Heterogeneous Catalysis and Catalytic Processes
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Lecture – 06

In the last lecture we were talking about catalysis preparation; so, let us continue the same chapter. The basic of catalysis preparation they said that you need a metal; you need a support and then how the metal is binded to a support is very importanted question. So, we have different treatment methods that we discuss last time also; the impregnation method is one, co-precipitation method, precipitation method, sol gel method, micro milson method, dry mixing.

They can be a verity of methods, right; that the carrel catalyst. When you look at the asymmetric catalysis based on ligand based stories; so, polymer matrix and you have something the complex as will or metal will binds to these polymer chains, right. So, these can be the, there can be the different processes for making these catalysis. But in general as I said it is a science as well as arts; so, you have to look at the possible way by which the metal can be well disposed in the part of nano particles on the support. So, that is very important. So, p H may play very ((Refer Time: 01:33)) role; concentration because lot of mass transport limitations may come between the catalyst preparation. So, you have to look at those.

So, any metal salt, if you look at here, right; you have to edit to a support which can be a just a mixing. So, and then you are adding a precipitating agent, so generally co precipitation is used when you have a support also prepared from its precursor. So, it may be a support precursor, right; say for alumina you can have aluminum tertiary butyl hydroxide. Same thing for silica also you can have a butyl silicates or some salts of the silicates which may dissolve just like a glass metal. You take glass and dissolve it in H 2 S O 4 or H of you will get a silicate solution for and then heat it; a heat treatment, so like that.

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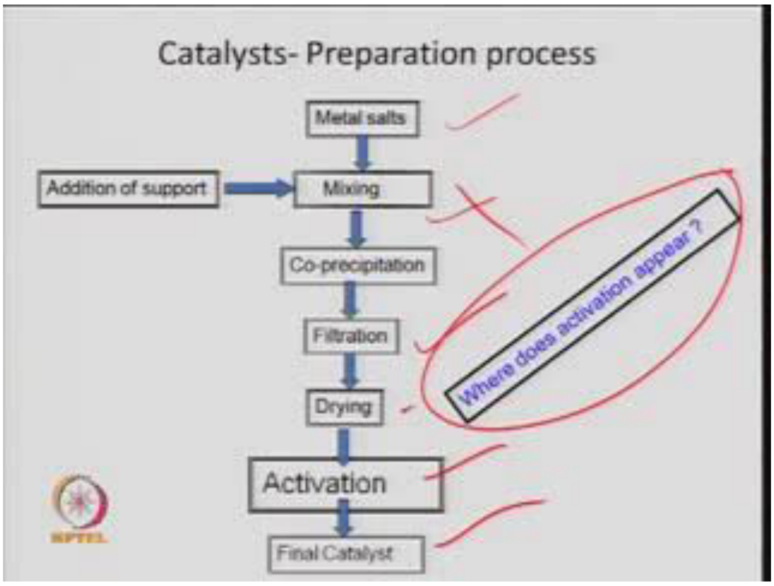

Catalysts- Preparation process

Metal salts

Addition of support

Mixing

Co-precipitation

Filtration

Drying

Activation

Final Catalyst

Where does activation appear ?

So, then followed by the filtration, drying, activation and you get the catalyst, right. So, where does activation appear? This is the crucial question here, but I will say in all steps. So, we have already discussed this last time. So, activation may occur at all step not only during mixing; but pro precipitation, how does it co-precipitates, which nucleating material has been added; because it is nothing but the growth of that crystal, so depending upon that.

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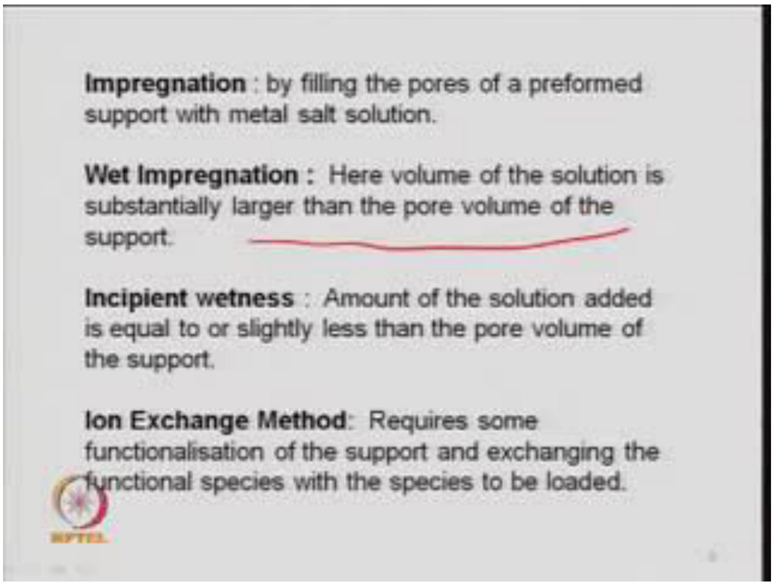

Impregnation : by filling the pores of a preformed support with metal salt solution.

Wet Impregnation : Here volume of the solution is substantially larger than the pore volume of the support.

Incipient wetness : Amount of the solution added is equal to or slightly less than the pore volume of the support.

Ion Exchange Method: Requires some functionalisation of the support and exchanging the functional species with the species to be loaded.

So, basically impregnation, when we use the terminology; so, it is nothing but the filling of that core of a perform support with metal solved solution, that we discussed last time. So, there can be wet Impregnation method, it can be Incipient wetness method. So, Incipient wetness means, the course of just filled, right. So, we do not add a large volume of the liquid or solution for filling the core, right.

There may be some times of problem, when you have a larger concentration of the metal is missing; we call it may aggrumulate on the support precursor or in the pore species, so it may block also. Sometime this may be problem; so, this incipient wetness technique is generally used, when no concentration of the precious metal is to be deposited on a large surface area support or larger volume of the pores.

Wet impregnation method also, as I said earlier that you can a larger volume, right. So, here you can have the probability that because you are using a dilute solution; so, dispersion may be better, when you have a wet impregnation technique. But since you are using a large volume, so we need extra energy for drying that solid, right. So, that also you have to check. And, it can be another method which ion exchange method, right,

It required some kind of functionalization; just like say you have a ((Refer Time: 04:14)) material right, which have narrow or pore size. The diffusion may be a phenomenal, but if you have a ((Refer Time: 04:20)) we can very easily replace this ions by some other, right like that. So, it is nothing but a cation or anion exchange methods and you can just do that.

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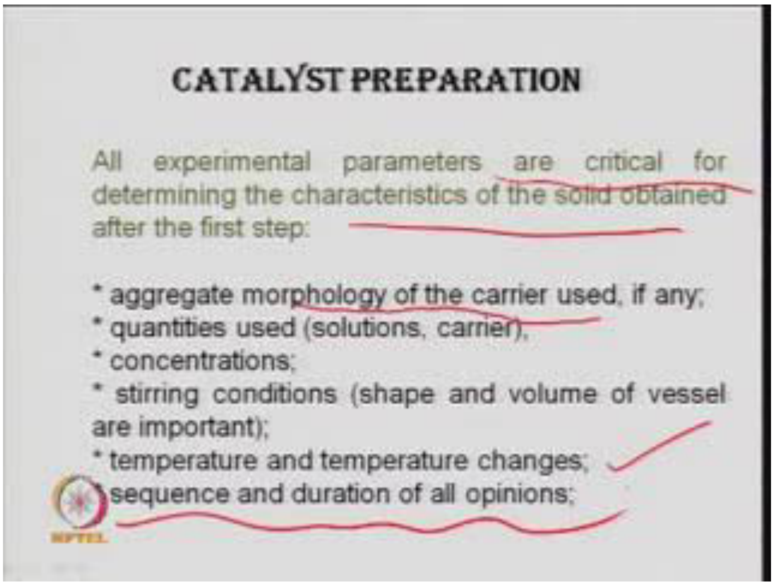

CATALYST PREPARATION

All experimental parameters are critical for determining the characteristics of the solid obtained after the first step:

* aggregate morphology of the carrier used, if any;
* quantities used (solutions, carrier);
* concentrations;
* stirring conditions (shape and volume of vessel are important);
* temperature and temperature changes;
* sequence and duration of all opinions;

So, catalyst preparation as I said the parameters, all parameters are critical for determining the characteristic of the solid obtained. So, every step is very crucial right in terms of drying calcination, when you say aging, right; then p H temperature. So, because this will decide the aggregate morphology of the carrier support, right. what is the morphology of the support which has been used, right. Then, quantity. How much quantity of the solution has been used like wet impregnation incipient wetness; there may be interference sometime.

Concentration of the solid; because of diffusion, right. Concentration of radiant from solution to the core of a solid. So, depending up, if the concentration is high the gradient will removed. But the higher concentration may have the agglomeration also. So, this may effect stirring condition; r p m, because you are removing the mass of external, mass transferred during the preparation. So, this may also decides, shape and volume of the vessel everything.

