

Physics of Renewable Energy Systems
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Lecture 43
Nanocatalysts

Welcome to the fourth lecture of this week and today we will focus mostly on Nanocatalysts which were mentioned when we were discussing fuel cells. So, in the previous two lectures we discussed about a lot of materials that are useful for batteries, supercapacitors, solar cells, wind turbine blades or any other system which were discussed in the earlier modules. And today we will focus on the synthesis or the kind of materials that are used in fuel cells.

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CONCEPTS COVERED

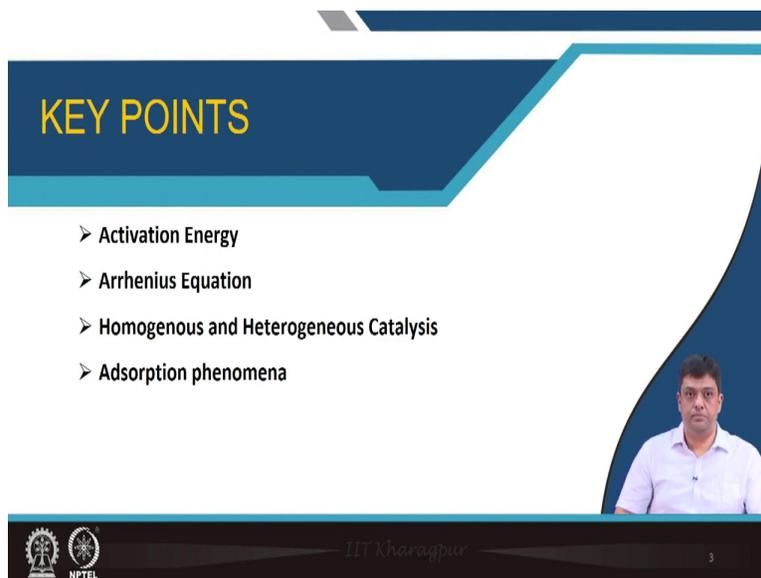
- Nanocatalyst
- Catalyst and its types
- Properties of catalysts
- Catalysis and its types

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So, you will be able to see what is a nano catalyst, what are catalysts and their types, how do they differ in properties, and finally, how do we define catalysis and what are the different types of catalysis processes.

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KEY POINTS

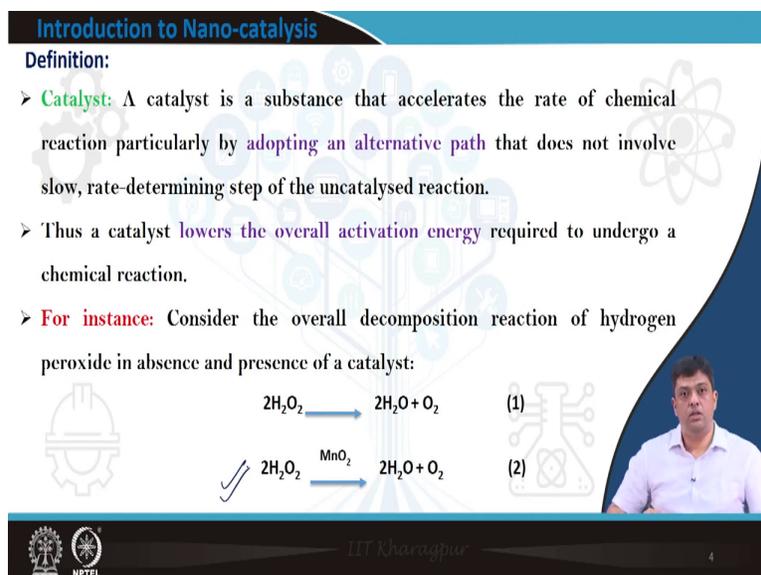
- Activation Energy
- Arrhenius Equation
- Homogenous and Heterogeneous Catalysis
- Adsorption phenomena

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Again, similar to the way we have discussed earlier, you will be able to see the importance of activation energy, the Arrhenius equation these two points have been discussed in earlier module, but we will repeat these concepts here and I hope that they will become even more clear to you. And two new concepts which will become known to you are dealing with homogeneous and heterogeneous catalysis and adsorption phenomena relate to these catalysts.

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Introduction to Nano-catalysis

Definition:

- **Catalyst:** A catalyst is a substance that accelerates the rate of chemical reaction particularly by **adopting an alternative path** that does not involve slow, rate-determining step of the uncatalysed reaction.
- Thus a catalyst **lowers the overall activation energy** required to undergo a chemical reaction.
- **For instance:** Consider the overall decomposition reaction of hydrogen peroxide in absence and presence of a catalyst:

$$2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad (1)$$
$$2\text{H}_2\text{O}_2 \xrightarrow{\text{MnO}_2} 2\text{H}_2\text{O} + \text{O}_2 \quad (2)$$

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So, a catalyst is defined as a substance that accelerates the rate of chemical reaction, but does not take part in the reaction as per se and how does it increase the rate it actually gives an alternative path for the reaction to take place. And what it also ensures that the rate determining step is actually able to follow this alternative path.

