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Lecture –18 Chemical Kinetics-Catalysis (Part-A)

Welcome everyone to our online NPTEL course of Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself Professor Anjali Pal. We are both from Civil Engineering Department, IIT Kharagpur. We have divided this course into two parts. The first part, Environmental Chemistry will be covered by me and the second part, Environmental Microbiology will be taught by Professor Sudha Goel.

In my first module I have covered acids, bases and salts. In the second module I have covered chemical equilibrium. In the third module I have discussed about the chemical kinetics (order, rate, rate expression, differential rate law, integrated rate law and procedure for determining the order have been discussed). This is my fourth module and this is on chemical kinetics. In this lecture I will cover the catalyst. Catalyst is also very important for chemical kinetics because it can change the rate of a reaction. It can make a reaction faster or slower.

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Now in this lecture I will cover the general concept on catalysis. I will tell you what is the catalyst and what are the different types of catalyst or catalytic reactions. I will talk about homogenous catalysis, heterogeneous catalysis, biocatalyst and then how the efficiency of a

catalyst is determined or what are the parameters we have to consider. I will discuss about turn over number (TON) and turn over frequency (TOF).

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Catalyst is a very important thing today in today's scenario. There are many reactions which are very slow. They can be made very fast by using some catalyst. Some reactions can be done with much less energy or heat if we use the catalyst. We will discuss those things.

In today's world green chemistry is very important topic of discussion. What is green chemistry? There are two persons named Paul Anastas and John Warner. In 2000 they have given 12 principles of green chemistry. The principles are as follows:

- 1. Prevent waste
- 2. Design safer chemicals and products
- 3. Design less hazardous chemical synthesis
- 4. Use renewable feedstock
- 5. Use catalysts
- 6. Use chemical derivatives
- 7. Maximize atom economy
- 8. Use safer solvents and reaction conditions
- 9. Increase energy efficiency
- 10. Design chemicals and products to degrade after use
- 11. Analyze processes in real time
- 12. Minimize the potential for accidents
- So, you can see here the catalyst is also under this green chemistry principles.

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When we talk about catalysis let us first come to H_2O_2 . H_2O_2 has wide applications including environmental pollution control (degradation of organic pollutants), as an antiseptic, in mouth wash, as bleaching agent etc.

Now if you just keep hydrogen peroxide in a say watch glass what you will see? H₂O₂ will decompose into water with the evolution of some heat. But the reaction will not be so vigorous. But if you keep some MnO_2 (pyrolusite) in presence of H_2O_2 , then you will find vigorous reaction. So, MnO₂ is acting as a catalyst making decomposition of H₂O₂ faster even at ordinary temperature. On the other hand, if you keep some phosphoric acid the reaction will be slow. So, it is also acting as a catalyst slowing the reaction (inhibitor). Now I do not know whether you have used H_2O_2 in your lab or not. But if you see the bottle of H_2O_2 then you will see that it is kept in black colored plastic bottle or brown colored plastic bottles. Why it is so? Why it is not kept in colorless transparent glass bottle? Actually, H_2O_2 is decomposed under heat or under light. That is why it is kept in black colored bottle. If you keep it under normal light then some diffused light also can cause the decomposition of H_2O_2 . There is another fact that the strength of H_2O_2 decreases with time gradually and it has to be standardized. If you are using the H_2O_2 bottle for long time (say for example three months) then after 3 months (i.e., on 90th day) you cannot tell that that the strength of H₂O₂ is the same because continuously it is decomposing and that is why from time-to-time you have to determine the strength. There are some standard procedures by which you can determine the strength of H₂O₂.

You will find that in many laboratories H_2O_2 is kept in a refrigerator at low temperature so that its decomposition is slow.

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Now let us come to catalyst and catalysis. The man who has coined this term is nothing but Berzelius. He observed that many chemical reactions were accelerated by the presence of some foreign substance that is not taking part in the chemical reaction. He described the process as catalysis. At the end of the reaction the foreign substance remained unchanged in mass and in composition. So foreign substance should have some specialty. What is that specialty? There is no change in mass and composition after the reaction.