Temperature and change in temperature, very crucial factor because you are aging or growth of the crystal depends on this temperature or what is the rate of change of temperature. Especially, when you are doing the calcinations, when you are doing aging at that instant. And, so this sequence and duration of all the steps; that is also that whether you are drying it for 24 hour, calcining it for 5 hour or 8 hour, because the nucleation is taking place or growth is taking place, solid-solid reaction is taking place. So, depending upon all these temperature, time, p H, concentration; they may effect the performance or efficiency of the final catalysis. So, we do the pre treatment as I said or also known as activation instinct.

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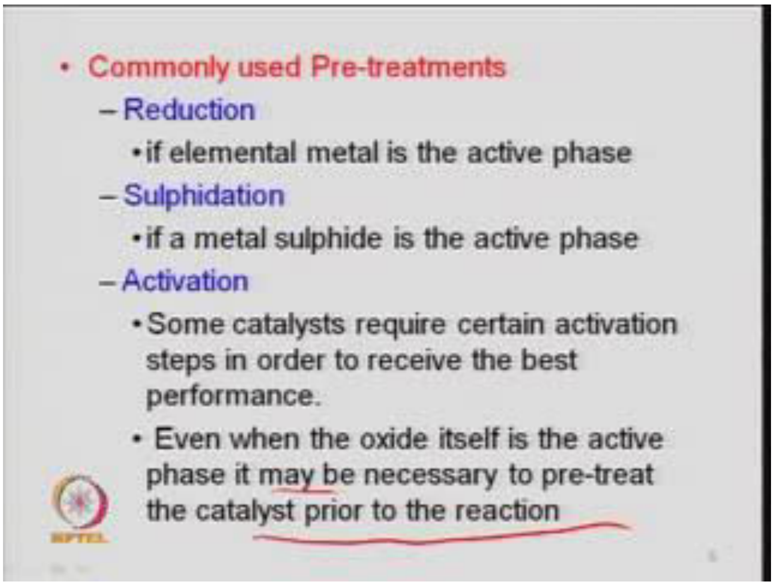

- Commonly used Pre-treatments
  - Reduction
    - if elemental metal is the active phase
  - Sulphidation
    - if a metal sulphide is the active phase
  - Activation
    - Some catalysts require certain activation steps in order to receive the best performance.
    - Even when the oxide itself is the active phase it may be necessary to pre-treat the catalyst prior to the reaction

So, reduction; you know reduction is done in c 2 with hydrogen, carbon monoxide; so, carbon monoxide may be give the carbide form, hydrologic of hydrogen you may get in the form of metal. If it is oxide form, so oxide form can be converted; if it is metallic form when you are hydrogenating under certain condition, you may get metal hydrides so like that. Sulphidation, sometimes t sulphidation is required, if the catalyst is very active; especially, as I said in the case of hydro de sulphidation reaction right or a formal reaction.

So, small concentration of sulphur treatment can be given for activation of the characters. So, some catalysts required certain activation step in order to receive the best performance. Sometime we do additional steps beside these regular right. So, say treatment with some say other components like chlorination sometime we do, for improving the dispersal. Sometime you add a kind promoters separately in order to improve, sometime you treat it with acids to remove the certain or inhales the certain kind of acidity or give the kind of protonation. So, these can be the additional treatment.

So, even when you have a oxide catalyzed the active phase, it may be necessary to pre treat the catalyst prior to the reaction. So, always the pre treatment is required; pre treatment may be in terms of just removal of gases from the core of a catalyst. When you because that you have to do under vacuum, the pores are may be filled with moisture, it may filled with gas; so, a pre treatment is required. Especially, when we determine the dispersion, we determine the pore city surface area. Pore volume of physical characteristics; then, also you need a kind of pre treatment. So, we will talk on that later.

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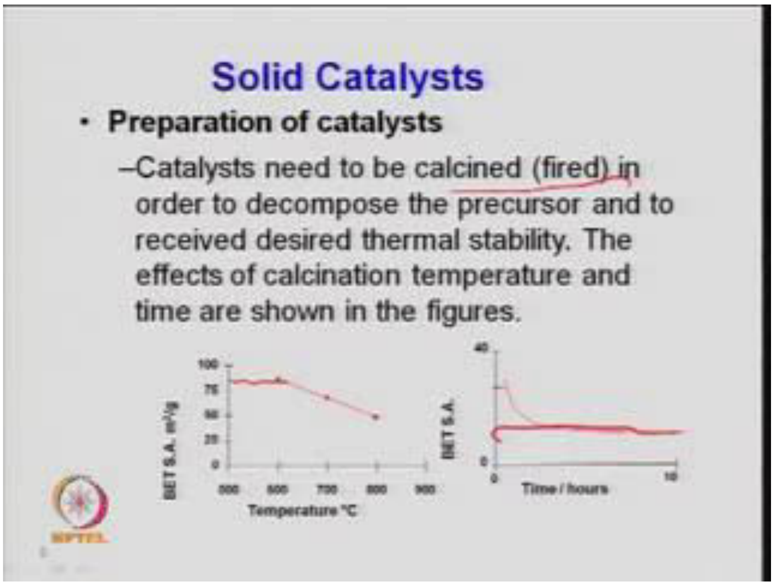

Solid Catalysts

- **Preparation of catalysts**
  - Catalysts need to be calcined (fired) in order to decompose the precursor and to received desired thermal stability. The effects of calcination temperature and time are shown in the figures.

So, this is just a graph; it shows that the calcination may effect the property of the catalysts, time may effect the property of the catalyst. So, generally we report that I said the active metal may have or should have a larger surface area. So, especially when you are looking support precursor, the surface area of the support should be high; this is the first thing in most of the chemical reaction.

Because it will give you a larger with a ray queue calculate based on surface area of the catalyst. So, although this is not object work is defined tunnel frequency; but sometimes a large surface area with assume that higher the surface area the rate may be higher right;

dispersion may be higher. So, do you have some things when you select a support material?

So, here you see that the catalysts is been calcined under a certain condition well say calcium carbonate decomposed. And, you get the calcium oxide same thing all metal salts may convert to the metal oxide. So, here the because during calcination you get a kind of the activation stabile; the metal gets agglomerate, particles come closer, size may grow, the crystal size may increase.

So, you can see here that is increase the temperature the surface area of the catalyst which is around 70 or 80 right 85, 80 and this 600. But if you heat it to so around 800 degree centigrade it reduces to value of roughly 50 meters square per 1. You do not you drastic decrease in the surface area of the catalyst during this calcination step. So, that is what I said with a 550 is the optimum temperature for a calcination for 5 whether or 450 may be the optimum temperature and time may be 6 hours right.

So, you have to look out and it should not be sudden heating of a crystal particle; it should be a gradual heating. So, it is a kind of reaction which is controlled by temperature. So, surface area of the catalyst may change during the reaction; same thing here if you do the same thing; so the same temperature but at higher time. For a higher time during the same 550 degree centigrade for 5 hour or 550 degree centigrade for 8 hour.

So, again because it is the growth of the nucleation. So, this is the function of time and temperature both. So, this is also important here say is the surface area drought thrown some value around 30 to a final value; say here if you look at here around so 20; so even less right. So, the surface area changes when you have the time course of the heating also. So, the surface area may be 30 here suppose; and it goes to a value of said may be 15 or 20 or 18. So, tropes that is ((Refer Time: 10:56)).

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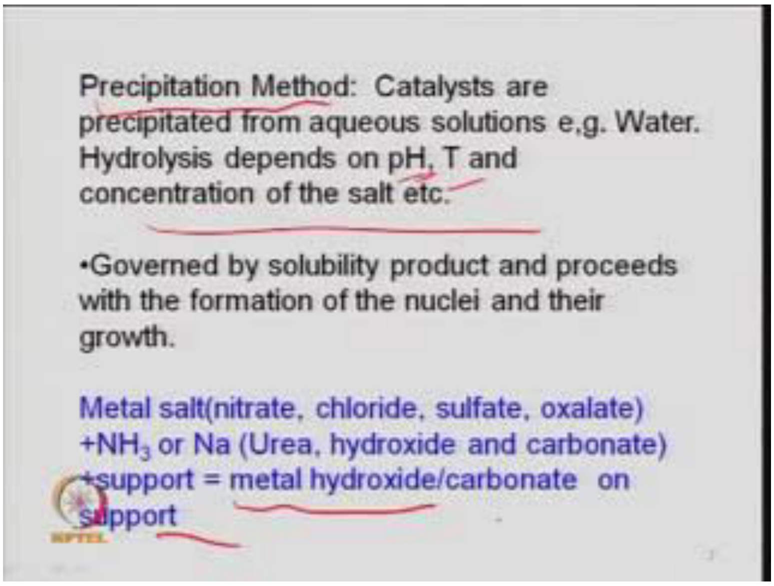

Precipitation Method: Catalysts are precipitated from aqueous solutions e.g. Water. Hydrolysis depends on pH, T and concentration of the salt etc.

