Chemical Reaction Engineering - II
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Module - 1
Lecture - 3
Catalyst Properties and Classification

Hi, in the last lecture we defined what a catalyst is and what are the implications or utility of catalysts in various systems and how it may affect the yield and selectivity. In this lecture we will start by looking at some properties of the catalyst.

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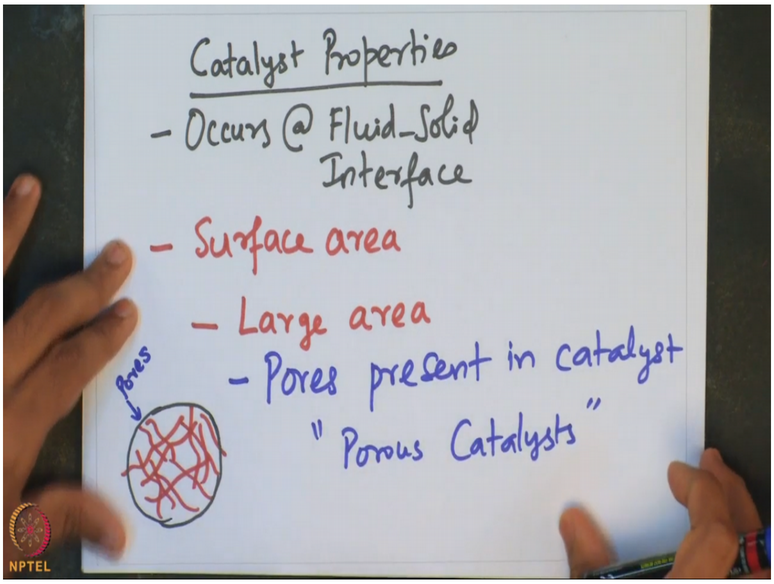

Catalyst Properties

- Occurs @ Fluid-Solid Interface
- Surface area
  - Large area
    - Pores present in catalyst
      "Porous Catalysts"

So, catalytic reaction typically occurs at the fluid-solid interface. So, therefore, clearly, the reaction would be a function of the surface area which is available for the reaction. Surface area available for the reaction or the interfacial area which is available for the reaction to occur. So, the large interface, so catalyst particles actually facilitate availability of large area for the reaction to happen.

And this actually is possible because of the various pores that are present in the catalyst. And these pores, there are several pores that may be present in the catalyst. And these pores together actually offer availability of large area at which the, in which the reaction can actually happen. So, such kind of catalysts are typically called as porous catalysts. Suppose we sketch a catalyst, let us assume that the catalyst is spherical in nature.

And there may be many pores which are actually present inside. And each of these pores will have surface which is present along the walls of the pores, which can actually facilitate or make available fluid-solid interface at which the chemical reaction can happen. So, these porous catalysts actually offer this unique advantage of providing large surface area for the reaction to happen. So, let us take a specific example and look at what is the kind of or what is the ballpark surface area which may be available for the reaction to happen.

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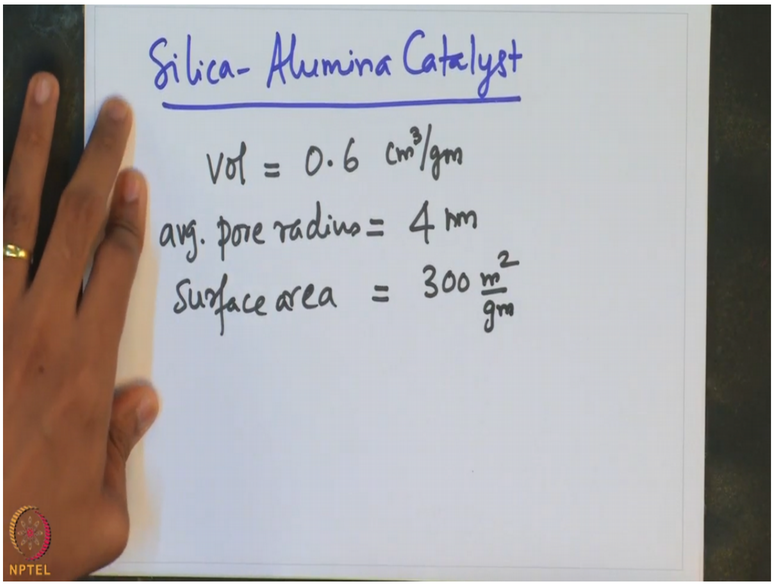