Now there are different types of catalyst as I told you. Positive catalyst means it makes a reaction faster. There may be some negative catalyst which is also called inhibitor. So, a very good example of catalysis is formation of HCl from hydrogen and chlorine in presence of active charcoal. Charcoal is a solid substance and it can act as a very good catalyst also. Now let us see an example of negative catalyst. When we store H_2O_2 then we do not want that it to get decomposed. Then we will use something which is a negative catalyst that means which will slow down the process of decomposition. Phosphoric acid can do that.

Auto catalysis is a very good experiment. It is the experiment of determination of the strength of permanganate. You know that permanganate (KMnO₄) is a pink colored substance and when the solution is prepared it is pink colored solution or purple colored solution. An important thing regarding the strength is that even if you take the proper weight and prepare the solution then also strength is not actual strength. That is why it is called secondary

standard. You have to determine the strength by using another standard and that is called the primary standard. Primary standard is something whose strength does not change with time and which you can take the weight properly. Oxalic acid is a primary standard. The reaction between potassium permanganate and oxalic acid this is a redox reaction. Here permanganate is an oxidizing agent. It is going to Mn^{2+} state. On the other hand, oxalate is reducing agent and it is going to CO_2 which has no color. Oxalic acid has no color, but KMnO₄ it has color. So, first take KMnO₄ in burette and oxalic acid in presence of acid in a conical flask and start your titration so by adding drop by drop the permanganate into this oxalic acid solution. The reaction is given as (1):

 $2MnO_4^{-}+16H^{+}+5C_2O_4^{2-}=2Mn^{2+}+8H_2O+10CO_2$ (catalyst: Mn^{2+}).....(1)

Theoretically, Mn^{7+} is reduced to Mn^{2+} and hence color of permanganate should be discharged. But at the initial stage of addition of first few drops of addition we will see that color is not going very quickly. So, the color is staying although color should go immediately. Why it is so? It is so because this reaction is slow reaction. But then after addition of few drops you will see that reaction has become faster and color is going fast. Why it is so? Why initially it is not going fast and after few drops of addition of KMnO₄ you see that color is going very fast? This is because this Mn^{2+} which is produced in this reaction is acting as the catalyst. This type of reaction is called autocatalysis (auto means self). The product itself is acting as the catalyst and that is why it is called auto catalysis.

Now let us see induced catalysis. What is induced catalysis? Let us consider an example as follows:

 $Na_2SO_3+Na_3AsO_3+O_2=Na_2SO_4+Na_3AsO_4....(2)$

In the above reaction (2), As(III) is converted to As(V). This can happen in presence but you will only in presence of oxygen it is not occurring. But if you add sodium sulfite (Na₂SO₃) it will be oxidized to sodium sulfate (Na₂SO₄) and As(III) will be oxidized to As(V). So, this is an example of induced catalysis. So, there are different types of catalyst and catalytic reactions.

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Now, what are the characteristics of catalytic reaction? A catalyst can only change the speed of a reaction. So, a reaction speed is only changed by a catalyst. It cannot change the final state of equilibrium. Now you know what is equilibrium and equilibrium constant (I have already discussed in my module 2). It helps to attain the equilibrium quickly. It means only the rate is changed by a catalyst, but thermodynamic parameters cannot be changed. It accelerates both the forward and reverse reaction to the same extent and that is why it cannot change the equilibrium constant.

A catalyst provides an alternative path. Say for example I want to go to one room. Suppose there are two routes. One route takes longer time and another route takes shorter time. So, route is different and that is why it is becoming faster. A small amount of catalyst is required to accelerate the reaction and a catalyst remains unchanged in mass and chemical composition that I already told you. At the end of the reaction, it remains unaltered in mass and chemical composition. However, the physical nature may change. Sometimes you may start with crystal, but it may go to amorphous stage. It can happen like this thing.

