Environmental Chemistry and Microbiology
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Lecture –20
Chemical Kinetics-Catalysis (Part-C)

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 of IIT, Kharagpur. We have divided this course into two parts. The first part is environmental chemistry that will be taught by me and the second part is environmental microbiology which will be covered by Professor Sudha Goel. Now in my module 1, I have discussed about the acids, bases and salts. In the second module, I have discussed about chemical equilibrium. In the third module, I have discussed about the chemical kinetics: the order, the rate expression, the rate and how to develop the rate expression, how to determine the order of a reaction, differential rate laws, integrated rate laws etc. In my fourth module I am discussing about the other aspects of chemical kinetics. I have discussed about the mechanism, how to develop the mechanism of a reaction and also how the catalysts are working, what are the different types of catalyst, what is the mechanism behind the catalysis etc. So, this is the module 4 (my 20th lecture) and it is chemical kinetics catalysis (Part C).

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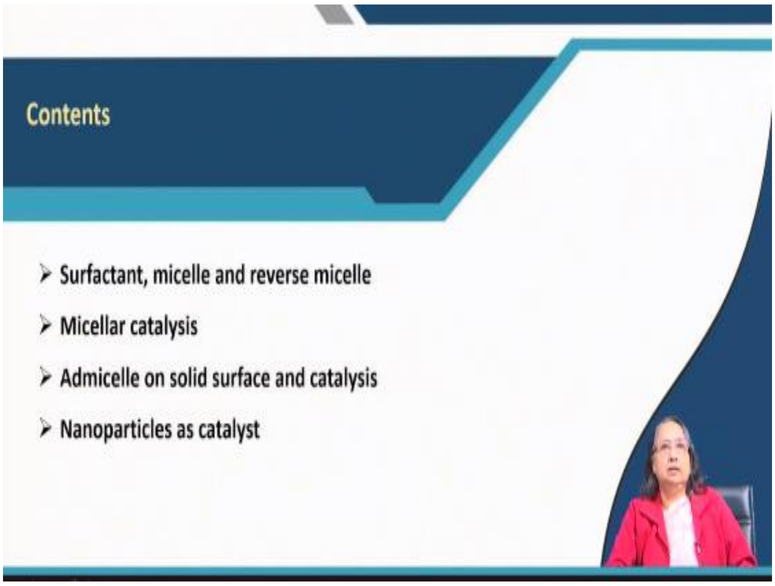

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- Micellar catalysis
- Admicelle on solid surface and catalysis
- Nanoparticles as catalyst

In this lecture I will talk about little bit of research related things, which are very important for catalysis. I will talk about surfactant. I will talk about the micelles and reverse micelles. I will discuss how the catalysis can happen within the micelle. Then I will talk about the admicelle and how admicelle can hold the catalyst and facilitate the catalytic activity. I will talk about the nanoparticles. Nowadays nanocatalyst is a very important field of research. So, I will cover all those things in this lecture.

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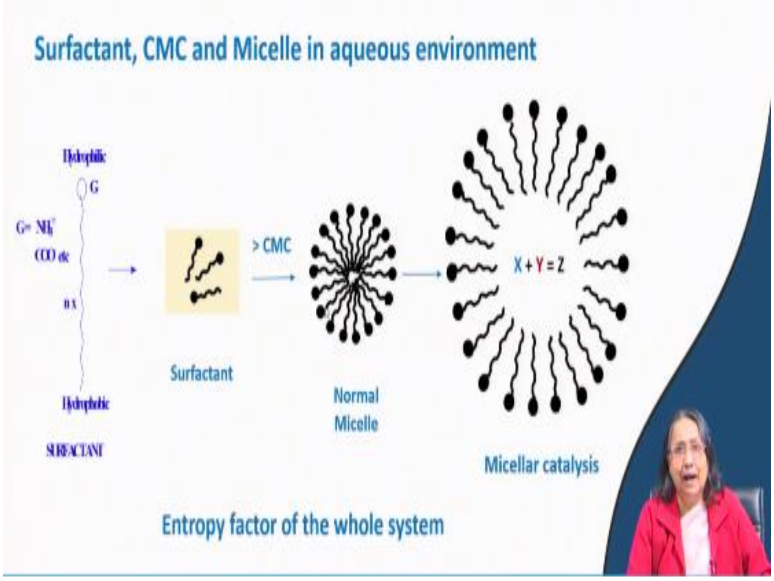
Surfactant, CMC and Micelle in aqueous environment