•Governed by solubility product and proceeds with the formation of the nuclei and their growth.

Metal salt(nitrate, chloride, sulfate, oxalate) +NH_3 or Na (Urea, hydroxide and carbonate) +support = metal hydroxide/carbonate on support

The other methods again I have already said last time that the precipitation method which is again generally used; when the metal precursor may be precipitated on the already available support. And, when you have the metal also to be precipitated support is also to be made; that you call it co precipitation right.

So, both matter pre cursor supports. In this precipitation technique it may be possible that support is already available. But suppose say magnesium oxide is acting as a catalyst you are taking it from a salt or magnesium nitrate. But you are not calcining it directly you are taking some salt other salt of magnesium. And, then using this sodium hydroxide or sodium carbonate; and then making it precipitate of sodium, magnesium carbonate right or sodium carbonate something like that. So, basically what I am saying here in the case the idea is that when you do that kind of reactions. So, your precipitates which comes that comes in the fine particle form right; idea is that you get a kind of nano particles of that and then you calcine it.

So, the step may be same that you have a magnesium carbonate; you can directly take magnesium carbonate and then calcine it. You will get magnesium oxide. The second thing is that I have taken another salts magnesium hydroid sydroid something and then reacted it with this right some sodium carbonate adjusted the p H. And, then arranged to got the nucleation of this. So, different type of steps may be here in order to prepare the catalyst. So, the important is that the catalyst are precipitated from the aqueous solution like water. Because the water is very food solubility, very good controlled acidity under certain p h condition. And, you can have the nucleation it is a kind of hydrolysis reaction hydrolyze it will give a kind of proton imprudence in the certain condition.

So, hydrolysis depends on p H they said ideal also temperature and concentration of the sore right. These are very crucial factors when you look at the precipitation of a catalyst or metal catalyst in the support. So, this also governed by solubility of the product and process with the formation of nuclei. And, their growth as I said the precipitation method is nothing but the super saturation is avoided; that is nothing but the larger and larger growth and the particle to agglomeration of the particle.

So, under certain condition, under certain periods in time you try to get the nucleation of that right and controlled crystal size; so those super saturation. So, this is this will depend on the p H, this will depend on the concentration. So, how the metal precursor gets participated right will depend on the temperature, p H and the concentration. So, this is just an example.

So, any metal salt can be taken like metal nitrate, chloride, sulfate, oxalate you react in the presence of ammonia; when you hydroxide or sodium what about the salts right sodium carbonate. So, urea, hydroxide they acts they form some kind of products or this can be a kind of the a gel right you are the gel structure may form. So, some organo metallic complexes can form or organic template can be taken here also like EDTA can be one right.

So, this is a kind of gel formation and then this gets hydrolyzed and you get the precipitate. So, gel method can also be a part of the and then here supporting is already available. But when you are co precipitation you can add that precursor also; you get a metal hydroxide or carbonate on the support. Then, you get the heat treatment and you get the catalyst. So, co precipitation so similar to precipitation but here you have preparation of the support also right on the supported catalyst.

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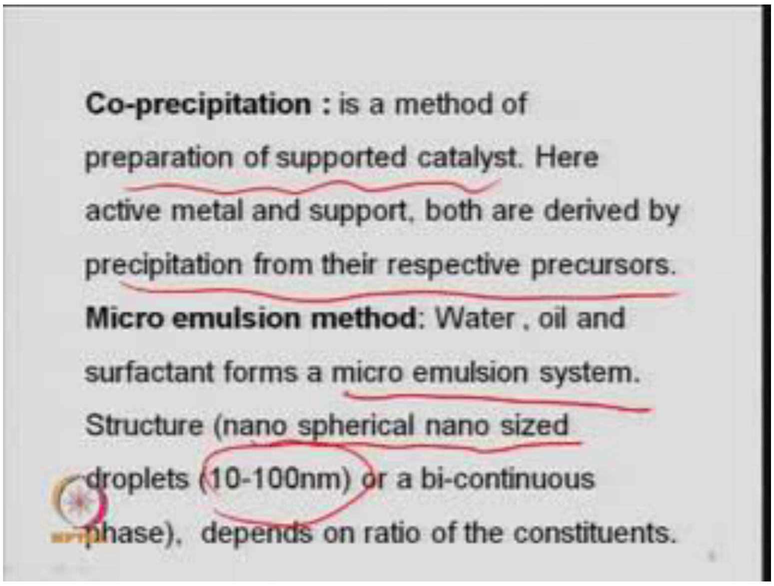

Co-precipitation : is a method of preparation of supported catalyst. Here active metal and support, both are derived by precipitation from their respective precursors.

Micro emulsion method: Water , oil and surfactant forms a micro emulsion system. Structure (nano spherical nano sized droplets (10-100nm) or a bi-continuous phase), depends on ratio of the constituents.

So, here the active metal and a support both are derived by the precipitation on there respective recursive. So, you have one pre cursor for the support, one pre cursor for the metal salt and then dissolve it may be alcohol or in water and then adjust that p H separately; and then mix them together. So, here again the because the solubility of each component will be different; it can be a multiple component right when you have a multi metallic catalyst solubility is different.

So, different condition the growth will take place; and that rate of growth will be different. So, nucleation rate will be different. So, final particle size will vary. So, generally in co precipitation method you can get the nano particles say 10 to 100 nano meter sized particles depends on the solid geometric reactions, shape everything you will get during this co precipitation technique; same thing in the micro Milson method also.

So, here you have one aqua space right another is the so what you call the hydro phobic phase and hydro phallic phase. So, aqua phase if I talk water right it is a kind of hydro phallic phase. So, metal salt can be dissolved inorganic salt will easily dissolve here. Then, second case may be oil right we say they scroll also. And, on this is a kind of hydro phobic phase right in general when you take these two depending upon the two different layers right in try to make emulsions. So, emulsion; now if you look at the macroscopic view, it appears to be a homogeneous solution; just say milk is also no mention. And, when you look at the microscopic picture of that it is a heterogeneous catalyst.

So, but the good thing is that now the oil can be tread by the water body that can be right and water. So, water gen continuous phase that may be one option; second thing is that the oil is in continuous phase; when the oil concentration is high then oil will be in continuous phase. And, water droplet will be trapped by this oil droplets; and if the some inorganic salts which is soluble in water. So, that will also be trapped in the water because it is soluble in the water. So, that that will form a kind globules right a small which itself acts as a reactor fine value if you the some reactant comes across this; so, then it can react.

So, they are well disposed; so that is the funda of the emulsify verification reactions right or emulsified reactors also; where you have a good kind of homogeneous solution you look like that homogeny its looks like that right. So, oil water or water in oil. So, depending upon the conditions r p m hydrophobic; you add a kind of surfactant also to reduce a surface tension. So, you can get; so reverse nicely funda is gain the same when you have the water and oil droplets is inside that end. Then, it is right if a kind of reverse micelle also.

So, all these can be used, these technique can also be used for the catalyst preparation. So, water oil and surfactant form a micro emulsion system; structure of this which can be nano spherical nano size droplet. But I am calling 10 to 100 nano meter in size or a bi-continuous phase as I said when oil is in continuous phase and water is inside that. So, the it will depend on the ratio of the constituents the oil is in larger amount or water is in larger amount.

So, you can have a bi-continuous or versus just a small droplets of water in continuous ways. So, this is again novel method of catalyst preparation and can be used. But the only thing that the process is very complex your to in both co precipitation method and Micro Milson method it is nothing but a kind of complication right formation. So, some kind of complex form or kind of gel form which is to be converted into zero gel; and then try it calcine it. The advantage of that Micro Milson is that you are getting in the nano particles inside the small water droplets; because they are trapped by that.

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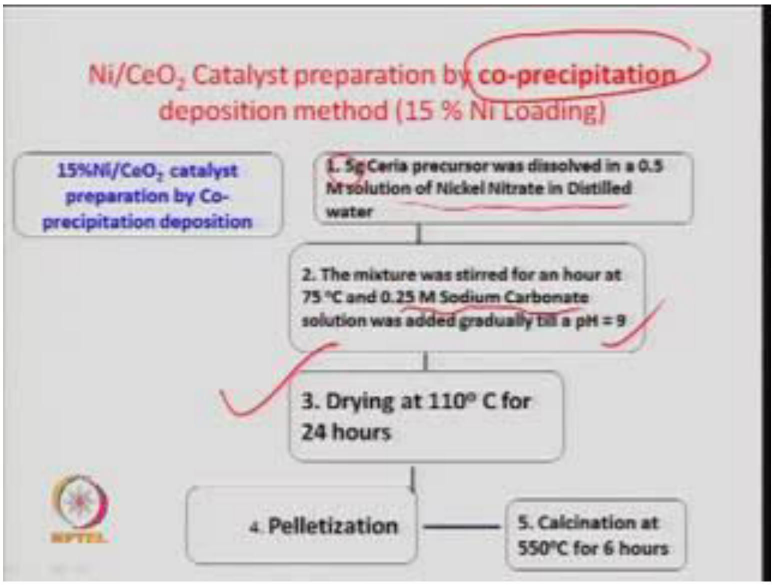

Ni/CeO_2 Catalyst preparation by co-precipitation deposition method (15 % Ni Loading)

15%Ni/CeO_2 catalyst preparation by Co-precipitation deposition

1. 5g Ceria precursor was dissolved in a 0.5 M solution of Nickel Nitrate in Distilled water

2. The mixture was stirred for an hour at 75 °C and 0.25 M Sodium Carbonate solution was added gradually till a pH = 9

3. Drying at 110° C for 24 hours

4. Pelletization

5. Calcination at 550°C for 6 hours

So, just an example of co precipitation method; where you have prepared the catalyst which is nickel ceria catalyst. And, the basic idea the ceria was developed from salts cerium nitrate it can be one right and same thing nickel nitrate can be taken. And, then we have co precipitator these two and we got that. Another option could have been you take the ceria right directly or take cerium nitrate directly calcine it first. And, then you will get nickel nitrate solution impregnation technique or wet impregnation technique. So, generally at the larger concentration like a 15 percent you can have a wet impregnation is to in sequent vectors matter.