A catalyst cannot start a reaction. So here I have given a very nice example (3) that we see in the school days in the laboratory method of oxygen preparation.

We take potassium chlorate and MnO_2 (catalyst). We mix these two things very well together and then we heat it heat at 250°C in a hard glass test tube. After that when oxygen is prepared, we collect it. But can you tell me that if I do not use MnO_2 and just take KClO₃, then whether oxygen will be produced or not, if I heat it. It can also happen (as shown in (4)), but it takes higher temperature (>600°C).

4KClO₃=3KClO₄+KCl

$KClO_4 = KCl + 2O_2 \dots (4)$

Now you know that we want everything fast and, in an energy efficient way. Energy is a very important thing in today's world. Now catalyst is helping us in that way.

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Now let us come to the classification of catalysis. There are many different kinds of catalysis, catalyst like acid (H⁺) catalyzed reactions, base (OH⁻) catalyzed reactions also, Lewis acid (AlCl₃). In acid base chapter I have told that what is Lewis acid and what is Lewis base. You know that aluminum chloride (AlCl₃) is a Lewis acid. So, this also can act as a catalyst. Organometallic complex can act as catalyst. Organometallic complexes are those where carbon metal bond is formed. Organic and inorganic polymers are the support material. They can also act as catalyst. In our body system there are many enzymes. Enzymes are very complex molecules and they have specific sites to carry out specific reaction. So, enzymes are also good biocatalyst.

How will you classify catalysis? Mainly the catalyst or catalysis is divided into three classes: homogenous catalysis, heterogeneous catalysis and biocatalysis. So, I will discuss those things, but let us first see what is catalyst promoter and catalyst poison. We know catalyst, but what is catalyst promoter. A very good example that is the ammonia synthesis. Ammonia synthesis we have seen when I discussed about (()) (22:15) principle I have discussed that hydrogen and nitrogen they can react to form the ammonia and it needs high temperature, high pressure. I also told that thereon catalyst is needed that is finally divided iron, but with iron if you use trace amount of molybdenum that is along with finely divided iron then it can enhance the reaction rate significantly. So, molybdenum actual catalyst is this one this finely

divided iron, but molybdenum is a catalyst promoter. It can enhance the rate further. So this is a promoter.

Now what is poison what is poison that is anti catalyst that is a poison. So poison means in which the catalytic action it poisons the catalyst catalytic action. Substances which reduces the catalytic activity, for example, in the contact process of H2 SO 4 synthesis you know that contact process and chambers process all those processes are very important for sulfuric acid synthesis. So there platinum is used as the catalyst, but if there is trace amount of arsenious oxide then it can destroy the catalytic activity of the platinum.

So this is a poison. We all know poison what is poison so it is poisoning the catalytic activity, it is poisoning the catalyst so this is the catalyst poison.

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Now what is homogenous and heterogeneous catalysis some example I will tell. In homogeneous catalysis, the catalyst is in the same phase as that of the reactants and products. So it is a homogenous condition it may be anything it can be gas phase, it can be liquid phase, but everything is there in the same phase. Catalyst and then substrate and then products everything is in the same phase then it is a homogenous catalysis.

There are many, many examples I have only taken a few. This is the biodiesel production very important topic today biodiesel production, transesterification of fatty acid triglyceride you know fatty acid, you know what is fatty acid triglyceride with methanol catalyzed by OH – that is this is an important reaction for biodiesel production there catalysis is OH – means base catalyzed reaction.

And this I already explained pseudo unimolecular reaction, pseudo first-order reaction. I have told you that cane sugar when hydrolyzed this is in presence of acids so it is acid hydrolysis. When it is hydrolyzed to glucose and fructose then I have told levulose, but glucose and fructose then inversion of cane sugar happen hydrolysis with hydrolysis. So this is catalyzed acid so it is acid catalyzed and everything is there in the liquid phase in solution so it is a homogenous catalysis.