Entropy factor of the whole system

Now what is surfactant? Surfactant is a very common thing which is used in detergents, toothpaste and the specialty about that surfactant is that it has a very special chemical structure. Why it is called surfactant? It is so because it is a surface-active agent. In abbreviated form it is called surfactant. Surface activation means it is reducing the surface tension of water. Now what is the specialty about the surfactant in relation to the chemical structure? The chemical structure is shown of the surfactant is shown in the last slide. You can see here that there is a long carbon chain. There may be 15 carbon or 18 carbon. You can see the two ends. In one end you see it is carbon. So, it is hydrophobic end. It is also called hydrophobic tail and at the other end it is written as G. G is some ionic end. It maybe NH_3 or COO^- or it can be SO_3^-. So, this is called ionic head. Now in a structure of a surfactant, one end can be represented as head and the other end as tail. So, if you put surfactant molecule in water in a small concentration then it will be acting as an electrolyte. So, it will start forming some layer in the interface of water and air. But if you increase the concentration and if you reach the CMC (CMC means critical micelle concentration in water), then these surfactant molecules will arrange themselves in some spherical structure. This is shown in two dimensions, but actually it is three-dimensional structure as it is a spherical structure. It is called micelle. Now what is the specialty about it? This is dynamic. It means it is forming and breaking. You can see here all the carbon ends inside the center at the core. It is called hydrophobic core and all the hydrophile end groups are exposed towards the water medium in water. The picture is shown in a bigger way in the last slide. Say, for example benzene or chloroform are not soluble in water. If you put a little amount of this type of molecule in water then they will form emulsion but they are not dissolved in water. Now but they can be dissolved in the hydrophobic core. This is called solubilization. But if you add too much of benzene or chloroform, then it will not be soluble. Now in the hydrophobic core some reaction can occur. This is called micellar core. So micellar catalysis can happen here. Say for examples, there are X and Y can react to form the Z. This can happen here in the micellar core. This is called micellar catalysis.

Now I will discuss about the entropy factor which is a little bit away from this catalysis. You may tell that why the micelles are formed? We know that in the natural process always entropy increases, but here when the micelle is formed entropy should decrease. It is opposite to our concept. Now to explain this phenomenon, you have to think about the whole system. When the micelles are formed, water structure is breaking and so entropy is increased. This is not catalysis related, but just I wanted to mention. Many reactions that will not happen in homogenous water or any solvent but can happen here in the micelle. Now instead of water medium, if you put similar surfactant molecules in organic solvent, but containing little amount of water then what will happen?

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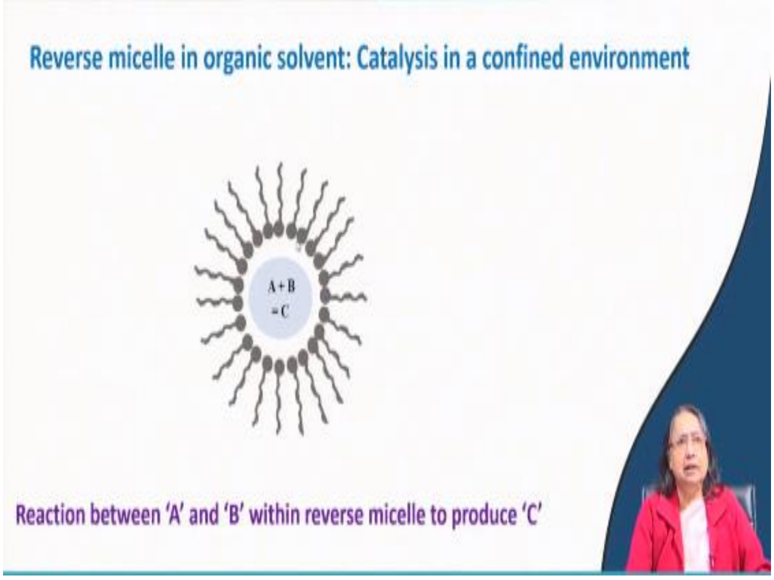

Reverse micelle in organic solvent: Catalysis in a confined environment

Reaction between 'A' and 'B' within reverse micelle to produce 'C'

it is just the reverse where mostly organic solvent with little amount of water is present. Then the reverse micelle will be formed. This is the reverse micelle you can see here that the head groups (because of little amount of water) will be inside the core and then these head groups are facing towards the water. So carbon end will remain towards the organic solvent because we know hydrophobic thing like hydrophobic things. So, in organic solvents like chloroform, hexane it will form reverse micelle. Here also some reaction is possible in the reverse micellar core. This is also very interesting.