This catalyst when used can lower the overall activation energy. Remember the concept of activation barrier when we were talking about the use of temperature in supercapacitor devices and how the effect of temperature which was increasing can reduce the barrier height and you can see significant change in the capacity of super capacitors.

Similarly, a catalyst lowers the overall activation energy required to undergo a chemical reaction. For example, let us see we are using manganese oxide as a catalyst here. Remember, we are at one point we have used manganese oxide as a very useful electrode material for energy storage device that is super capacitors. And MnO₂ based super capacitors are already available in the market. But now we are going to use MnO₂ as a catalyst.

Hence, if you synthesize material, do not think that material can only be used for one application. You will see that nanomaterials have a wide range of applications and they are mostly associated with functionality. What do I mean by functionality, that means that these materials can be simultaneously used for more than one application. So, either you can use the synthesize MnO₂ powder for electron or if you want you can use this MnO₂ for catalytic activity.

So, if you take this overall decomposition reaction of hydrogen peroxide then what happens, you will see that you have the decomposition into 2H₂O plus O₂ of this hydrogen peroxide, but in the second case we are using the catalysts.

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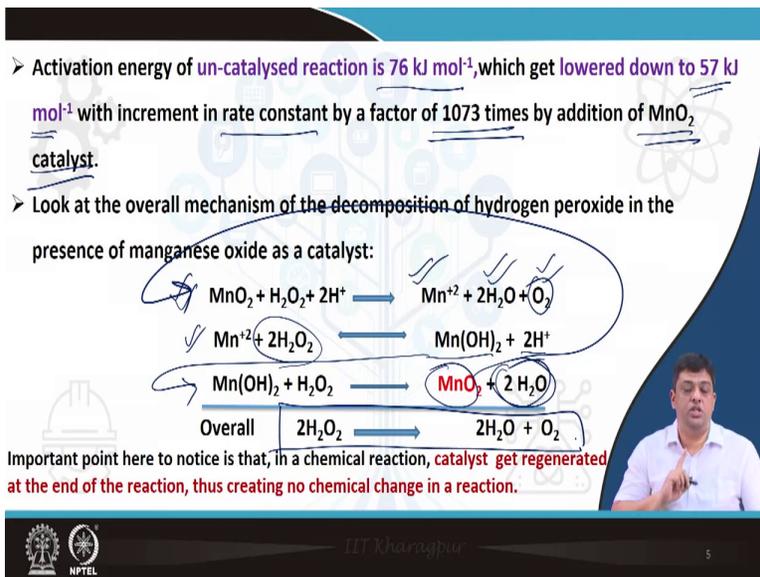
➤ Activation energy of un-catalysed reaction is 76 kJ mol^{-1} , which get lowered down to 57 kJ mol^{-1} with increment in rate constant by a factor of 1073 times by addition of MnO_2 catalyst.

➤ Look at the overall mechanism of the decomposition of hydrogen peroxide in the presence of manganese oxide as a catalyst:

$$\text{MnO}_2 + \text{H}_2\text{O}_2 + 2\text{H}^+ \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{O}_2$$
$$\text{Mn}^{2+} + 2\text{H}_2\text{O}_2 \longrightarrow \text{Mn(OH)}_2 + 2\text{H}^+$$
$$\text{Mn(OH)}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$$

Overall $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$

Important point here to notice is that, in a chemical reaction, catalyst get regenerated at the end of the reaction, thus creating no chemical change in a reaction.



So, what happens if a catalyst is used, then you will see that the uncatalyzed reaction was having the activation energy of 76 kilojoules per mole this activation energy is actually lowered to 57 kilojoules per mole with an increment in the rate constant by a factor of 1073 times. So, that is what is happening your reaction is happening at a much, much faster rate and that is obtained because of the addition of this catalyst.

So, what happens if you look into this process if you have added MnO_2 MnO_2 plus hydrogen peroxide plus protons will give you Mn^{2+} plus $2 \text{H}_2\text{O}$ plus O_2 and this 2 plus of Mn will react with H_2O_2 give you manganese hydroxide plus 2H^+ plus. So, what happens again this manganese oxide hydroxide reacts with H_2O_2 gives back MnO_2 plus water. So, you are actually getting back MnO_2 and this MnO_2 can then again take part in the reaction.

So, you are obtaining the completion of the reaction at a much faster rate. So, you have obtained O_2 and you have obtained water and this is what your reaction is. So, the catalyst is getting regenerated at the end of the reaction. Hence, there is no chemical change in the reaction which you had initiated.

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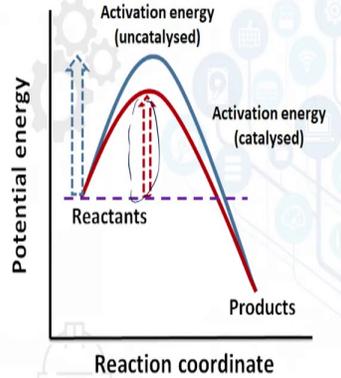


Fig.1 represent the effect of catalyst on the activation energy of a chemical reaction.