Chamber process of sulfuric acid synthesis there nitrogen oxide is used as catalyst to convert mixture of SO 2 and oxygen and water vapor to H2 SO 4 this is a very important method of production of H2 SO 4 their nitrogen oxide is there nitrogen oxide is used as catalyst. I will tell you the mechanisms later, but these are just the examples. Now in heterogeneous catalysis the catalyst and the substrate are in different phases.

One may be solid, one may be liquid or one may be solid, one may be gas. So this is gas solid or solid liquid something like that. Now finely divided iron in ammonia synthesis by Haber process obviously this is ammonia is gas phase and iron is in solid phase so it is an example of homogenous catalysis. Active charcoal in a formation of phosgene you know it is very poisonous gas phosgene.

So it can be synthesized from carbon monoxide and chlorine so their active charcoal is used so all are gas, but this is the solid. Now platinized asbestos for the conversion of S0 2 to SO 3 in H2 SO 4 synthesis by contact process this is another process of H2 SO 4 synthesis where platinized asbestos is used so it is also heterogeneous catalysis. So for heterogeneous catalysis the advantage is that.

What is the advantage? The catalyst can be easily separate from the reaction mixture. So this is a very good advantage in homogenous catalysis after the reaction how can you take out the catalyst. Although catalyst is doing many cycles running many cycles, but still at the end if you want to recover it or if you want to separate it out then how will you separate this is the problem, but for heterogeneous catalysis this problem is not there.

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Now when there is a catalyst or there are two catalysts how to know which catalyst is better. So to know this we have to consider two things one is the turnover number another is the turnover frequency both are similar. Turnover number and turnover frequency. Now catalyst turnover number and turnover frequency are two important quantities used for catalyst efficiency.

And they are defined in different ways in homogenous catalysis, in heterogeneous catalysis, in biocatalysis. The definition of TON is different. What is this in homogenous catalysis we define TON as a number of cycles that a catalyst can run through before it gets deactivated. How many runs it can go so before it gets deactivated that is the homogenous catalysis and TON is the number that is TON is the number of X molecules that one molecular catalyst can convert into Y molecules.

Say for example X is going to Y so how many X molecules are converted to Y molecules by one molecule of catalyst for homogenous catalyst that is the definition and TOF is nothing but TON by time. So, similarly is similar but this (()) (29:29) time factor is coming in TOF. Now heterogeneous catalysis TON and TOF are defined for active site because it is solid if you think about it is solid so active sites will be there or per gram of the catalyst.

So here it is defined in this way so that means how many number of molecules it is converting per gram of catalyst. Now that is the heterogeneous catalysis we use and it is difficult to know exactly how many catalyst molecules are there on the surface that is why it is defined in this way per gram because we know how many sites are there, exactly how many catalyst molecules are there that is also very difficult.

How many sites also it is very difficult per gram is easier most of the cases we see per gram. Now biocatalyst again definition is different TON and TOF are defined by the rate measured when all the enzyme molecules are complexed with a reactant divided by the total enzyme concentration. So there are different ways to tell the TOF and TON, but there is a relation you have understood that what is TON and TOF by time TON by time is TOF very, important any good paper you will see that they have calculated these two values.

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Industrial application of catalysts: Synthesis of ammonia by Haber's process (finely divided Fe as catalyst and Mo as promoter) $3H_1 + N_2 \rightarrow 2NH_2$ Hydrogenation of unsaturated oil and fat (finely divided Ni as catalyst) >C=C< + H, → >CH-CH< Synthesis of HCI from hydrogen and chlorine (active charcoal as catalyst) H₂ + Cl₂ → 2 HCl Oxidation of ammonia to nitric oxide (Ostwald process) (platinum gauge as the catalyst) 4 NH₃ + 50, → 4 NO + 6 H₂O Oxidation of sulphur dioxide to sulphur trioxide (in the contact process platinised asbestos or vanadium pentoxide as catalyst) $2SO_{2} + O_{2} \rightarrow 2SO_{2}$

Now industrial there are many industrial applications also for catalyst so for example this I have already this is nothing, but the Haber process you know it is also nitrogen fixation when I will talk about nitrogen cycle then I will again tell it about this. Now this is you know for ammonium fertilizer synthesis ammonia is so important. So this is important, but you know that when Haber process the yield if you know the yield you will be surprised to know although it got the Nobel Prize the yield is only 7%.