Silica- Alumina Catalyst

$\mathrm{Vol} = 0.6\ \mathrm{cm^3/gm}$

avg. pore radius = 4 nm

Surface area = $300\ \frac{\mathrm{m^2}}{\mathrm{gm}}$

So, let us take the example of silica-alumina catalyst. So, the typical volume of the catalyst is about 0.6 centimetre cube per gram of the catalyst. And the average pore radius is approximately 4 nanometres. And the surface area which is available for the reaction is about 300 metre square per gram of the catalyst. So, the kind of surface area which is available is actually phenomenal as one can see from this example.

And these are typical numbers which is applicable for most of the catalytic systems. So, the pore radius is very very small. It is in the nanometre scale. And so, in a catalyst whose typical diameter could be about 3 millimetres or so, the pores are actually very very small. It is about 4 nanometre pore through which the fluid can actually go through. And when the fluid goes through, the surface area which is available for the reaction is approximately in the order of 300 metre square per gram of the catalyst.

So, this is a phenomenal amount of surface area which is available for the reaction or the phenomenal amount of fluid-solid contact area which is available for the reaction to happen.

So, such catalysts having very high surface area because of these pores are typically referred to as what is called as the porous catalyst. There are several examples of these.

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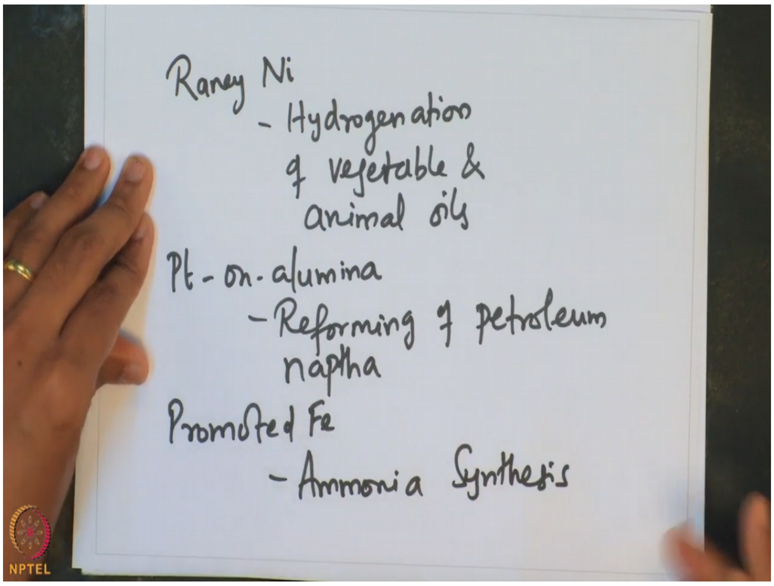

Raney Ni
- Hydrogenation of vegetable & animal oils

Pt-on-alumina
- Reforming of petroleum naptha

Promoted Fe
- Ammonia Synthesis

For example: Raney Nickel is 1 type which is actually used in hydrogenation, hydrogenation reaction; hydrogenation of vegetable and animal oils. It is, and another example is platinum on alumina. So, platinum is actually coated on a support called alumina. And we will discuss in a while, what the supported catalysts are. And this is typically used in reforming of petroleum naptha.

And another example is promoted iron, which is used in ammonia synthesis. So, these are some of the typical examples of catalysts which is used in different processes. So, sometimes pores are very small.