- (1) Introducing the catalyst **lowers down the activation energy** required for the chemical reaction.
- (2) According to **Arrhenius equation**, that relates the rate constant of a reaction with the activation energy required to carry out the overall reaction:

$$k = A e^{-E_a/RT} \quad (3)$$

where, k = rate constant,
 A = Arrhenius constant,
 E_a = Activation energy(kJ mol^{-1})
 R = gas constant($\text{J } \text{K}^{-1} \cdot \text{mol}^{-1}$),
 T = absolute temperature in Kelvin.

Fig. 1 Activation energy profile in presence (blue) and absence (red) of catalyst

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6

And as you can see, the addition of the catalyst reduces the barrier height so, it reduces the barrier height quite significantly. And we had already seen that according to the Arrhenius equation that relates the rate constant of a reaction with the activation energy required to carry out the overall reaction you know, k is equal to $A e^{-E_a/RT}$, where E_a is the activation energy, k is the rate constant, R is the gas constant, T is the absolute temperature in Kelvin.

So, if the activation energy comes down that immediately your rate constants also increase because you have this negative term in the exponent and that is the use of the catalyst. So, if you want to have high performing fuel cells, where you are going to use catalyst, then you should choose the right catalyst which can lead to significant enhancement in the rate constants.

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It is important to know that the catalyst neither change the equilibrium position nor does it alter the value of equilibrium constant in a reversible reaction.

7

Till now, what have we understood that catalysts can reduce the activation energy required to complete the reaction the rate constants can increase but the catalysts neither change the equilibrium position nor does it alter the value of equilibrium constant in a reversible reaction. So, catalyst is not taking part in the reaction if you say, so, it is recovered back.

(Refer Slide Time: 10:06)

Properties of a catalyst:

- (1) During a chemical reaction, a catalyst may undergo a physical change but never undergoes a chemical change, i.e. it does not chemically react with either reactants or products.
- (2) A catalyst can only activate a chemical reaction it can never initiate it.
- (3) In a reversible reaction, catalyst catalyzes both forward and backward reaction, thus does not alter the equilibrium position.
- (4) A catalyst can be stereoselective (i.e. catalyst prefer predominately a single stereoisomer as major product in a mixture of products) or stereospecific (i.e. catalyst particularly catalyzes the formation of one of a pair of stereoisomers among the mixture of products).

8

What happens during the chemical reaction, the catalyst may actually go a physical change, but it never undergoes a chemical change, that is it does not chemically react with either the reactants

or the final products. The catalyst is actually activating a chemical reaction, but it is never initiating the same.

So, it can activate, but it is not the initiator and in a reversible reaction, the catalyst catalyses both forward and backward reaction. Thus, it does not alter the equilibrium position. You can have steel selective catalyst or stereo specific catalyst. Stereoselective the catalyst prefer predominantly as single stereoisomers as the major product or stereospecific where the catalysts particularly catalyses the formation of one of a pair of stereo isomers amongst the mixture of products. So, you can have stereo selective catalyst or stereo specific catalysts.

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Negative catalysts

- It is not always necessary that a catalyst will always enhance the rate of chemical reaction. It may be the case when some catalyst inhibits the chemical process and thereby slow down the chemical reaction.
- For instance: Consider again the decomposition of hydrogen peroxide but this time with phosphoric acid as the catalyst.

$$2\text{H}_2\text{O}_2 \xrightarrow{\text{H}_3\text{PO}_4} 2\text{H}_2\text{O} + \text{O}_2 \quad (4)$$

- Here, the phosphoric acid increases the activation energy requirement.

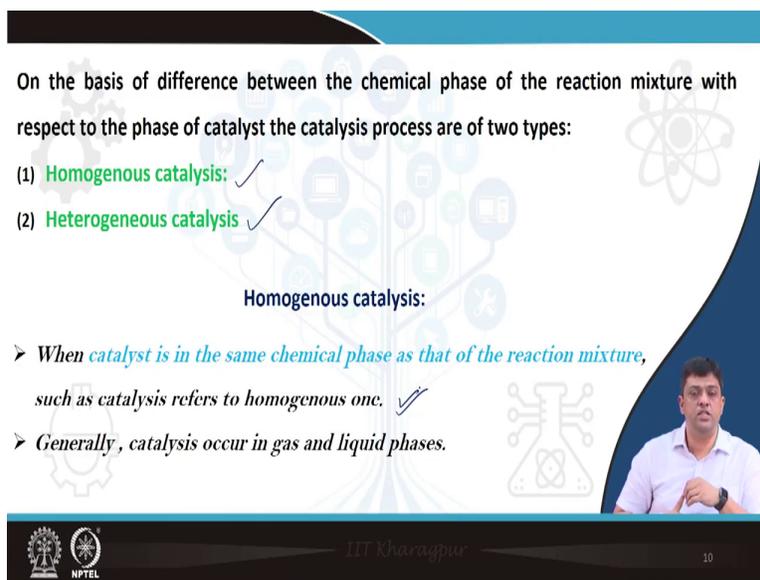
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9

You can also have negative catalysts. So, these catalysts are not necessarily actually increasing the rate of reaction, they can actually also slow down the reaction, for an instance let us consider the hydrogen, hydrogen peroxide decomposition case once again, but this time we are using phosphoric acid as the catalyst.