So after such huge temperature and pressure application and even catalyst you see the yield is very less, but still it got noble prize that is very interesting to see that time it was so much important. Now hydrogenation of unsaturated oil and fat. So unsaturated oil and fat this double bond is there so hydrogenation can be done in presence of (()) (32:03) finely divided nickel as catalyst.

So this is also heterogeneous catalysis. Synthesis of HCL from hydrogen and chlorine this already I have told active charcoal this is also very important procedure for HCL synthesis. Now oxidation of ammonia to nitric oxide ammonia oxidation by oxygen to nitric oxide then nitrogen dioxide then nitric acid it is Ostwald process. Here also platinum gauge is used as the catalyst.

These are all industrial large scale production so here you see so much application of catalyst. So if you can develop a very good catalyst even patent you can take and that can be really useful for some good synthesis. There are many awards also for catalyst synthesis. Here you can see that oxidation of sulfur dioxide to sulfur trioxide. This also for sulfuric acid preparation in contact process.

Platinum asbestos or vanadium pentoxide is used as the catalyst. So I have picked up only few, but there are so many.

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Now what is catalytic converter you know that this is most important although I have not described much, but you can see that most widely used chemical catalysis in everyday life in the catalytic converters installed in the exhaust of automobile. What is happening in the automobile we know that in automobile we used the gasoline that is nothing, but the hydrocarbon.

So hydrocarbon is oxidized to carbon dioxide and water, but if it is incomplete combustion then it goes to carbon monoxide and some of the gasoline is kept out so it is polluting our environment. So what should be our goal? Our goal is to use some good catalyst so that it goes to complete oxidation that means it goes to carbon dioxide and water and for this purpose we use some catalyst as platinum.

There is another thing is going on when we use the gasoline there in the vehicles automobile what is happening the air is (()) (34:35) at high temperature what is there in the air there is the nitrogen and oxygen so they combine to form the nitrogen oxides NO x they form the NO x. So when NO x is formed that is also polluting. So if we can use a very good catalyst then if we can reduce the NO x to N 2 then it can go back to the atmosphere and then it will be good for environmental purpose.

So for that reason in the catalytic converter platinum and rhodium is there are many other, but these are most common platinum and rhodium are used or deposited on a fine honeycomb mesh of alumina to give a large surface area. So for catalyst surface area is also very, very important that increases the contact time of the exhaust gas with the catalyst and then what is happening our desired thing is happening.

Then platinum and rhodium those are the two catalyst, but they are used for different purpose. So in one case we need to oxidize the gasoline to carbon dioxide into water in another case we want to reduce, but these two catalysts are used catalytic converters can be poisoned, but those catalyst are easily poisoned by certain metals that block their active sites and reduce their effectiveness.

Lead is one such metal. So unleaded petrol must be used in automobile now it has come in a market unleaded petrol because lead is very dangerous not only for health purpose, but also as a poison in this type of catalytic converters. So, unleaded petrol must be used in automobiles with catalytic converters. So this briefly I am telling you just giving the brief it is a large field the catalytic converter, but it is daily basis this is a good application of catalyst.

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Now the references I have shown here the same references actually this book and two books all three our books actually, but this book is very good this is also good. Here for catalysis it is also some parts I have collected, some information I have collected from this books.

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So as a conclusion I can tell that in this lecture we have discussed about different types of catalyst and their industrial applications. Various catalytic reactions have been elaborated the turnover number, turnover frequency of a catalyst is discussed for various types of catalyst. So these are very important for catalyst. Thank you.