So, this could have been one the second could have been precipitation value just take the salt of the nickel. And, allow it to precipitate and then take already prepared ceria support. So, here this co precipitation means the nickel nitrate was taken as a precursor and cerium nitrate was taken as a precursor; and then these two are allowed to precipitate.

Now, in the final ((Refer Time: 19:43)) you can have a distributed fine particles of the ceria; and since you have controlled the condition. So, the morphology of the ceria will depend under what condition this has been prepared.

If you take it from a commercial you have market you have to just depend on there available property of the ceria. So, this is just a typical example here 15 for preparing so you have taken ((Refer Time: 20:07)) for 10 gram 1.5 gram ceria precursor which is cerium nitrate here. And, 0.5 solution of the and molar solution of the nickel nitrate; the these two are dissolved in distilled deionized water. So, just a typical procedure then you stirred it for given time; so say 75 degree at 75 degree centigrade for 1 hour. But this time may be different; temperature may be different you have to check it out right.

And, sodium carbonate is acting as a precipitating agent here right I have to control the p H. Now, because the p H is dissuasive factor as I said that zero point or zero charge. So, and then accordingly you have to get the precipitation; so here the p H use was 9 right. So, we got the precipitation of this nickel and the ceria, right. Ceria in the form of cerium oxide then this cerium hydroxide. Then, you get the drying at 110 degree centigrade for 24 hour followed by the make the pallet.

So, generally you make the pallet and calcine it or reverse can also be done. So, these two can be interchangeable like this but most of the time you first palletize and then calcine it. So, the so that you can have a final pallet which is binded right well binded. And, then you can take the size depending upon the mass transfer diffusion limitation for the catalytic reaction.

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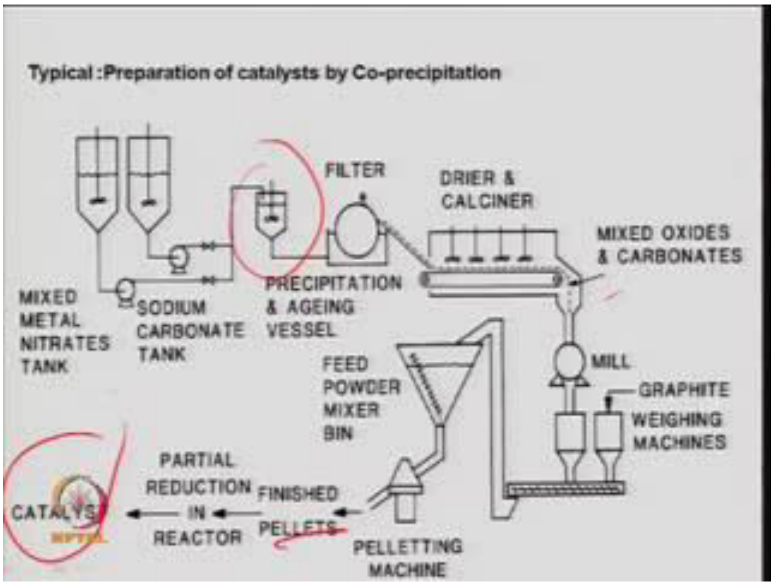
Typical :Preparation of catalysts by Co-precipitation

This is just a commercial flow sit out in a because the in large skill generally we prepare the small amounts of this. But when you look at the convesalisation you have to be very particular in terms of the well mixing good kind of stirrer is required. And, also if you are making a emulsify; good kind of emulsifying agent their concentration the type of system which you are using there will be batch or ((Refer Time: 22:00)). So, there size, there diameter, height stirrer type of stirrer blades imperial blades. So, everything is very crucial when you look at a pilot plant or large scale commercial catalyst of questioning. So, this is typical flows you that what you need in order to the to prepare the catalysts in commercial unit.

So, this co precipitation that is similar flow sheets that you will see for the other systems also. So, here you have say mixed metal nitrate tank; one tank, another tank, sodium nitrate tank. So, these two are palmed and taken into a reactor vessel here where you are these two will get precipitates. So, you have precipitate precipitation of these two precursors; then agents then you have to filter it right and then you dry in a calciner, right. So, it is can a root retile system right drying in a calcination step.

And, then you can mixed oxides of carbonate you will get here. And, then you have just mixed oxides and whatever unconverted carbonate you just take it in a mill right; where you grind it to a given size. You can add the pore former in between if you needed additives it is right some other additives as well as pore former. So, graphite is one of the pore former and then you just taken a feed powder mixer you make a pellet of that tablets; depending upon your size of the characteristic required. And, then you just look at the heat treatment calcine or reduce it and you get the final catalyst here.

So, the same ((Refer Time: 23:37)) which I shown in the beginning the steps are just a getting the metal precursor followed by drying calcination and activation; which can be a reduction right n c 2 in the presence of hydrogen and you get the catalyst. So, this is just a preparation but in between you have to take the sample you have to check the degree of crystallanity. So, do the x-ray diffraction of that if you what to see the concentration or composition do the some atomic objection spectroscopy right.

After extracting it or do the couple coupled plasma methods, inductive coupled plasma method, I c p technique for determine or you do the scanning electro micro graphs, you do x-ray diffraction, you do transversal electro ((Refer Time: 24:10)). So, all these steps are required to criticize catalyst or in order to get a given particle size; metal dispersion comes concentration of these active metals. So, everything is very important when you look at the final catalyst. So, very crucial method or crucial approach in terms of development of the catalyst.

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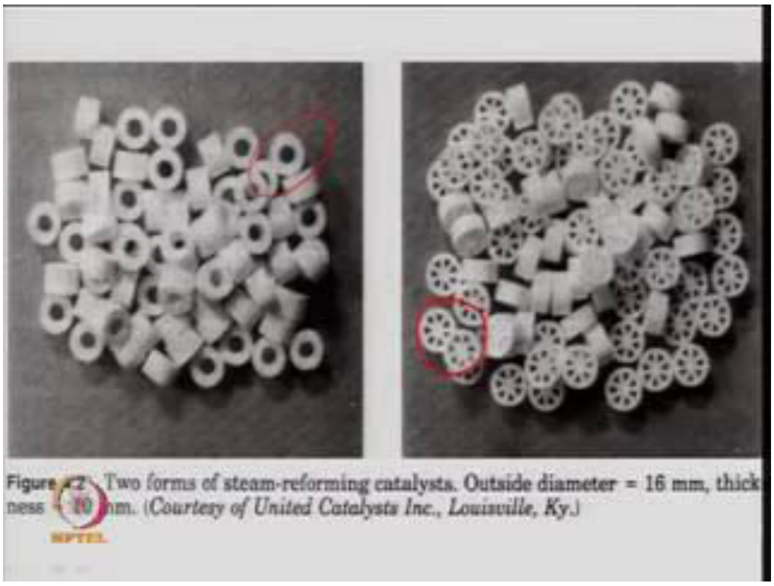

Figure [illegible]2 Two forms of steam-reforming catalysts. Outside diameter = 16 mm, thickness [illegible] mm. (*Courtesy of United Catalysts Inc., Louisville, Ky.*)

The diffusing that is what I was taking I will come to that but before that I just wanted to show these are some kind of catalyst pallets. So, this can the pellet can be of different shape, different size. So, as I discussed in the beginning that this depends on the type of p r c; whether it is a mass transfer controlled reaction or diffusion control reaction. So, you have to select the pellets. So, here you can see the these are kind of rings ((Refer Slide: 25:04)). So, the idea of this kind of shape or structure is to get the larger interfacial area right or external surface area per unit volume.

So, these will be probably that used for the mass transfer control reaction where the kinetic size less importance; kinetics is very fast less importance may it is fast. But the problem is associated with the external mass transport property. So, we give the catalyst of different shape which this can be used; where because the pressure will be less in this kind ((Refer Time: 25:37)) right a kind of ring structure catalyst.