(Refer Slide Time: 12:04)



On the basis of difference between the chemical phase of the reaction mixture with respect to the phase of catalyst the catalysis process are of two types:

- (1) **Homogenous catalysis** ✓
- (2) **Heterogeneous catalysis** ✓

Homogenous catalysis:

- When *catalyst is in the same chemical phase as that of the reaction mixture, such as catalysis refers to homogenous one.* ✓
- *Generally, catalysis occur in gas and liquid phases.*

10

And you will see that here you can have the slowing down of the reaction. Similarly, on the basis of difference between the chemical phase of the reaction mixtures with respect to the phase of catalysts, the process can either be homogeneous catalysis or heterogeneous catalysis. The homogeneous catalysis means that the catalyst is in the same chemical phase as that of the reaction mixtures and you are having the homogeneous catalysis. And in these examples, you will see that they are more prevalent when you are talking the occurrence of catalysis in gas or liquid phases.

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Heterogeneous catalysis:

- When the chemical phase of catalyst is different from that of the reaction mixture, such as catalysis refers to heterogeneous catalysis
- Generally such catalysis occur on the surface of solid catalyst which has high surface area and porous structure.
- For instance:

(1) Consider Haber's process

$$\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \xrightleftharpoons{\text{Fe(s), Mo(s)}} 2\text{NH}_3 (\text{g})$$

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In comparison you have heterogeneous catalysis, where the chemical phase of the catalyst is different from the reaction mixtures. And generally, such catalysis occur on the surface of a solid catalyst which has high surface area and porous structures. So, you can consider the Haber's process where you are using iron ore molybdenum based solid catalysts and you are obtaining the nitrogen gas. So, more like heterogeneous catalysis.

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Adsorption are of two types:

(1) Physical adsorption or Physisorption,

Weak adsorption

Through Vander Waal force of attraction between adsorbent and adsorbate.

Reversible and non-specific

Enthalpy of adsorption in the range of 20-40 kJ mol⁻¹

(2) Chemical adsorption or Chemisorption

Strong adsorption

Adsorption occur via forming chemical bonds between the adsorbent and adsorbate.

Irreversible and specific

Enthalpy of adsorption in the range of 80-240 kJ mol⁻¹

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Based on the absorption processes you can have various kind of processes associated with catalysis you can have physisorptions or physical absorptions where which are weak absorptions

they are mostly associated with Van der Waals forces between the adsorbent and the adsorbate. Mostly they are reversible and nonspecific, you will see the importance of this process when we start talking about the BET technique for determining the specific surface area. And the enthalpy of adsorption lies in the range of what 20 to 40 kilojoules per mole.

You can have chemisorption, which is much stronger than physisorption. And here the adsorption takes place in a way that you obtain chemical bonds between the adsorbent and the adsorbate. If you are talking about chemisorption, then mostly you are talking about cases which are irreversible and specific. And they are associated with much higher enthalpy, maybe up to 240 kilojoules per mole.

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How to improve the chemical activity of catalysts?

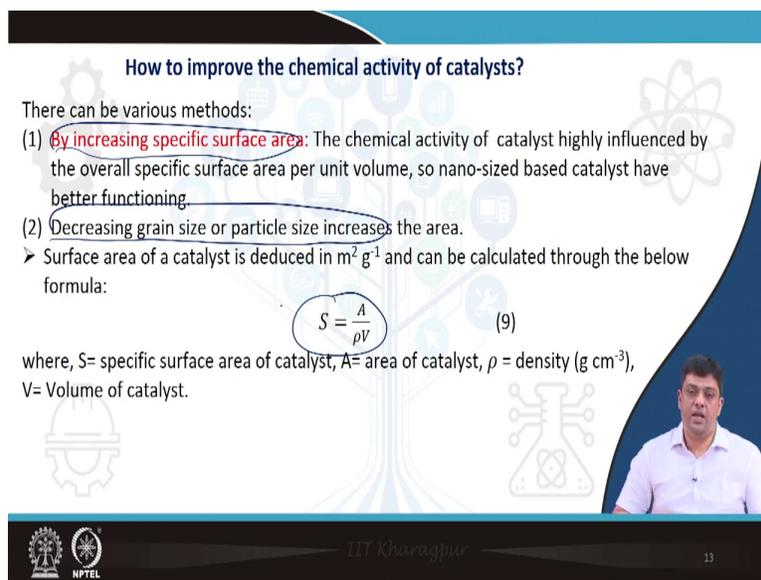
There can be various methods:

- (1) **By increasing specific surface area:** The chemical activity of catalyst highly influenced by the overall specific surface area per unit volume, so nano-sized based catalyst have better functioning.
- (2) **Decreasing grain size or particle size increases the area.**

➤ Surface area of a catalyst is deduced in $\text{m}^2 \text{g}^{-1}$ and can be calculated through the below formula:

$$S = \frac{A}{\rho V} \quad (9)$$

where, S= specific surface area of catalyst, A= area of catalyst, ρ = density (g cm^{-3}),
V= Volume of catalyst.