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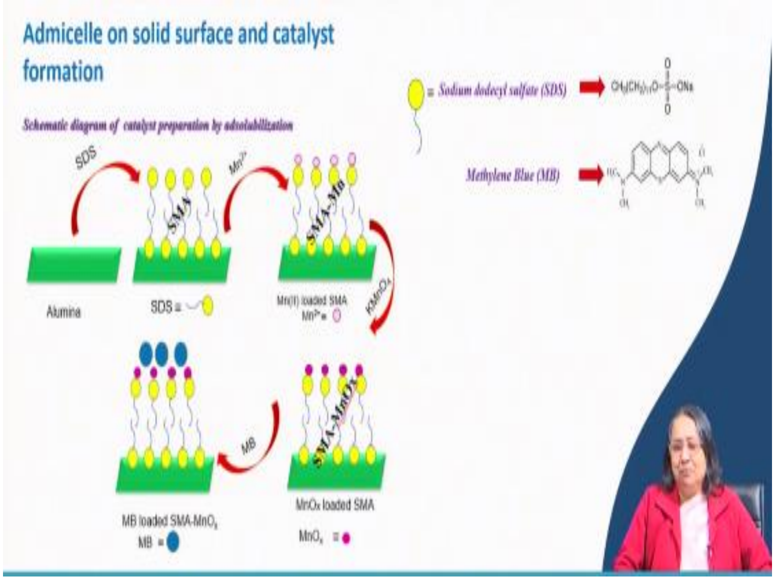

Admicelle on solid surface and catalyst formation

Schematic diagram of catalyst preparation by adsolubilization

I already told you that in heterogeneous catalysis it is easier to separate the catalyst after reaction. Now considering the similar concept in the micelle, how can you separate. Once the reaction is happening, then how can you separate the micelle or surfactant. It is very difficult. But if we can do it on solid surface, then the solid is easier to remove by filtration or settling. In the last slide, you can see here similar type of thing happening, but it is happening on the micelle adsorbed on the solid surface. This type of micelle is not spherical micelle, but it is adsorbed on to the solid surface. That is why it is called admicelle (means adsorbed micelle). Here you can see in the last slide, that this type of hydrophilic end of the surfactant is facing towards the solid surface (i.e., the surface alumina). It depends on the pH_{zpc} of alumina. PH_{zpc} is a characteristic for a solid surface. It is actually a pH. At pH_{zpc}, some solid surface is neutral. It means its charge is zero. But if you lower the pH of the solution, then the surface will become positively charged. If you go to higher value then the solid surface will be negatively charged. In case of alumina, the pH_{zpc} is 9.1. So, if you make the solution pH below 9.1, say for example 4 or 5, then alumina will be positively charged and, in that case, you know hydrophilic head of the sodium dodecyl sulfate (SDS) (negatively charged) will be towards the alumina surface. Over the first layer, the second layer will arrange themselves as shown in the last slide. So, basically it is micelle type structure, but it is adsorbed on solid surface and that is why it is written SMA (alumina is modified with SDS or surfactant).

How it is formed? To alumina in water, you have taken you have added SDS in very high concentration. You have made the solution pH around 4.5 (much below the pH_{zpc} of alumina) Then SDS is arranging on the alumina surface in a bi-layer fashion. Now the hydrophilic head group is negatively charged. If you put Mn^{2+} (cation), it will be adsorbed in a negative head group and then manganese loaded SMA will be formed. So, you have loaded manganese to SMA and now if you put $KMnO_4$, then a redox type reaction will occur. See in the catalyst it is written MnO_x. Actually, we have told oxygen is in mixed oxidation state. So, we have written MnO_x. You have learned that MnO_2 is a very good catalyst for H_2O_2 decomposition. Here we will use it as a catalyst. Now as the solid surface (SMA) is negatively charged, the cationic dye (methylene blue) will be adsorbed on this negatively charged head group. So, catalyst as well as the dye are on the solid support. We will show you how the catalyst can degrade the methylene blue dye here in presence of H_2O_2. So basically, you are preparing a heterogeneous catalyst with MnO_2 or MnO_x and you are trying to degrade the methylene blue by using H_2O_2.