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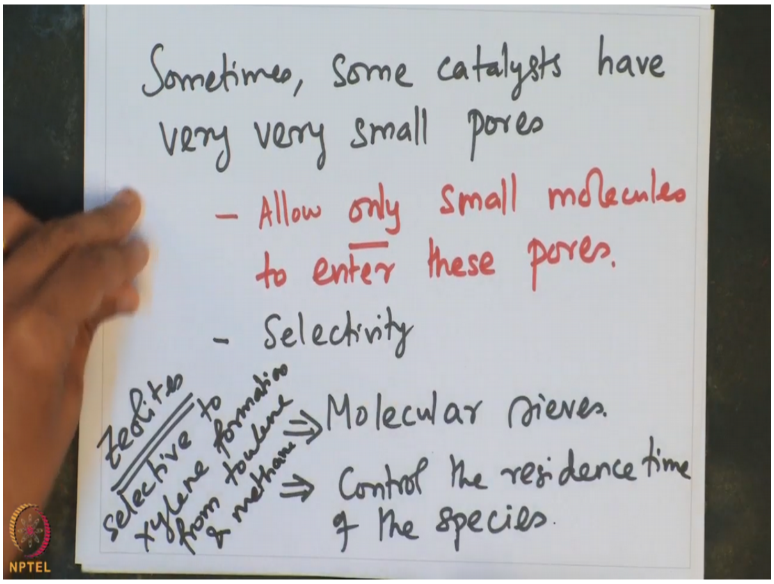

Sometimes, some catalysts have very very small pores

- Allow only small molecules to enter these pores.
- Selectivity

⇒ Molecular sieves.

⇒ Control the residence time of the species.

Zeolites

selective to xylene formation from toulene & methane

Sometimes some catalysts have very very small pores. And such catalysts actually have unique advantage because they allow only small molecules to enter these pores. This has a unique advantage because, only small molecules are allowed. And therefore, only certain molecules which may be participating or available in the reactant mixture would be allowed to enter the catalyst pores.

So, as a result, this can actually facilitate good selectivity for a desired product. And such kind of catalysts are called as molecular sieves. These molecular sieves are becoming very popular these days. It is used in many many different systems because it has this ability to facilitate high selectivity because it only permits a certain small molecules to enter the catalyst pores. And thereby, it prevents the other species from participating in the reaction.

Remember that the reaction is actually happening at the fluid-solid interface in the walls of the pores inside the catalyst particle. Moreover, it actually allows one to actually control the residence time of the species inside the catalyst. So, one of the important factor that actually controls the reaction is basically the total time for which the species which is participating in the reaction is actually staying inside the pores and is in contact with the fluid-solid interface.

So, the fact that these molecular sieves have very tiny pores, it has very selective ability to selectively allow only certain species to go inside the pores. It can, one can actually have a ability to control the residence time of these species in the catalyst particle. And thereby, actually provides an ability to control the reaction better. A good example of this is the use of zeolites catalyst.

Zeolites catalyst for selective, which is selective to xylene formation from toluene and methane. It is a very good example of such molecular sleeves, which is actually very selective to a particular product formation. So, it is not that all catalysts are actually having such kind of extended surface. Then it is not necessarily required. So, there are typically 2 classes of catalysts one can think of. So, one is called the supported catalyst.

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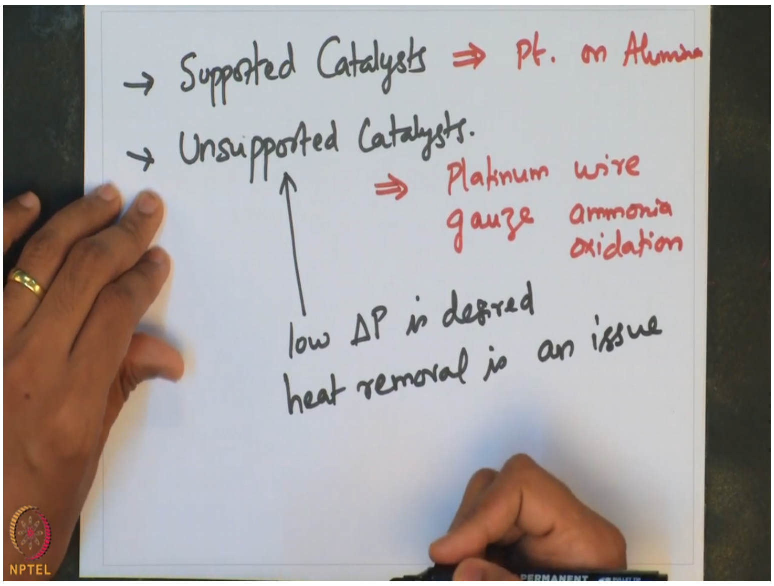

→ Supported Catalysts ⇒ Pt. on Alumina

→ Unsupported Catalysts.