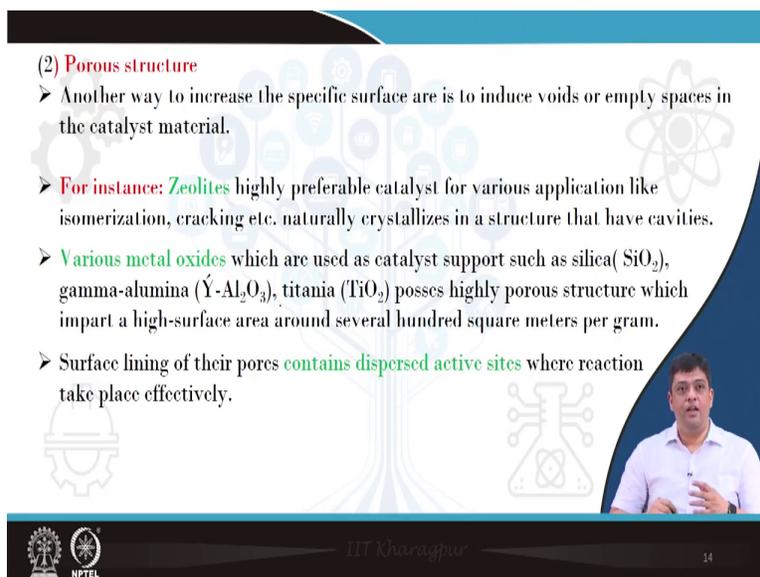
So now, we have understood that they are catalysts, the catalysts actually help to increase the rate constant, the catalysts actually will not take part in the reaction. So, I would like to have a catalyst which actually is giving me a much enhanced performance than the earlier case that means, I have used MnO_2 with the given shape and size and now, I want to again use MnO_2 but the performance should be enhanced even further from this catalyst.

So, what can I do, so there are various strategies which are proposed and one of the most common is by increasing the specific surface area because the chemical activity of the catalyst is highly influenced by the overall specific surface area of these particles which are constituting the catalyst and the second strategy which is there to increase the chemical activity is by decreasing the grain size or particle size.

So, you can go to nano sized structures, but with much higher specific surface area. So, you will understand why this topic is being discussed in this way, we have talked to you about nanomaterials, we have talked to you about various synthesis protocols which are used to obtain nanomaterials, you can go to very low dimension structures and you can also have various types of oxides or structures using complex combination of different metal ions these can have very different specific surface area.

And therefore, I already know a strategy of having a better catalyst that means, I am indicating please synthesize catalysts which are having dimensions in the range of nanometres and you ensure that they do not agglomerate, so that the available surface area remains high, you will get a high performance catalyst. So, surface area of a catalyst is mostly therefore, given in terms of meter square per gram and is given by A by ρV , where A is the area ρ is the density and V is the volume of the catalyst.

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(2) **Porous structure**

- Another way to increase the specific surface area is to induce voids or empty spaces in the catalyst material.
- **For instance: Zeolites** highly preferable catalyst for various application like isomerization, cracking etc. naturally crystallizes in a structure that have cavities.
- **Various metal oxides** which are used as catalyst support such as silica (SiO_2), gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$), titania (TiO_2) possess highly porous structure which impart a high-surface area around several hundred square meters per gram.
- Surface lining of their pores **contains dispersed active sites** where reaction take place effectively.

14

Along with that you can improve the performance of catalyst by making pore structures, so that you ensure more and more particles taking part in the overall process and they are contributing in increasing the rate constant because the absorbent or the absorbate have larger number of sites where they can interact. So, you will have porous structures which can give you improve performance.

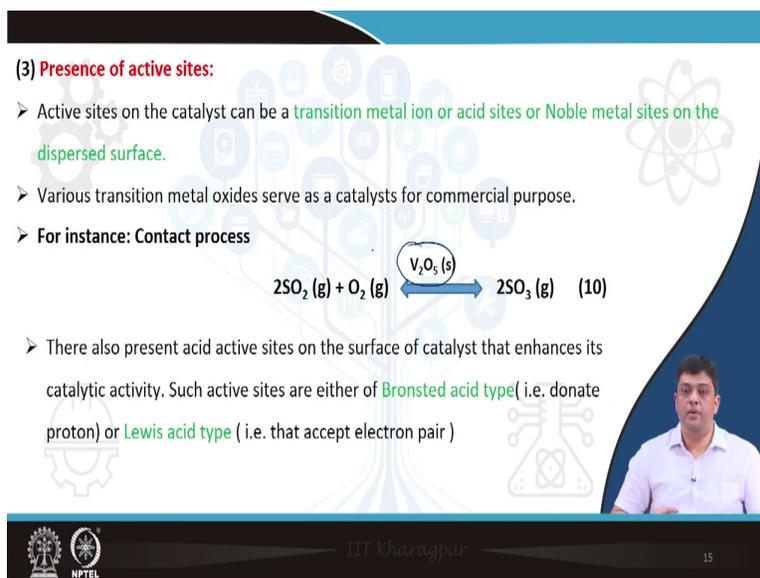
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(3) **Presence of active sites:**