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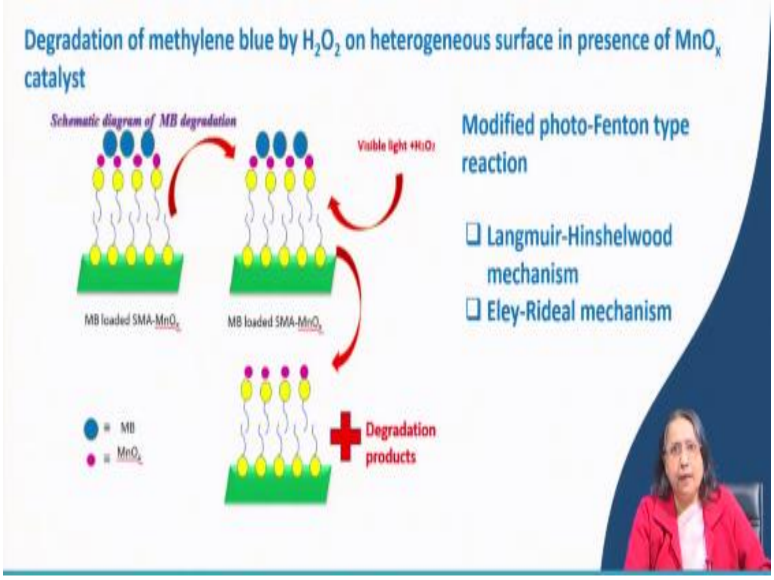

Degradation of methylene blue by H_2O_2 on heterogeneous surface in presence of MnO_x catalyst

Modified photo-Fenton type reaction

☐ Langmuir-Hinshelwood mechanism
☐ Eley-Rideal mechanism

Now you see in the last slide that you got SMA-MnO_x as the catalyst and the dye i.e., methylene blue is adsorbed there. So, as already mentioned both the catalyst and the substrate together is adsorbed on the same surface. Now you are putting H_2O_2 and light. Light can also decompose H_2O_2 (you have already learned). Now H_2O_2 will be decomposed and here in this case it is not oxygen, but it will be hydroxyl radical. So, this type of degradation is called advanced oxidation process or AOP. $OH^{\bullet}$ is very powerful oxidizing agent and that is coming from the H_2O_2 in presence of catalyst. So, $OH^{\bullet}$ will oxidize the methylene blue and some degradation products will be formed. Now after that the product will go out. So, the catalyst is remaining free for another molecule of methylene blue again to come and react. So, this is called modified Fenton type catalyst. Why it is called modified Fenton? It is so because in the classical Fenton, reaction is happening with Fe^{2+} and H_2O_2. This is first it is observed by Fenton and he did the oxidation of tartaric acid. But after that for a long time this reaction remains unattended. Finally, again from 1960 this Fenton type of reaction is being used for pollutant degradation. In this type of reaction, $OH^\bullet$ radical is generated and it is much powerful oxidant than H_2O_2 and it is taking its role to oxidize the organic pollutant. Now it is modified Fenton because H_2O_2 is there, but catalyst is different (MnO_x). It is also photo Fenton because you are using the visible light also.

Now there are two types of mechanisms to explain this type of reactions. One is the Langmuir Hinshelwood mechanism and another is the Eley Rideal mechanism. So, in this type of heterogeneous catalysis, you know there is substrate and reagent. At least one substrate has to be adsorbed. It can be two also may be adsorbed. Say for example A and B are reacting and both A and B are adsorbed on the catalyst surface. Then this is called the Langmuir Hinshelwood mechanism, but if one is adsorbed and another is in the liquid phase or gas phase and it is not adsorbed, but it is coming from the gas phase or liquid phase and reacting and then it is going out then it is the Eley-Rideal mechanism. So, these two types of mechanism are proposed. I hope you have understood what are the difference between these two. So, what we have seen here that micelle can be used on adsorbed phase to get the catalysis. Mn Ox is a good catalysis and it is very easy to separate just by keeping for some time this is settling down and then you can easily take out the water from the upper part. I have already disused about the mechanism. So, if you want to know the mechanism then you have to isolate the intermediates or products. So here it is observed that there are many products where $OH^\bullet$ is attached.