So, catalyst can be of different size, different shape and different type of geometry also right intellectual just like an mass transfer packing. You see the similar fundamental things can be used here when you look at a larger surface area per unit volume of the reactor. For diffusion control reactions or kinetic control reaction generally we take the x to dates, cylindrical x to dates right. So, because there the mass transfer is not a problem.

So, very large interfacial area is not rigged. So, smaller particle we will do the job or this structure because this manufacturing of this kind of pellet or these kind of pallets is not easy.

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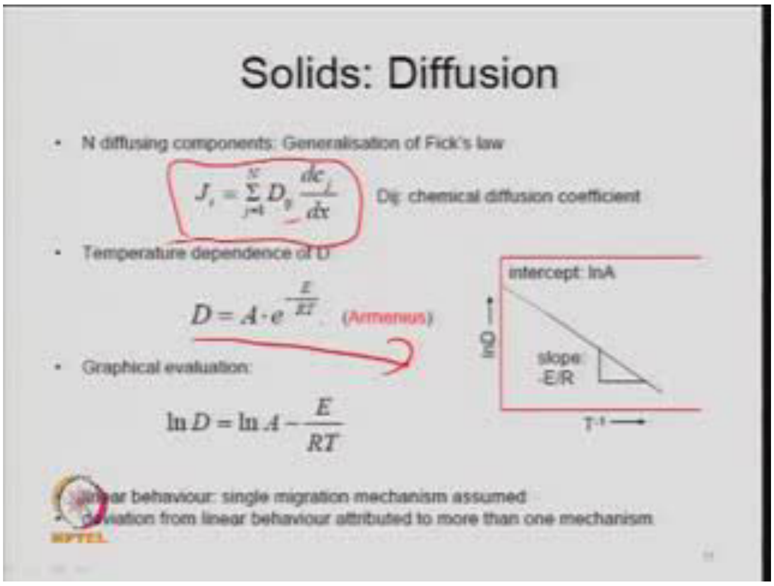

Solids: Diffusion

- N diffusing components: Generalisation of Fick's law

$$J_i = \sum_{j=1}^{N} D_{ij} \frac{dc_j}{dx}$$

Dij: chemical diffusion coefficient

- Temperature dependence of D

$$D = A \cdot e^{-\frac{E}{RT}}$$

(Arrhenius)

- Graphical evaluation:

$$\ln D = \ln A - \frac{E}{RT}$$

- Linear behaviour: single migration mechanism assumed
- deviation from linear behaviour attributed to more than one mechanism

So, before this now just I was talking a kind of reaction which takes place. So, this is the last time I was talking a catalytic reaction whereas told you that the one method can be just by dry mixing. Well, I said that preparation of calcium aluminate.

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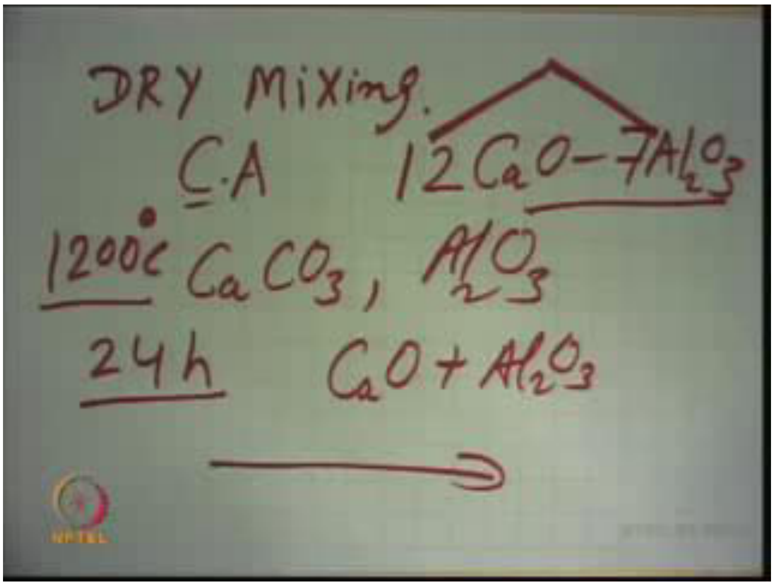

DRY MiXing.

C.A $12CaO-7Al_2O_3$

$1200^\circ C$ $CaCO_3, Al_2O_3$

24h $CaO + Al_2O_3$

So, I can write it something like C.A which will define something like 12 C a O 7 Al 2 O 3 a kind of phase right or a kind of basic catalyst which was made by dry mixing of these two precursor sulfate can be calcium carbonate right, it can be calcium nitrate, it can be here it can be alumina directly or aluminum nitrate; either precursor. And, then you have taken this in drafted ratio like this whatever you have seen here in terms of molar in order to get that back ((Refer Time: 27:19)).

So, might the same thing can be done with nickel also nickel aluminates So, calcium aluminates, nickel aluminates so these catalyst can be used for cracking that can be used for reforming reaction because they are relatively basic in nature. And, also they have excess oxygen in there lattice structure. But when so you are just taking the powder and heating them to a temperature say 1200 degree centigrade. And, time may be 24 hour very high time it is nothing but the fusion reaction a solid-solid reaction between the particles of calcium oxide and aluminum oxide.

So, there it is making a structure which is something like this right. So, it may there is a diffusion in solid-solid diffusion. So, lot of models may be available here right then you try to get ((Refer Time: 28:14)) phase as I said that depending upon temperature depending upon time; you may have a different kind of rigged that may available in your final catalyst.

But when you are selective say you want to get only this type of phase 12 so ((Refer Time: 28:27)). So, you have to just identify under what condition this ((Refer Time: 28:32)) phase can form. And, then you focus on that condition which can be a function of temperature, which can be the temperature function of time and which can be a function of initial particle size of these solid-solid materials.

So, the fundamental thing is that there is a kind of diffusion between solid-solid also; in the other methods also when you have a liquid or a solid which is diffusing along the solution in a pore right to the kind of diffusion will take place. So, there can be different models for developing these kind of mathematical equation or define the diffusion phenomena or the concentration distribution in a pore of a catalyst. So, the basic idea is that these any diffusion components say Fick's law; I think all of you know. So, this is just for the mass transfer.

So, chemical diffusion coefficient d i j; so depending upon that say there may be a multiple component you can have the say platinum you can have a little concentration of nickel right; solutions of these may be there. So, every molecule will have a different. So, it is a kind of transport phenomena is very important and at which rate these are migrated. And, this rate will be different depending upon the value of this right. So, the concentration flux or flux of a species is defined by this kind of equation. And, so that is what I said the concentration is important; high concentration, low concentration when there is a equilibrium there will not be any transport after that right; same thing diffusion coefficient is a function of temperature.

So, high temperature, low temperature that is important because of this phenomenon. So, diffusion may be higher suppose your rate of transport low you just heat it slightly. So, that will inhale the diffusion and this is what how the equation is collated. So, what I mean to say then all the mathematical understanding the diffusion phenomena mass of the phenomenon this is also to be known when you are looking a catalyst preparation. So, ((Refer Time: 30:35)) understand understanding in terms of how diffusion takes place in the solid reaction? So, there may be variety of models again I said when you look at a precipitation agent. So, several models are available in order to define the preparation conditions. So, nucleation as I said right.

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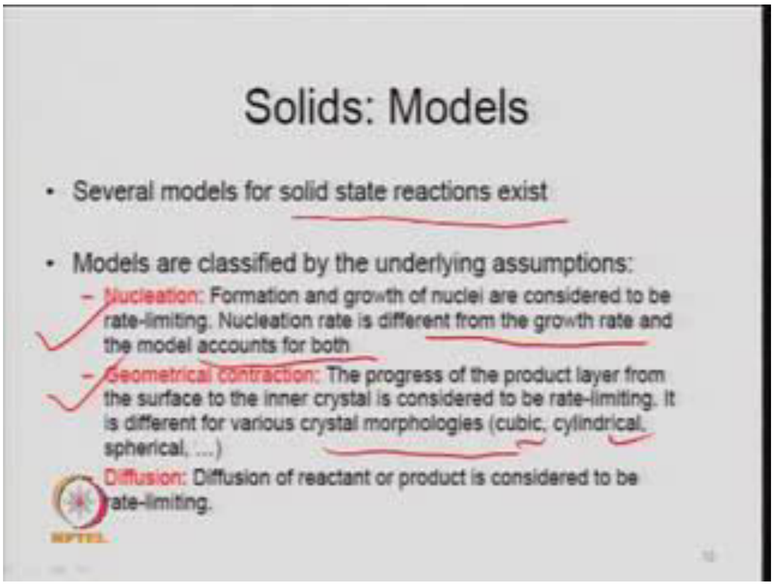

Solids: Models

- Several models for solid state reactions exist
- Models are classified by the underlying assumptions:
  - Nucleation: Formation and growth of nuclei are considered to be rate-limiting. Nucleation rate is different from the growth rate and the model accounts for both
  - Geometrical contraction: The progress of the product layer from the surface to the inner crystal is considered to be rate-limiting. It is different for various crystal morphologies (cubic, cylindrical, spherical, ...)
  - Diffusion: Diffusion of reactant or product is considered to be rate-limiting.