- Active sites on the catalyst can be a **transition metal ion or acid sites or Noble metal sites on the dispersed surface.**
- Various transition metal oxides serve as a catalysts for commercial purpose.
- **For instance: Contact process**

$$2\text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \xrightleftharpoons{\text{V}_2\text{O}_5 (\text{s})} 2\text{SO}_3 (\text{g}) \quad (10)$$

- There also present acid active sites on the surface of catalyst that enhances its catalytic activity. Such active sites are either of **Bronsted acid type** (i.e. donate proton) or **Lewis acid type** (i.e. that accept electron pair)



What do I mean by presence of active sites as I just said, so active sites on a catalyst can be a transition metal ion or acid site or noble metal sites on a dispersed surface. So, active sites are those where this catalyst or catalysis will take place. How are you going to ensure that, either you can have pore structures, high surface area structures or you are going to tune their morphologies, so that you can allow accessibility of interaction between the absorbate and absorbent. So, if you talk about contact process, you can use medium pentoxide and then you can have these kinds of activities taking place much faster.

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Properties of porous materials:

- ❖ *Ordered pore network*
- ❖ *High pore volume*
- ❖ *High surface area*
- ❖ *Controllable structure*

Porous structures you can have ordered pore network, you can have high pore volume, you can have high surface area and while you have these structures you can also have control structures. So, it is not true that if you have porous structures then they are not ordered structures you can have quiet ordered structures in them also.

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Importance of porous structure

For energy storage application, the porous materials have a large number of advantages

- (1) The facilitated charge transfer reactions at the electrode/electrolyte interface due to the large surface area of the porous materials
- (2) The presence of the pores at the surface of the electrodes provide good access to the electrolyte
- (3) The shorter diffusion lengths for the electrolyte ion transfer as the walls of the active material surrounding the pores are very thin
- (4) The excellent cycling stability, due to the presence of the void space created by the separation of the particles in the active material, can help to constrain growth of material during cycling
- (5) The small feature sizes permit increased utilization of active material (more utilized volume, deeper cycling)

As a result, improved electrochemical activity can be obtained

For energy applications which we have discussed till now, the porous materials have large number of advantages because, first of all they facilitate the charge transfer reaction at the electrode interface as I just discussed. It provides good access or improved accessibility for the

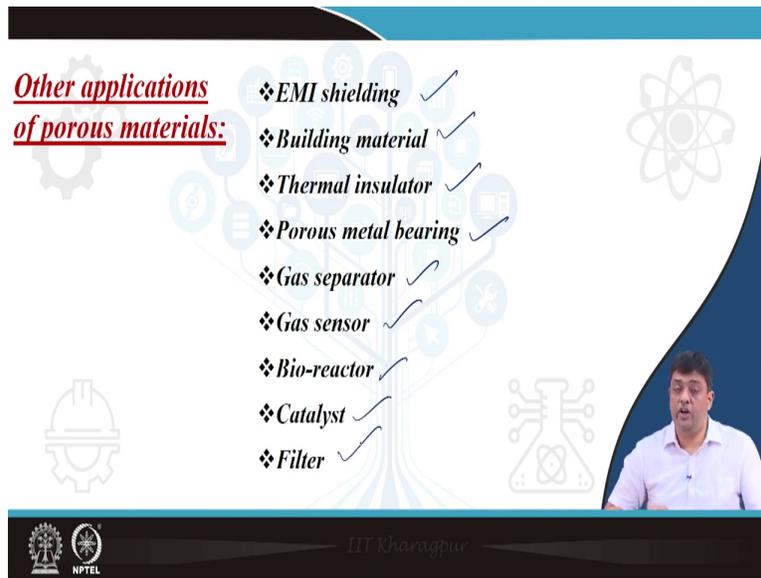
electrolyte ion to intercalate inside the electrode and then deintercalated after we process is complete, so during charging or discharging.

So, you can have improved intercalation processes if you have porous networks. The shorter diffusion length for the electrolyte ion transfer at the wall of the active material surrounding the pores are very thin and hence you are having lowered charge transfer resistance. And hence, the overall drop or loss is much reduced. These kinds of advantages lead to excellent cycling stability and a higher performance is obtained from the material. So, porous networks are very useful in energy devices and more so, in devices which we have discussed over the last three weeks.

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Other applications of porous materials:

- ❖ EMI shielding ✓
- ❖ Building material ✓
- ❖ Thermal insulator ✓
- ❖ Porous metal bearing ✓
- ❖ Gas separator ✓
- ❖ Gas sensor ✓
- ❖ Bio-reactor ✓
- ❖ Catalyst ✓
- ❖ Filter ✓