⇒ Platinum wire gauze ammonia oxidation

low ΔP is desired

heat removal is an issue

Another one is called the unsupported catalyst. So, supported catalysts are those where the catalytic material which can typically be oxides of noble metal, so on and so forth. These will be impregnated in the particle form on the surface of a supporting material. For instance, a supporting material could be silicon or it could be alumina. And may be the catalyst particle such as platinum are actually impregnated on the surface or the sites which are actually available in this support material.

Good example is platinum on alumina. And these are basically minute particle which are actually impregnated on the local surface of the catalyst particles, local surface of the supported, support system. So, unsupported catalyst is where such a support is not required and directly the catalyst particles are actually used as a catalyst material is used as a reacting fluid-solid interface.

For example: platinum wire gauze which is used for ammonia oxidation. Normally a supported catalyst would actually require, you know higher pressure drop, because the pores in the catalyst are very tiny and the fluid particle actually has to go inside the pores. So, in case there are situations where we require low pressure drops and heat removal is an issue, then one would actually want to consider unsupported catalyst for such type of reactions.

So, unsupported catalyst is typically favoured when low pressure drop is desired and heat removal is an issue. In both these cases unsupported catalyst is actually preferred over supported catalyst. So, let us look at some examples.

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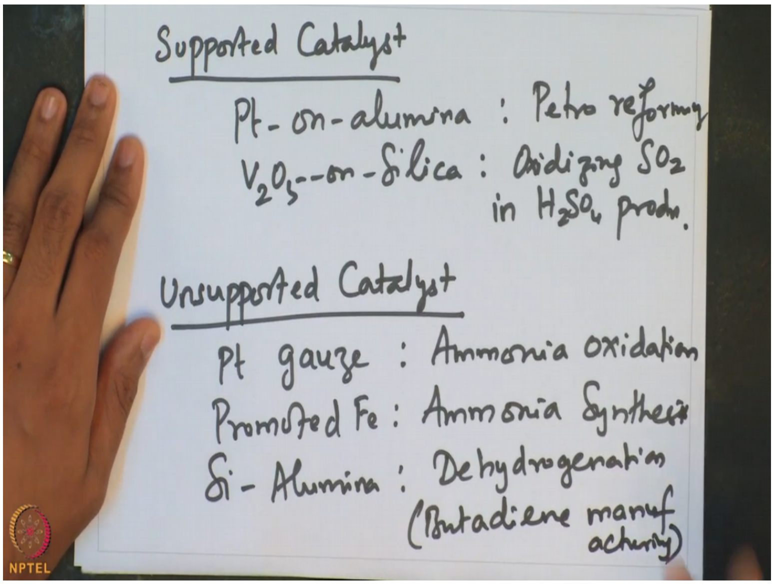

Supported Catalyst

Pt-on-alumina : Petro reforming

V_2O_5--on-Silica : Oxidizing SO_2 in H_2SO_4 prodn.

Unsupported Catalyst

Pt gauze : Ammonia oxidation

Promoted Fe : Ammonia Synthesis

Si-Alumina : Dehydrogenation (Butadiene manufacturing)

So, for supported catalyst, platinum on alumina which is used for petroleum reforming. And vanadium pentoxide on silica, which is used for oxidising S O 2 in H 2 S O 4 production process. And for unsupported catalyst, platinum gauze, which is typically used for ammonia oxidation. And then, promoted iron, which is used for ammonia synthesis. Silica alumina which is used for dehydrogenation and typically used in butadiene manufacturing.

So, these are the typical examples of supported versus the unsupported catalyst. And remember that supported catalyst will require a substrate on which the active catalyst material is actually impregnated in the substrate material. So, let us ask this question as to how does a catalyst work.