So, nucleation the formation and growth of the nuclei and these are considered; these may be considered to rate limiting. So, that will depend on the type of your metal component p H; well I said right and concentration also. So, the because super saturation is avoided you do not want super saturation but growth of nucleate and the control both of these nucleate that is very important. So, here the that nucleation rate is different from the growth rate and the model accounts for both. So, the model there you can say that solid and solid transport is related to the control of the growth of these particles. So, that is what important when you look at a nano particle formation.

So, the formation of nano particle is a separate sign. So, it is not a easy job; you have to look at with understand the particle chemistry of that reaction and then time, temperature, p H, concentration you have to look at those. So, higher concentration may just give the agglomerated particles. So, that may not be good for the catalytic reaction; same thing geometry. So, particle shape and size that again which forms that is again related to this model. So, this may be controlling factor and this also a function of concentration again and p H right and time out. Because depending upon time the crystal grow inside and depend that will decide your growth rate.

So, the progress of the product layer from the surface of the inner crystal is considered may be considered to be a written team. So, another model you have to look at which rate model is rate controlling in terms of the particle size or growth of the crystal; there can be different morphologic cubic form; shape you may get cylindrical, spherical. So, different kinds of particles may form and same thing diffusion of reactant or product that can be rate controlling. So, there can be so that is what I mean to say; again when you are looking a catalyst preparation transfer limitation has to be known or you should understand the basics of the transport limitation.

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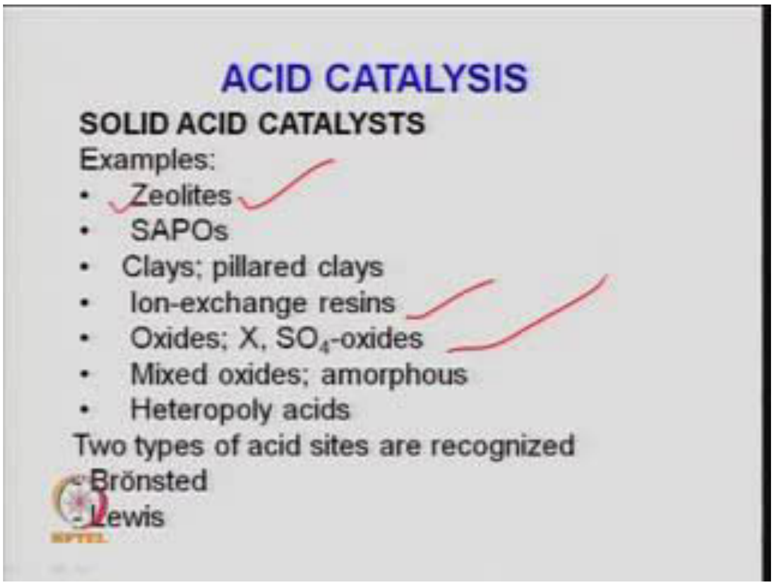

ACID CATALYSIS

SOLID ACID CATALYSTS

Examples:

- Zeolites
- SAPOs
- Clays; pillared clays
- Ion-exchange resins
- Oxides; X, SO_4-oxides
- Mixed oxides; amorphous
- Heteropoly acids

Two types of acid sites are recognized

- Brönsted
- Lewis

Well, just a area send what I said here is that it is a kind of solid-solid reaction here. So, here you have a nickel oxide, here you have aluminum oxide and when these two react at high temperature you may need nickel and alumina. So, it can be either case you may need nickel and alumina. But because of your temperature and time during certain concentration of this may also this may form; which may not be good for reaction. In some cases this phase is desired but since your temperature and time is not sufficient. So, most of this remain like this just nickel on alumina.

You want nickel oxide, aluminum oxide they should react together they will react only when there is a diffusion. So, it is a kind of solid-solid reaction but your temperature is not sufficient time for reaction is not sufficient. Then, you may get only 50 percent nickel aluminate and rest of the phases will remain as such nickel oxide and aluminum oxide. So, depends on the what is your ultimate lead and then only accordingly you have to look at. So, reaction can be addition reaction it can be spinal formation.

So, here also you have to look at that controls right how the temperature time where I said that 1224 hour 1200 degree centigrade and 24 hour may be important. And, but the surface area may be very low here right particle may agglomerate centering may be a problem. So, you can have 1000 degree and 36 hour; another option right lower temperature and larger time. So, temperature time collation has to be understood fast. In order to look at the catalyst phase or the particles. So, everything is important when you look at catalyst preparation.

So, there can be a variety of catalyst Zeolites I will cover later; but as I said that the acid catalyst are very common for the ((Refer Time: 34:54)) reaction. So, what you are talking the preparation part catalyst preparation; but the before that you should understand that what kind of acidity you need? So, you have to immediate the acidity of a catalyst, you can titrate it with some basic gas right; simple you can define some hamate function right which can talk in terms of that p H. So, it means this factor becomes very crucial right.

So, acid catalyst if look at there are variety of acid catalyst as I said the Zeolites are one right. Because they have large number of silicon to aluminum in a same work. So, if you have silica Si you not get any kind of acidity; same thing if you have aluminum along aluminum o, aluminum that will also not give you any kind of acidity. The acidity comes because the Al 3 and SI 4 right. So, when the aluminum enters in that silicon map rates then there is a kind of heterogeneity in the substance.

So, that electro negativity which generates right and that has now when I say Zeolite catalyst and I say that it has a Bronsted type of acidity which is stronger kind of acidities. So, acidity means the ability of a catalyst to donate a proton or accept a electron. So, when it has a ability to donate a proton we call it Bronsted acid site; when the catalyst has the ability to accept an electron. So, accepting electron from the catalyst right or from the molecules. So, that is hydrate formation basically right so that is known as Lewis type of acidity. So, all these kind of acidity or acid side concentration can be determined experimentally right the characterization part. So, we will talk on that later.

So, acid catalyst can be a Zeolites which are the most promising in terms of the high acidity. Then, SAPOs silica alumina phosphate catalyst right; SAPOs are again the variety of this Zeolite catalyst basically right again a molecular say catalyst always. Clays are again something like this calcium aluminate. So, they have a kind of basicity. So, they are they are generally seen ((Refer Time: 37:11)) also clay. So, it can be used as catalyst the only thing that it is a non crystalline in nature; when you look at Zeolite catalyst or SAPO it is highly crystalline in nature.

And, that crystallinity gives you the crucial catalytic activity a clay metal may not be active for a catalyst. But Zeolites becomes active because it has high degree of crystallinity. It has control silicon to aluminum ratio and that provide that how many aluminum metals have been added to the few more work of a Zeolite provide its acidity. So, depending upon that. So, you can if you have more acidity you can control the acidity by removing the aluminum from its frame work right same thing ion exchange agents.

So, cation exchanger's; anion exchanger's they can also act as a catalyst right all this the Zeolite also has a ability to have exchange of the anions, cations that exchanger, anion exchanger they are used as the water purifier also. Because calcium magnesium on the hard dusk can be removed by using these an exchanger agents. They can act as a catalyst also, week acid, week base, strong acid, strong base or different combination of these kind of ion exchange agents are available and can be used as a catalyst.

Oxides you can have a halide, sulfate they are can also be a verity in terms of to metal oxides right calcium oxide, magnesium oxide right halides, chlorides which can be used as a catalyst also and hetero poly acids right. They can also be different kind of acids which have the kind of activity for the catalytic reaction. So, they can also be used. So, in generally I said that acidity can be brownest type or Lewis type; so let us we will see later.

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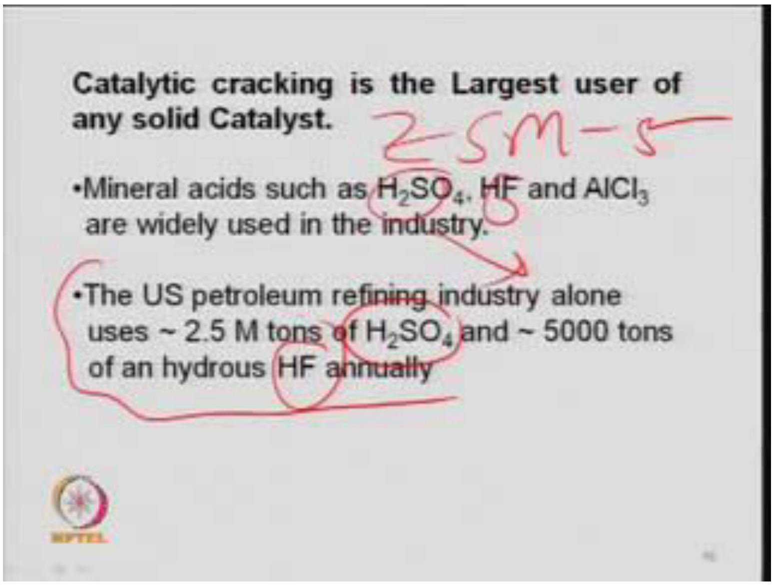

Catalytic cracking is the Largest user of any solid Catalyst.