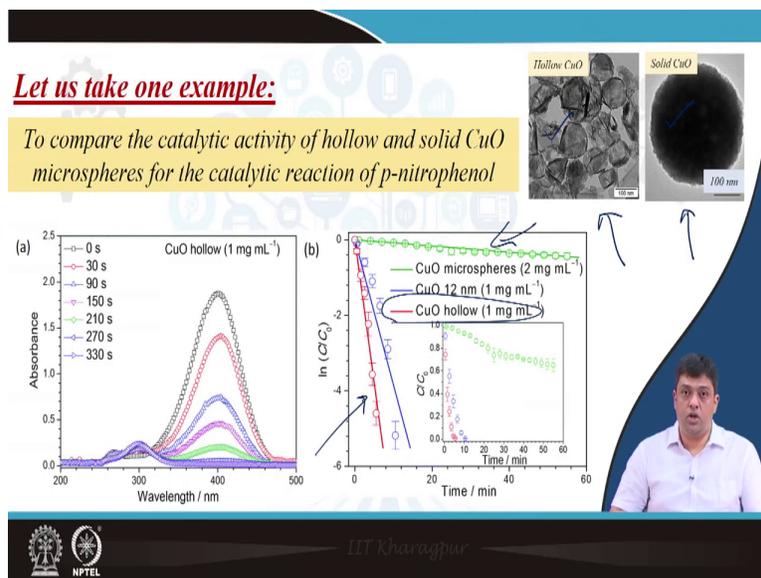


The other applications of these porous networks or porous materials lie in electromagnetic shielding, they can be used as building materials insulators, gas separators, gas sensors, bio reactors for catalysis obviously, or for filtration processes.

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Let us take one example:

To compare the catalytic activity of hollow and solid CuO microspheres for the catalytic reaction of *p*-nitrophenol



❖ *p*-Nitrophenol ions attain an equilibrium state following the adsorption and desorption from the active sites on the CuO surface.
 ❖ Once adsorbed on to the surface, *p*-nitrophenol reacts and is reduced to *p*-aminophenol, which can desorb in solution.

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Just to give you an example, this is an example where you have used copper oxide of two morphologies this is solid and this is hollow, the one on the left is also porous. You can see that if you are using this copper oxide for the reduction of P nitrophenol which is common waste or pollutant in the industrial waste which is being directly thrown in reverse at it at many places then if you can reduce them, then the pollutants which are actually entering the water can be significantly reduced.

And if you use these porous networks then you can increase the rate constant by 6 to 7 times in comparison to hollow structures. So, if you use solid structures, then you can reduce let the given amount of pollutant in, let us say 30 minutes, then using the hollow structures or the poorer structures you can complete the reduction process in as low as 5 to 6 minutes.

So, you have more efficient more faster processes and then you do not need to store water which is coming out from the industry for larger duration and then you can let them flow out and then you have much more efficient management of the waste water.

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Comparison of rate constants for reduction of p-nitrophenol using various CuO structures

Catalyst	Cycle	Catalyst concentration (mg mL ⁻¹)	Rate constant (s ⁻¹)
Commercial CuO microspheres	1	2	1.3×10^{-4}
Commercial 12 nm CuO particles	1	1	6.4×10^{-3}
CuO hollow nanostructures	1	1	1.3×10^{-2}
CuO hollow nanostructures	2	1	8.6×10^{-3}
CuO hollow nanostructures	3	1	8.3×10^{-3}
CuO hollow nanostructures	4	1	8.2×10^{-3}

Similarly, you can talk about the rate constant calculations and you can see that the rate constant of copper oxide which is commercially available or copper oxides which are used, then they actually vary by an order of magnitude and the ones which you would use would be the one which have very high rate constants.

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Various porous materials:

The slide displays five scanning electron microscope (SEM) images of porous materials. Each image is labeled with the material name and a scale bar indicating its porous structure. The materials shown are:

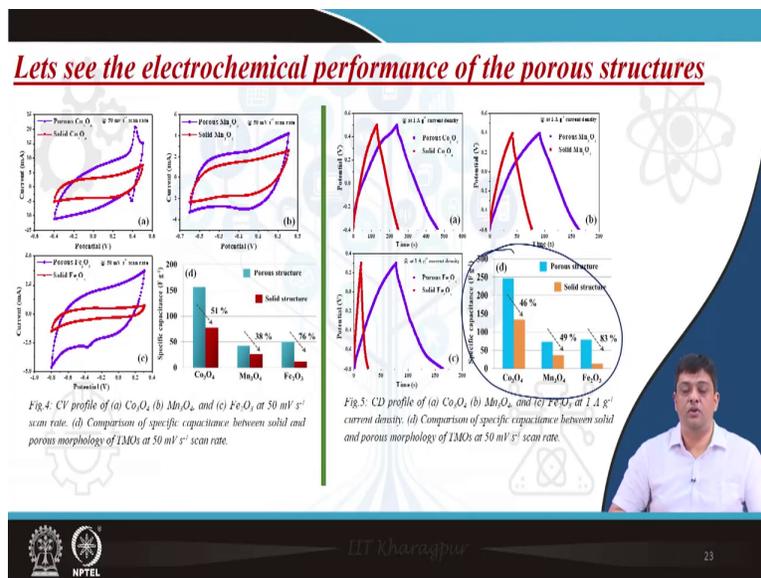
- Co₃O₄**: Porous structure with a scale bar of 500 nm.
- Fe₂O₃**: Porous structure with a scale bar of 4 μm.
- Carbon**: Porous structure with scale bars of 2 μm and 4 μm.
- Mn₂O₄**: Porous structure with a scale bar of 600 nm.
- SnS₂**: Porous structure with a scale bar of 600 nm.