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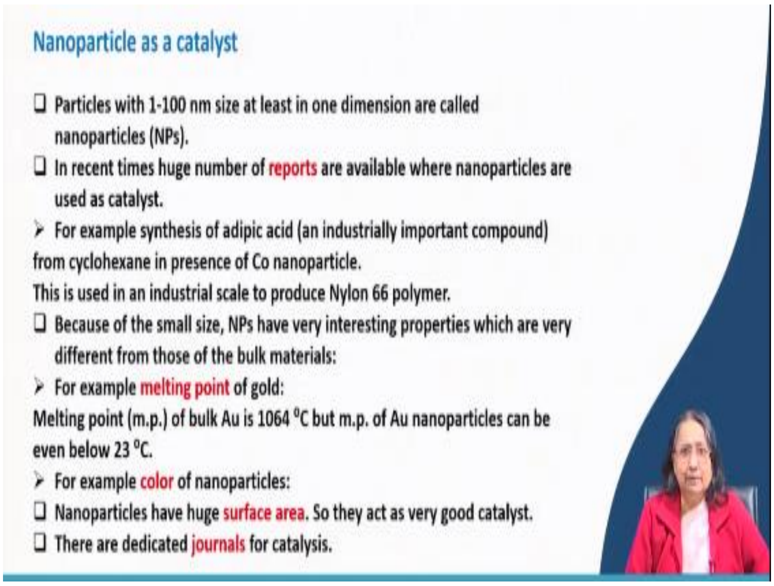

Nanoparticle as a catalyst

- ❑ Particles with 1-100 nm size at least in one dimension are called nanoparticles (NPs).
- ❑ In recent times huge number of reports are available where nanoparticles are used as catalyst.
- ➢ For example synthesis of adipic acid (an industrially important compound) from cyclohexane in presence of Co nanoparticle.

This is used in an industrial scale to produce Nylon 66 polymer.

- ❑ Because of the small size, NPs have very interesting properties which are very different from those of the bulk materials:
- ➢ For example melting point of gold:

Melting point (m.p.) of bulk Au is 1064 °C but m.p. of Au nanoparticles can be even below 23 °C.

- ➢ For example color of nanoparticles:
- ❑ Nanoparticles have huge surface area. So they act as very good catalyst.
- ❑ There are dedicated journals for catalysis.

Now I am going to another very important topic i.e., nanoparticle. Nowadays, it is enormously as a catalyst. Those who are not very much familiar with nanoparticle I can tell you that particles with 1 to 100 nanometer sizes at least in one dimension are called nanoparticles. Why I told in one dimension because say for example, you can think about one wire. Say for example the diameter of the wire is 15 nanometer, but the length of the wire may be 1,000 nanometer then my question is whether it will be called as nanoparticle or not. As one dimension here is 15 nanometer even if the length is much higher still it will be called a nanoparticle (nanowire). Nanometer means 10^{-9} m. So, you can understand how small it is. In recent times huge number of reports are available where nanoparticles are used as catalyst. I will tell some applications of nanoparticles as catalyst. Adipic acid is an industrially important compound. Adipic acid can be synthesized from cyclohexane by using cobalt nanoparticle. I will not go into the details, but I can tell you that cobalt nanoparticle is acting as a catalyst in this reaction. If you remove the double bonds of benzene ring of cyclohexane, then it can be converted to adipic acid which is very much important for preparing nylon 66. Now, why nanoparticle is so much important? It is because of their small size. Say for example melting point, color, surface area is very different from the properties of the bulk materials. Say for example melting point of gold the melting point of bulk gold is this one 1064° C, but melting point of gold nanoparticles can be even below 23° C. Color of nanoparticle is different from the bulk. Say for example gold nanoparticle can have purple color, blue color etc. Same is true for silver. Silver nanoparticles may have different colors than the bulk metal. Now nanoparticles have huge surface area. So, they act as a very good catalyst as I have already told you that the adsorption is required. So, if surface area is more then more number of molecules can be adsorbed. You can see that many journals are dedicated for catalysis. So, you know how important now it is to develop some catalysis or to do some reaction by using some good catalyst.

