing agent that you have to see the relative potentials the relative potentials of the oxidizing agent with respect to the redox potential of this F e 2 plus F e 3 plus couple. The oxidizing agent should be chosen such that it should have a more positive potential with respect to F e 3 plus F e 2 plus. That means the valence band should be lower than the valence band of the F e 2 plus F e 3 plus so the energy required.

So, you will be able to transfer a whole into the iron 2 plus to convert to iron 3 plus if the energy of this the valence band of the semiconductor is lower than the energy of this F e 3 F e 2 plus F e 3 plus couple. Whereas the if you do want to do a reduction then of course, you will have to chose a different kind of photocatalyst. And where you will be dealing with the conduction band and you want to transfer electrons to carry out the reduction here we are talking of oxidation. And hence we are talking about holes which are important which will carry out the oxidation. And if you are dealing with the reduction reaction then you will discuss the electrons which are normally present in the conduction band. And which can be transfer to the couple so depending on whether you are doing oxidation or reduction. You have to know which system to chose potentials which are all tabulated in several books.

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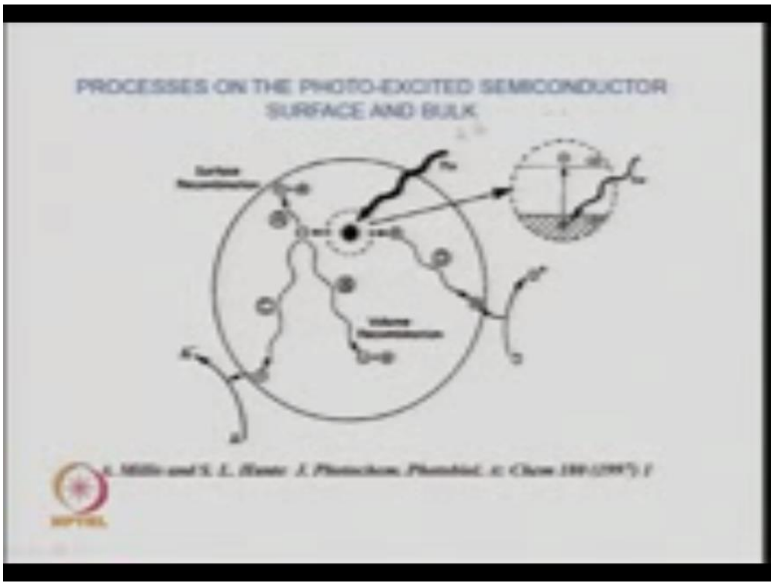

PROCESSES ON THE PHOTO-EXCITED SEMICONDUCTOR SURFACE AND BULK

A. Mills and S. L. Hunte J. Photochem. Photobiol. A: Chem 108 (1997) 1

Now, if this is a catalyst particle several processes occur when light falls on this catalyst which is a semiconductor. So, in the bulk certain processes will occur when light in pinches on this catalyst particle. So, in the bulk you have this band diagram for the material for the catalytic material. And when light strikes actually you will be generating holes in the valence band and electrons in the conduction band. Now, the electron and hole together is called as exciton and this pair of charges is very important that they should not recombine. So, if they recombine then they will give out a photon. So, recombination between these 2 levels will not allow you to carry out any catalytic reaction. So, it is important a for light to produce this holes and electrons but then it is also important that these 2 do not recombine fast and the time of recombination is long.

So, if that is true than the electron, which is here in the conduction band can go in one direction. And if the whole can be taken to another direction then you can do 2 things you can reduce using the electron and surface recombination. You can reduce something and on this side using the hole on this part of the surface you can oxidize D to D plus. So, both these things can happen so you can take electron you can go to the surface. So, actually this is the process the electron is going to the surface if it recombines. Then it is lost the electron will be lost if it recombines with the say a positive surface defect that if the electron goes to the surface without meeting a plus charge then the electron can reduce a to a minus.