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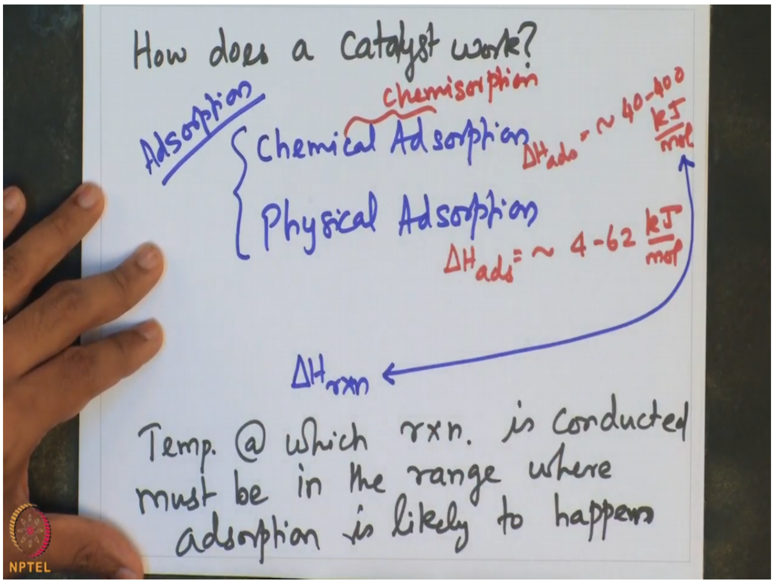
How does a catalyst work?

Adsorption

Chemical Adsorption (Chemisorption) $\Delta H_{ads} = \sim 40\text{-}400 \frac{kJ}{mol}$

Physical Adsorption $\Delta H_{ads} = \sim 4\text{-}62 \frac{kJ}{mol}$

ΔH_{rxn}

Temp. @ which rxn. is conducted must be in the range where adsorption is likely to happen

How does it facilitate acceleration or deceleration depending upon the situation, how does it facilities affecting the rate of the reaction. So, what happens is that the species which needs to react actually goes into these pores or into gets access to the surface of the catalyst. And this catalyst somehow interacts with the species which is present, the species which is participating in the reaction, somehow interacts with the catalyst material.

And this interaction can be of typically of 2 types. So, the interaction can be a chemical adsorption or a physical adsorption. So, typically, the adherence or the species which adheres to the material that process is what is called as adsorption process. And this is a very typical process which actually is involved in the gas phase reactions, which is catalysed by solid surface.

Now, usually one or all the molecules which is participating in the reaction have to adsorb onto the surface or they have to interact with the surface in order for the reaction to happen at the solid surface. So, the physical adsorption essentially involves physically the species come and bind onto the surface of the catalyst. And this of course is a function of temperature. It is an exothermic reaction.

And it turns out that the typical delta H which is actually corresponding to the physical adsorption is of the order of 4 to 62 kilojoules per mole. And in a similar fashion, the chemical adsorption the delta H adsorption is once again and exothermic reaction. So, one needs to supply heat for the species to actually adsorb onto the surface. And so, the delta H adsorption is typically of the order of 40 to 400 kilojoules per mole.

And you may recall from your first course on reaction engineering, that the delta H reaction for many reactions is also typically in the same order as that of this. The delta H reaction is in the same order of magnitude as that of the delta H of the adsorption. In fact, most of the cases, most of the reactions, the adsorption typically is actually a chemical adsorption. And therefore, because the, it is a exothermic process and it requires higher temperature and also the chemical reaction itself may be an exothermic reaction or an endothermic reaction; it may be temperature sensitive.

And if one has to conduct such a reaction at the solid surface, the gas fluid system at the solid surface, then the temperature at which the reaction actually is conducted must be in the same range where the adsorption of the species is likely to happen. Otherwise, what will happen is that the species is not readily adsorbed at that temperature. And so, conducting reaction at a temperature where the adsorption is not likely to happen will lead to low productivity because the species is not available at the surface for the products to be formed.

So, thumb rule is that, the temperature at which reaction is conducted must be in the range where adsorption is likely to happen. So, this process of chemical adsorption is also typically referred to as chemisorption. So, we will use this word quite often. Chemical adsorption is also called as chemisorption. So, when the species actually binds to the active material, what happens is that the species actually binds to what is called as the active sites which is present in the catalyst. So, let us define what is an active site.