There are various types of porous materials which we have used as electrode materials earlier in the devices. So, similar types of materials can also be used as catalysts. So, if you use let us say

cobalt oxide in super capacitors do not think that they are not going to be used anywhere else, they are as useful in let us say fuel cell or gas sensing or filtration or similar processes, where porous networks are required. You have used iron oxide in magnetic super capacitors, but they are also useful at many other places.

So, these kinds of metal oxides which we have been discussing in this course, are having large number of applications. So, I will repeat once again, material they can resynthesize using large number of techniques.

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They can have very different performance and you can choose the material as per the desired or requirement of the end user. If the user wants to use the material in energy storage device, you will use different structure of the metal oxide and if the user wants to use the same metal oxide that is the metal oxide having the same chemical formula, but for catalysis then you will use a different morphology with different porous structures, because they can clearly tune the response characteristics of these devices.

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Importance of porous structure over solid structures

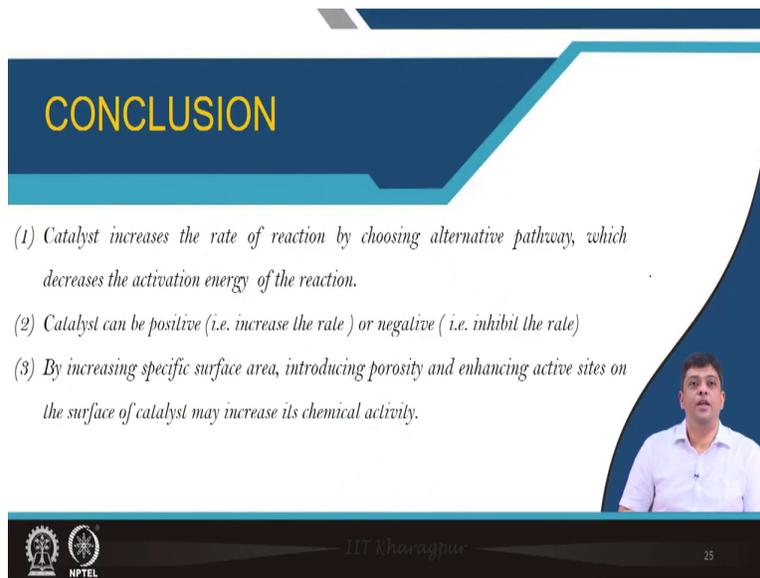
- ❖ *Significant enhancement of effective surface area of porous structures over the solid one makes them useful for catalytic applications.*
- ❖ *Accessibility to the inner pores enhances the reaction kinetics.*
- ❖ *As a result, there is a large increment in the reaction rate constants, proving improvement in the catalytic activity.*

The slide features a blue and white color scheme with a background of faint icons including a gear, a tree, a chemical flask, and a person. A video inset in the bottom right corner shows a man in a light blue shirt. The bottom of the slide contains the IIT Kharagpur and NPTEL logos.

And the importance of these structures is driven by the fact that they are having surface area which is high they also ensure improvement in the accessibility of electrolyte ion inside the material. So, that larger number of active sites become accessible for either catalytic processes to get initiated or even charged storage processes, which we have discussed earlier.

Because of this improved accessibility, what do you get, you have announcement in the reaction kinetics. And therefore, you get significant increment in the reaction rate for constants, which can improve catalytic activity or sensing activity if you are using these materials in for gas sensing or you can have improved double layer formation or enhanced double layer formation if you are using these kinds of materials in energy storage devices.

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CONCLUSION

- (1) Catalyst increases the rate of reaction by choosing alternative pathway, which decreases the activation energy of the reaction.
- (2) Catalyst can be positive (i.e. increase the rate) or negative (i.e. inhibit the rate)
- (3) By increasing specific surface area, introducing porosity and enhancing active sites on the surface of catalyst may increase its chemical activity.

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Hence, after today's lecture, it must be very clear to you that synthesis of materials will play a critical role in ensuring the usability of the various devices which we have discussed in this course. There are various techniques by which you can fabricate these materials, you can use these materials from solar cells to fuel cells, they have large number of functionality but one thing which will remain unanswered till now is that you have made these materials and we are talking directly about the application.

How do we understand that whether we have made these materials or not, whether they are single phase material or impure materials and are these materials giving me the physical or chemical characteristics by which I can decide the application of these materials. Therefore, the characterization of these materials are paramount before they can be used in the device. As a result, you must also know the characterization techniques which are used to characterize these materials.

Because in this course, you have seen that materials will play a very important role to obtain the desired device. So, you must also know the characterization techniques which are used to characterize the physical or chemical properties of these materials. And in the final two weeks of this course, we will therefore, focus on the characterization techniques that are used to

characterize these materials. And also, the details of the characterization techniques used to characterize some of the devices discussed in this course will also be presented.

(Refer Slide Time: 31:13)



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NPTEL 26

These are the major reference from where the data were obtained and I thank you for attending today's lecture.