So, this is the electron that is important and is fruitful as in the catalytic process. And this is the hole which is fruitful so you do not want process like this these are volume recombination. That means the electron meta whole in within the solid particle this is a volume recombination here the electron met the hole on the surface. And so it is called surface recombination either of the recombination are not good for photo catalysis for photo catalysis. You want both the electrons and the holes to migrate to long distances to different parts of the mol of the particle. And do catalytic reactions on the surface and 2 processes can occur both oxidation as well as reduction.

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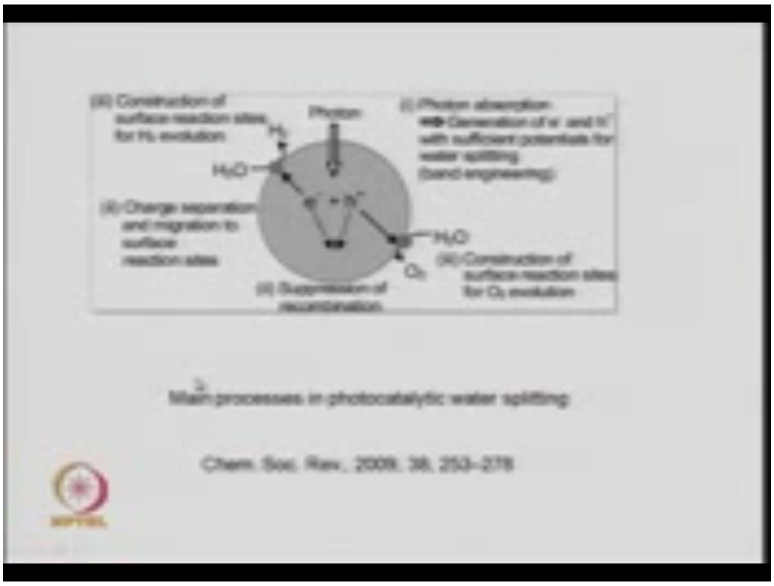

Main processes in photocatalytic water splitting

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And this is again shown here that if you have a photon electron hole pair is generated. And the electron goes to the surface and will reduce water to hydrogen and the hole goes to another part and will oxidize water to oxygen. So, this is a water splitting reaction the water using the electron and hole can change to hydrogen and oxygen. So, this process basically is explaining the photocatalytic water splitting.

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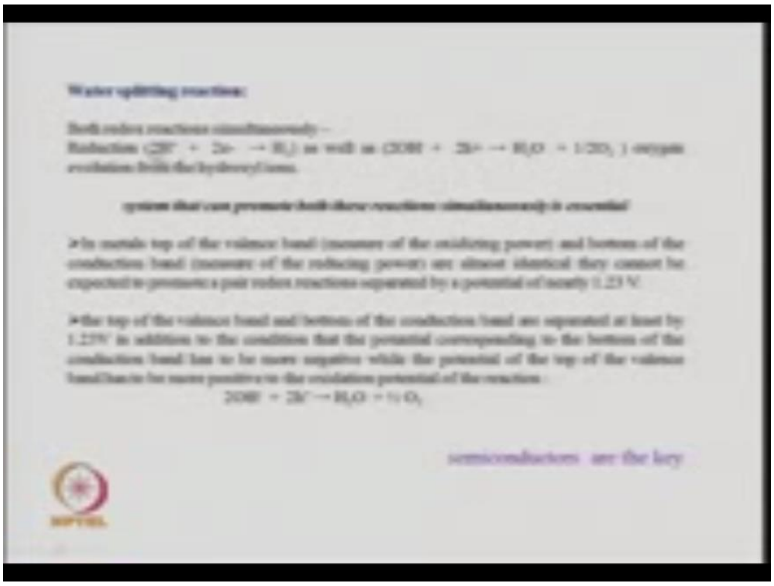

semiconductors are the key

So, in a water splitting reaction both redox reactions occur simultaneously. You have reduction photons to give hydrogen as well as hydrol hydroxyliones will react with holes and to give you oxygen.So, hydrogen and oxygen both will be produced and a good photocatalyst is for water splitting is one, which can promote both these reactions simultaneously. Now, it is known that the water couple that is give an in this diagram this couple that you know H plus H 2 and water oxygen this energy gap is around 1.23 volts. So, you have to give energy 1.23 volt a potential of nearly 1.23 volts by any reaction which you are doing using the photocatalyst. Now, the top of the valence band and bottom of the conduction band are separated by this.