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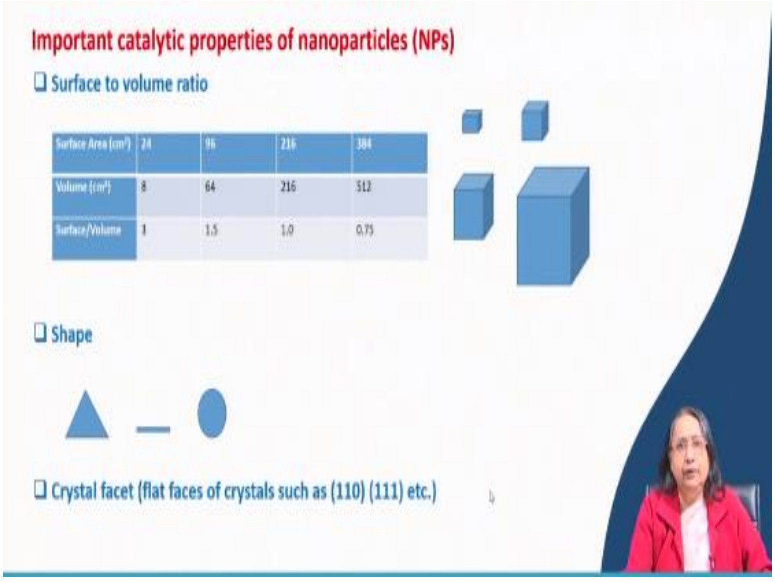

Important catalytic properties of nanoparticles (NPs)

☐ Surface to volume ratio

Surface Area (cm^2)	24	96	216	384
Volume (cm^3)	8	64	216	512
Surface/Volume	3	1.5	1.0	0.75

☐ Shape

☐ Crystal facet (flat faces of crystals such as (110) (111) etc.)

Now when I am talking about the nanoparticles you can see in the last slide that how the volume, surface to volume ratio and the surface area is related. Volume means length×length×length. You can easily calculate surface area and then surface to volume ratio. For cube there are 6 surfaces. So, you can see from the last slide that as the size is increasing, then the surface to volume ratio is decreasing. This is very important term for the catalytic property. When surface to volume ratio is high then it will have better catalytic properties. So smaller particles are better catalyst. Now shape also matters for catalytic property. There may be different shapes such as triangle shape, rod shape, spherical shape etc. Now crystal facets are also important for catalysis. Facets are flat faces of crystals such as (110), (111). There are some catalysts which are facet dependent. So, all those topics are now very important for nanocatalyst.

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References

- "Visible lighted assisted Fenton type degradation of methylene blue by admicelle anchored alumina supported rod shaped manganese oxide", S. Biswas, A. Pal, J. Water Process Engineering, 36 (2020) 101272

I have already discussed about the MnO_x supported on SMA. From SEM analysis it was found MnO_x nanorods. The reference for this MnO_x nanorods is given in the last slide. Regarding nanoparticles I have not discussed much. I have discussed a very general thing. You can get from any nano related book. So, I am not giving any reference.

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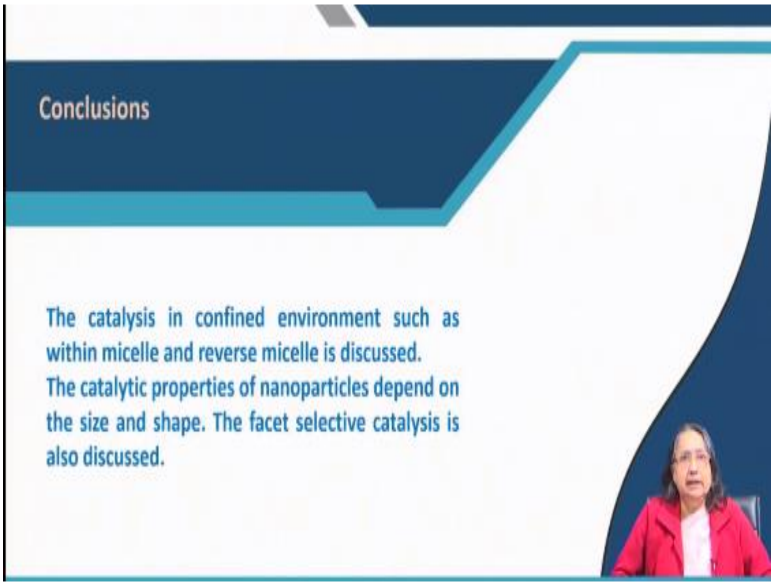

Conclusions

The catalysis in confined environment such as within micelle and reverse micelle is discussed. The catalytic properties of nanoparticles depend on the size and shape. The facet selective catalysis is also discussed.

Now in this last lecture I have discussed about the catalysis in confined environment such as within micelle and reverse micelle. I have also discussed the catalytic properties of nanoparticles. They are depending on the size, shape and facet. Thank you very much.