ZSM-5

- Mineral acids such as H_2SO_4, HF and $AlCl_3$ are widely used in the industry.
- The US petroleum refining industry alone uses ~ 2.5 M tons of H_2SO_4 and ~ 5000 tons of an hydrous HF annually

So, cracking as I said this is one of the largest user of the solid catalyst right; acid catalyst where ZSM 5 is used widely because it has higher acidity. So, generally accessing cracking is done over this kind of catalyst. There it the other catalyst can be your just like a the silica materials because there is five may not sustain a very high temperature.

So, additives may be added to it; in order to provide them the sufficient stability at higher temperature. Because now it is the faddish talk which is generally used for this cracking reaction for production of gasoline is heavier faddish talk. And, your naphtha was used right naphtha cracking catalytic cracking of naphtha. But since now sources are limited route sources; so the alternatives are to be ((Refer Time: 39:50)).

So, whisks residue atmospheric residue or blende they can be used for this cracking reaction. So, when they are heavier faddish talk you need a higher temperature for cracking Zeolite may not be stable at that temperature. So, new technique or new kind of Zeolites is to be searched in order to utilize them effectively for the catalytic reaction.

Because otherwise they will deactivate faster; because they are not stable at higher temperature. So, if you just look at this data previous before the US petrol refine industry along itself used 2.5 million tons of sulfuric acid right and 5000 tons of hydrochloric acid annually.

So, acid catalyst are widely used in general the just one idea but in all refine you see right the Zeolite catalyst, acidic catalyst but the liquid catalyst like mineral acid within say H 2 S O 4, H F they are also widely been used. So, alkylation process, polymerization process and most of the inorganic reactions again the bio diesel product so small concentration of the catalyst are used. So, the rodents may be that you just convert them these H 2 S O 4, HF and find a solid acid catalyst.

So, this is just a idea here that the alternative need to be looked into; to find out a solid catalyst where the handling will become easier. So, over this HF alkalization because hydrochloric acid is highly concentrated, H 2 S O 4 is highly concentrated. So, metal of construction becomes an issue if you have a solid catalyst then the process can be the advantage of this that since it is liquid free reaction. So, activity will be higher right because it is a now homogeneous reaction.

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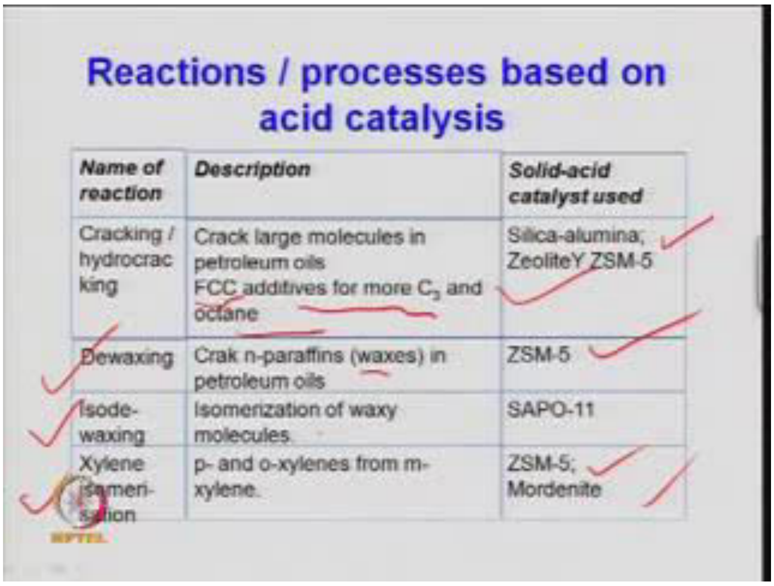

Reactions / processes based on acid catalysis

Name of reaction	*Description*	*Solid-acid catalyst used*
Cracking / hydrocracking	Crack large molecules in petroleum oils FCC additives for more C_3 and octane	Silica-alumina; ZeoliteY ZSM-5
Dewaxing	Crak n-paraffins (waxes) in petroleum oils	ZSM-5
Isode-waxing	Isomerization of waxy molecules	SAPO-11
Xylene isomerisation	p- and o-xylenes from m-xylene.	ZSM-5; Mordenite

So, there these just a flow sheet of table showing that different catalyst or acid type catalyst which are generally used for most of the catalytic reaction. So, cracking, hydros cracking right both use the acid catalyst. So, cracking in generally it is a larger molecule converting into a smaller molecule. So, bond breaking basically large molecular weight compound can be converted into small molecular weight compound; same thing for that petroleum oil I said food catalytic cracking as it is for c 3 and c 3 octane enhancer.

So, which during the gasoline production when you have a abscising cracking you idea is to get the gasoline right; same thing for additives right you can crack them. And, you can get the additives for the gasoline iso octane but which can be the additive for the gasoline right higher octane number or octane booster; this can be done. And, you have cracking so cracking is a multiple reactions. So, you can have olefins also ethylene, propylene, butadiene which are the raw material for the petro chemical industries.

So, this cracking can be done for variety of purpose though that the catalyst will be different accordingly. So, silica alumina, ZSM 5 type, Zeolites right they are used as for access where as silica alumina type catalyst are generally used for petro chemical raw material for that same. So, ethylene, propylene, butadiene if you want to crack everything into this small of olefin range of hydro carbon; then a kind of silica alumina catalyst will be desired. But when you need the hydrocarbon larger molecular hydrocarbon. And, then want to get something like a gasoline or iso paraphrase from that then ZSM 5 type catalyst will be required. Because they have a activity toward the hydrogenation, aromatization, cyclization. You have to understand the chemistry of that reaction first and then you have to select the particular catalyst values right same thing for d waxing right.

So, d waxing of patrolling fraction because state change hydrocarbon or wax compounded they the generally if you are temperature is low. So, they will become solid at low temperature. So, they will just deposit or especially in the cold countries you cannot use them as a fuel. So, the pore point that is the ideas of cloud point these are some properties which is generally use to characterize the petrol or crude oil or petroleum products. So, this pore point is one right we have to look at depressant pore one depression. So, or you remove these the say clod point as I said the hygeinness which comes because of the presence of the wax metals. So, which cannot be used directly in the fuel because at the; it becomes viscous also when it gets solidified. So, you have to remove these wax compounds.

So, waxes are nothing but larger molecular weight state change paraffin hydrocarbon. So, either you crack them or remove them. So, there again you can have different kind of catalyst which is Zeolites type catalyst in uniform hydro d waxing you call. iso d waxing again is nothing but the Isomerization of waxing molecule because directly when you have the iso d vexing you are getting the iso paraffin. So, you are cracking them and converting into iso paraffin. So, that can directly be used as the component for the gasoline or petrol.

So, from Fischer Trop synthesis if you look at the Fischer Trop synthesis you got a variety of the product. Fischer Trop synthesis as I said the reaction of scion hydrogen; so any hydrocarbon can be formed by using this; in the first lecture I was talking. So, generally if you have a iron based catalyst or cobalt based catalyst or a combination; so you can have different products from this. So, if you look at here cobalt based catalyst are generally used for diesel manufacturing.

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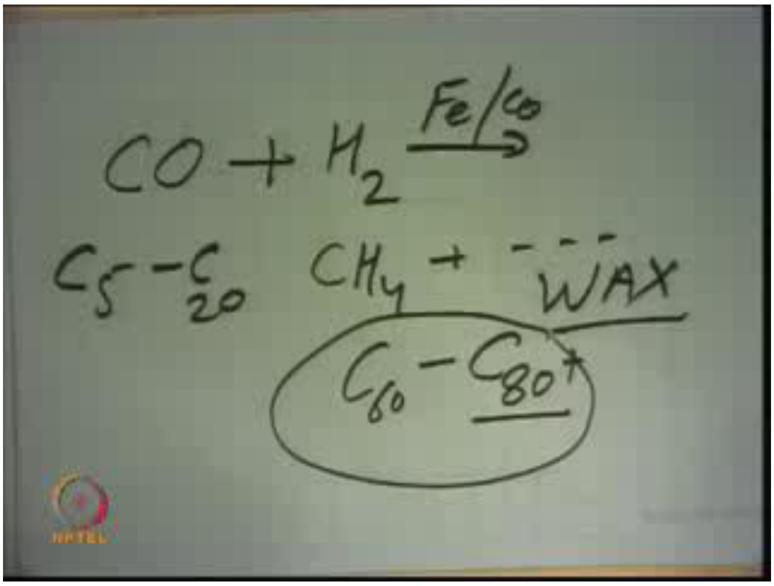

$$CO + H_2 \xrightarrow{Fe/Co}$$

$$C_5 - C_{20} \quad CH_4 + \text{---} \ \underline{WAX}$$

$$\boxed{C_{60} - \underline{C_{80}}^{+}}$$

So, they are good in type of diesel when I say it may you are requiring more and more straight chain carbon hydrocarbon. And, when you look at a iron based catalyst you get more and more gasoline type products. So, gasoline will come in a iso paraffin type component. So, but sometime you can have a combination of these two iron cobalt. So, this can give a product like methane also undesired and so on so on gasoline. And, finally you can get the wax from here; which is wax when I say c 80 range of paraffin's c 80, c 40, c 60 also I can say as a wax.