That is what it means an in addition to the condition that the potential corresponding to the to the bottom of the conduction band has to be more negative. And so not only you must have this difference 1.23 volts is the gap at least should be there between the conduction band and the valence band of the semiconductor. But it is also necessary that the potential corresponding to the bottom of the conduction band has to be more negative while the potential of the top of the valence band has to be more positive compare to the oxidation potential of the of this reaction. So, these are some key factors to choose semiconductors which can act as photocatalyst for water splitting reactions.

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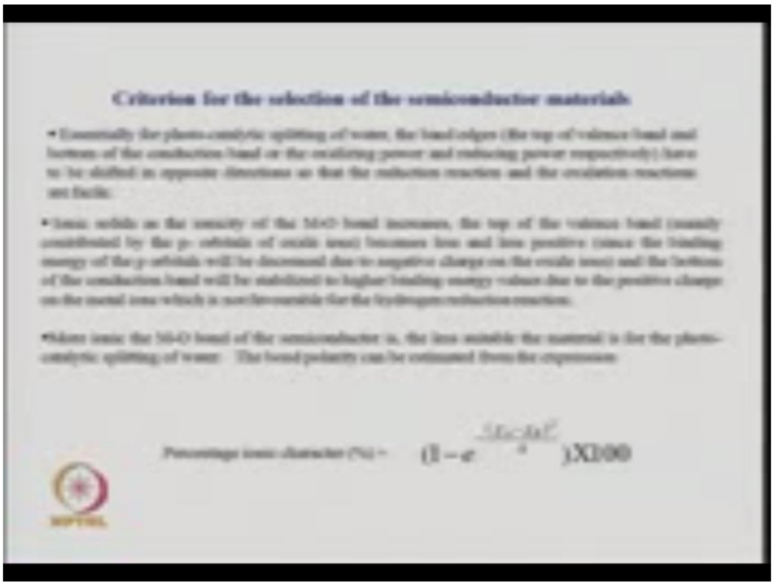

Criterion for the selection of the semiconductor materials

So, the criteria for the selection of the semiconductor materials. Essentially we discussed what kind of band gap should be there where should be the top of the valence band and where is the bottom of the conduction band. So, top of the valence band bottom of the conduction band and the band gap these 3 factors are very important in deciding which semiconductor you will use to achieve photocatalysis for a particular given system. Typically ionic solids, in ionic solids the iconicity of the metal oxygen bond increases the top of the valence band becomes less and less positive. And this is due to the bonding between the orbital's and the of the metal and the oxide ions.

And the bottom of the conduction band will be stabilize to higher binding energy due to the positive charge of the metal ions which is not favorable for the hydrogen reduction reaction. So, because you want the bottom of the conduction band you want it to become lower the bottom of the conduction band should become higher. And the top part of the valence band should become lower for the reaction to occur. So, more ionic the m o bond of the semiconductor the less suitable the material is for the photocatalytic spitting of water.

And so if you take something like titanium dioxide and cadmium sulfide, titanium dioxide is more ionic and cadmium sulfide is less ionic. The cadmium sulfide is a better material for photocatalytic splitting of course, it may have other problems etcetera. Now, the bond polarity or the ionic bond can be given by this expression parentage ionic character. And it is given as exponential of the difference the square of the difference of the electro negativities of the binary systems say suppose it is a metal oxide metal and oxygen.