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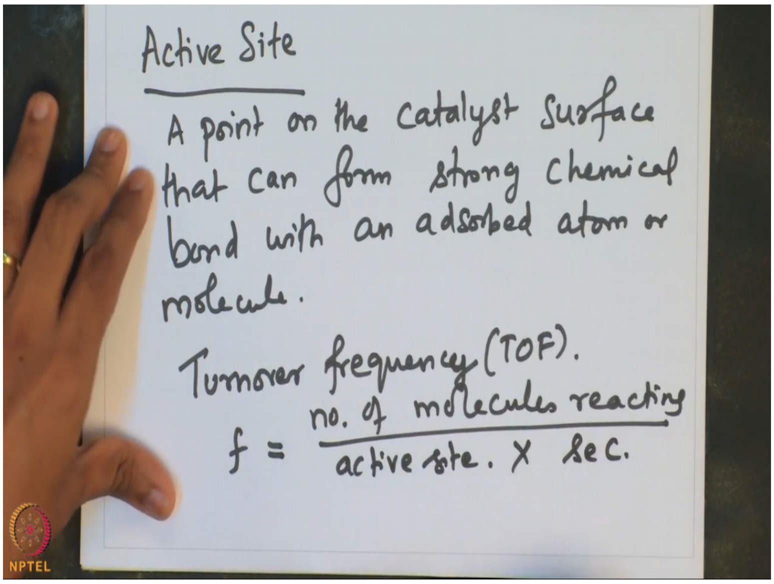

Active Site

A point on the catalyst surface that can form strong chemical bond with an adsorbed atom or molecule.

Turnover frequency (TOF).

$$f = \frac{\text{no. of molecules reacting}}{\text{active site.} \times \text{sec.}}$$

So, active site is a point on the catalyst surface that can form strong chemical bond with an adsorbed atom or molecule. In fact, the active sites is actually quantified by what is called as a turnover frequency or TOF in short. So, if I use this symbol f for turnover frequency, it is essentially defined as number of molecules reacting per active site per second. That is what is called as a turnover frequency. And this is typically measured or calculated at a certain experimental condition.

So, the active sites is essentially quantified by what is called as a turnover frequency, which is essentially reflects what is the number of molecules that is actually reacting per active site per second at a certain experimental condition. So, since the reaction is happening at a certain temperature and the temperature also affects the adsorption process, one can actually classify catalysts based on the temperature at which the reaction happens and the turnover frequency.

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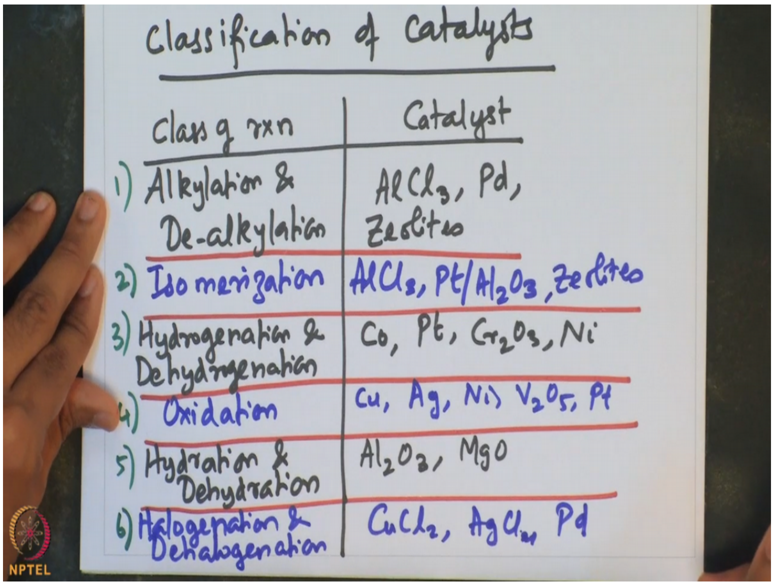

Classification of Catalysts

Class of rxn	Catalyst
1) Alkylation & De-alkylation	$AlCl_3$, Pd, Zeolites
2) Isomerization	$AlCl_3$, Pt/Al_2O_3, Zeolites
3) Hydrogenation & Dehydrogenation	Co, Pt, Cr_2O_3, Ni
4) Oxidation	Cu, Ag, Ni, V_2O_5, Pt
5) Hydration & Dehydration	Al_2O_3, MgO
6) Halogenation & Dehalogenation	$CuCl_2$, AgCl, Pd

So, there are several classes of catalysts. So, let us list down what these classes are. So, class of a reaction and the typical example of catalyst that is used for each of these classes. So, alkylation, for example: alkylation and dealkylation reactions. Typical catalyst that is used is A l C l 3, palladium and zeolites. Then isomerization reaction; and typical catalyst that is used is A l C l 3, platinum on alumina which is a supported catalyst and zeolites.