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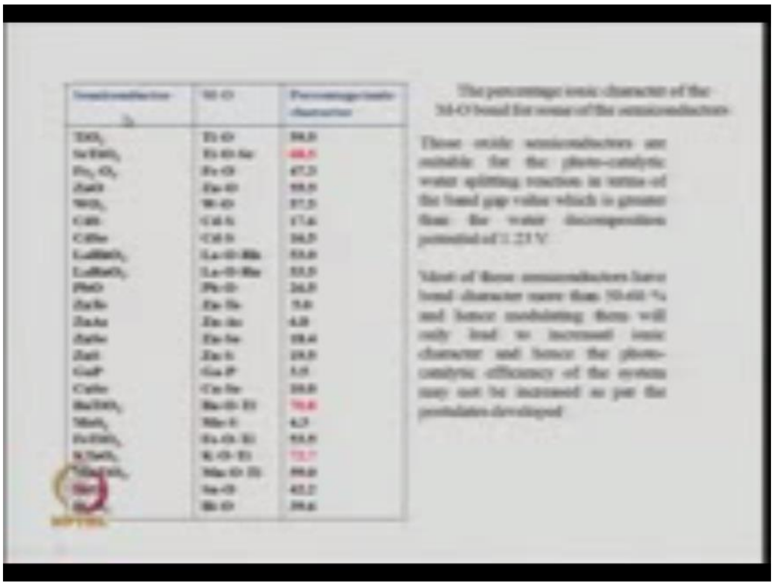

So, based on that you can see there are lot of materials which are semiconductors and there metal oxygen percentage ionic character is listed here. And you see the red once strontium titanate or barium titanate or potassium titanate; very high ionic character. And may not be suitable for the photocatalytic water splitting in terms of the band gap, which is greater than the water decomposition. The percentage ionic character you want is to below and you see some many of these telluride, arsenide, selenide semiconductors have very low percentage ionic character. So, that way they are much better but they may have other defects for the photocatalytic reaction. So, one has to make a judicious choice of various properties to chose a final photocatalyst.

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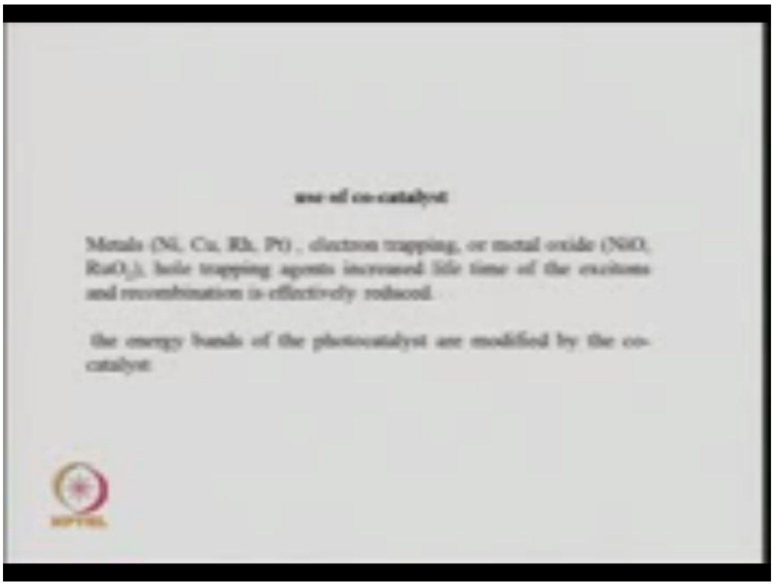

use of co-catalyst

Metals (Ni, Cu, Rh, Pt) , electron trapping, or metal oxide (NiO, RuO_2), hole trapping agents increased life time of the excitons and recombination is effectively reduced.

the energy bands of the photocatalyst are modified by the co-catalyst

Now, run can also use a co catalyst along with the photocatalyst. So, people many times use metals like copper, nickel, platinum, ruthenium, etcetera. People have used for trapping electrons along with the catalyst these metals help to trap electrons. And then so the hole is separated from the electron the hole is in the semiconductor and these cocatalyst can trap the electrons. Or if you use a metal oxide as a cocatalyst like nickel oxide ruthenium oxide they can trap the holes.

And eventually what you do you increase the life time of the excitons an recombination is effectively reduced. So, the energy bands of the photocatalyst are modify by the co catalyst. And hence these electrons trapping or whole trapping will increase on depending on whether you are using a metal or a metal oxide. Overall the result is you help slow down the recombination of the electron hole pair. So, with that we come to the end of our lecture today. And this is the first lecture on photocatalysis and will continue two more lectures on photocatalysis.

Thank you.