And then, you have hydrogenation and dehydrogenation reaction. The typical catalysts used are cobalt, platinum, C r 2 O 3, nickel. Then we have oxidation reaction which is very very common. There are several oxidation reactions that is actually possible; copper, silver, nickel, vanadium pentoxide, platinum, so on and so forth. Then we have hydration and dehydration reactions.

These typical examples of catalyst that is used for this type of reaction are A l 2 O 3 and magnesium oxide. Then we have halogenation and dehalogenation. And the typical catalyst that is used are C u C l 2 to silver chloride and palladium. So, these are the typical examples of catalysts, actually that is used for different types of reactions. So, we have classified these into 6 classes of reactions.

Alkylation and dealkylation which uses A l C l 3 and palladium and zeolites as catalysts. We have isomerization which uses supported catalysts such as platinum alumina. We have hydrogen and dehydrogenation which uses cobalt, platinum, so on and so forth. And then we have very very well-known oxidation reactions for which copper, silver and nickel palladium oxides are used.

Then hydration and dehydration reaction for which alumina and M g O are used. And then halogenation and dehalogenation for which copper chloride, silver chloride and palladium are actually used. So, these are the typical catalysts that are actually used for different processes that are actually in place. So, to summarise this lecture, what we have learnt is that, there are different properties of the catalyst particularly the presence of the pores which facilitates large area for the reaction, availability of large area for the reaction.

And then, we looked at supported and unsupported catalyst. We looked at the, how the catalyst works. The catalyst typically uses this process of adsorption where the species comes and actually binds to the active sites. And this can be a chemical bond or a physical bond. The physical bond, physical adsorption actually has a much lower heat of adsorption, whereas the chemical adsorption which is also called as chemisorption has a relatively higher heat of adsorption, which actually is comparable to that of the heat of reaction.

And the key take home point is that, if one needs to conduct a reaction at a certain temperature, then that temperature particularly when chemisorption is involved, the, that temperature has to be in the same range at which the adsorption of the species can actually occur. Otherwise the reaction will not happen due to lack of species that is actually adsorbed onto the surface.

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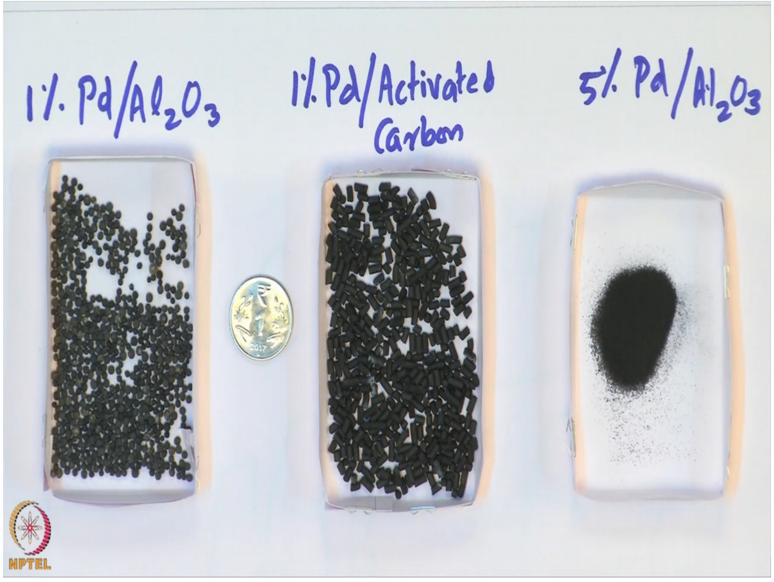

Let us look at a few examples of the actual catalyst. Here is the first example where you have 1% palladium which is actually coated or impregnated on the substrate alumina A l 2 O 3. And you can see that the particles are actually spherical in nature. There are small balls hear in about 2 mm is the diameter of each of these. And if you look at another example where you have 1% palladium which is actually impregnated on activated carbon.

And you can see that the catalysts are actually, the substrate is cylindrical in nature. And you will have lot of pores in which the 1% palladium is actually impregnated on this. And let us look at a third example where the catalyst is tiny spherical particles which are actually powdery. And it is actually 5% palladium which is actually coated on the substrate of alumina. So, these are a few examples and of course there are catalysts which actually come in many many different shapes. And these are just a few examples of these. Thank you.