So, generally the c 60 or c 40 to c 80 these are to be cracked further and ionized hydro ionized; because they cannot be used as a gasoline product or as a diesel product. So, this is what the larger components of this Fischer Trops which cannot be used for the gasoline; because for gasoline we need something in the range of c between c 5 and c 20; same thing for diesel also or we can that in one case you need iso paraffin more and more iso paraffin.

And, in diesel you need more and more straight chain hydrocarbon but it larger than that they can be isomerized right; they de waxing that is that can be cracked. So, you have to take it in separate reactor and again do the conversion. And, that is the concept of the Fischer Tropy reaction or gas to liquid reaction, biomass conversion to liquid reaction. So, the new technology needs to be developed for these kind of reaction; new catalyst need to be developed but this these steps are required here. Same thing Xylene isomerization which is generally for petrochemical industry also. So, Para Ortho Xylene that can be produced from meta Xylene right it could petrochemical product. So, again ZSM 5 Mordenite so these kind of catalyst can be used in the process.

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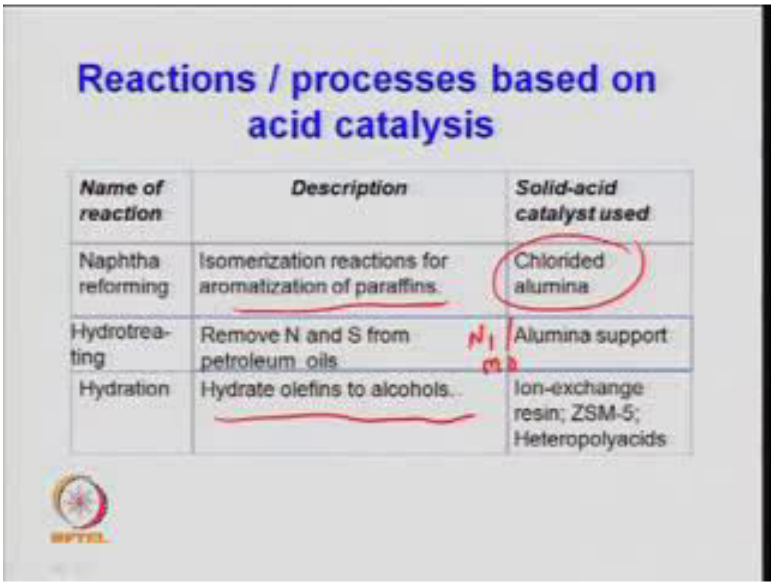

Reactions / processes based on acid catalysis

Name of reaction	*Description*	*Solid-acid catalyst used*
Naphtha reforming	Isomerization reactions for aromatization of paraffins.	Chlorided alumina
Hydrotreating	Remove N and S from petroleum oils Ni mo	Alumina support
Hydration	Hydrate olefins to alcohols.	Ion-exchange resin; ZSM-5; Heteropolyacids

So, we will talk on these catalysts later again; same thing for naphtha reforming if you look at the isomerization reaction for aromatization of the paraffin. So, reforming of naphtha is you are converting the crude naphtha into gasoline range of hydrocarbon or blending for the gasoline product which is known as reformed gasoline. The basic idea of using reformed gasoline is that you are getting improved octane number anti knocking tendency in the gasoline. So, the iso paraffin have higher octane number, aromatic have higher number; that benzene is casinogenic. So, its concentration should be less than one volume percent that is important. So, other iso paraffin and aromatic hydrocarbon can be used, alkylated aromatic may be deserted.

And, that is what you see alkylated gasoline also that is another a product which is after alkylation or HF alkylation what I said earlier. So, here the chlorinated alumina can be used because this can in dispersion when you chlorinated; and that used as a catalyst for the reform. So, generally it is a platinum on alumina which you also known as plat forming. So, platinum on alumina; platinum range on alumina by metallic catalyst. So, metal side, acid side; so part of this provides the hydrogenation activity, dehydrogenation. And, part of that provide you the aromatic aromatization activity, cyclization activity. So, combination of these two can give you the more and more iso paraffin and aromatic in your product. So, alkylated gasoline right which is generally used for blending with the traditional gasoline which is obtained from the crude oil distillation in it.

So, up gradation of this gasoline as per new environmental norms or aero file norms is to be done. And, the for that purpose these catalyst play a very important role. You need to look at this same thing hydro treating as I said removal of this nitrogen, sulfur from the petrol and diesel. So, Promox, Newmox on alumina support so this type of catalyst are desired here. So, they are basically Nickel Moly here. Nickel Moly with done something like that on alumina known as newmox, chromox hydration. So, hydrate olefins to alcohol; so for alcohol from the olefins.

So, you need a kind of reaction right for that ion exchange resumes ZSM 5, hetero polyacids; so these kind of catalyst can be used for the reaction. So, there can be a variety of other catalysts right also which may be used for this purpose and new R and D can be taken; in order to upgrade this catalyst or develop a novel catalyst for the process. Because the new concept requires that you should have high atomic efficiency 0 best charges or E efficiency what you say is low. So, keeping those things in mind and that is the concept of green catalysis that develops new catalysis or upgrade the existing catalyst. And, try to get more and more desired product compared to the undesired product.

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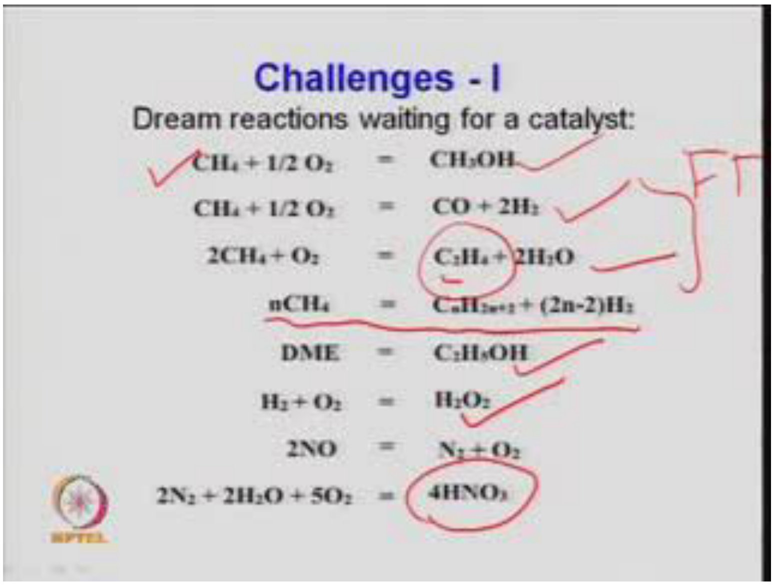

Challenges - I

Dream reactions waiting for a catalyst:

$CH_4 + 1/2\ O_2 = CH_3OH$

$CH_4 + 1/2\ O_2 = CO + 2H_2$

$2CH_4 + O_2 = C_2H_4 + 2H_2O$

$nCH_4 = C_nH_{2n+2} + (2n-2)H_2$

$DME = C_2H_5OH$

$H_2 + O_2 = H_2O_2$

$2NO = N_2 + O_2$

$2N_2 + 2H_2O + 5O_2 = 4HNO_3$

FT

So, there are lots of challenges if you look at in terms of the green chemistry and catalysis. So, some them which briefly I am talking. So, the partial oxidation of methane is again a very important reaction always because methane generally natural gas is available in a kind of ((Refer Time: 51:13)). And, this can be converted to series of petrochemical product; it can be converted to hydrogen. And, it can be converted to a aromatics or petrol diesel. So, that the catalysts need to develop. So, this is what the difference reaction where the challenges are required. So, conversion of methane to methanol partial oxidation right single is to not from that methane to sin gas; and then sin gas to methane which is a set of reaction. So, that becomes the energy intensive in some gases the catalyst development the reactor configuration.

So, if you have some technology, if you can develop some catalyst for oxidation of methane on into methanol in single step it will very good. And, the traditional is this methane convert to oxygen you get C o plus 2 hydrogen and then again it reacts and gives you ethylene and water. And, then this is in this is Fischer Trop reaction here. The second is not Fischer Trop but generally for oligopolization reaction; this is used which is known as basically you can have the coupling of methane oxidative coupling of methane or lanthanum oxide catalyst by you can convert that olefins from that. And, in one way when you look at the dimethyl ether formation the important reaction; where the natural gas can be converted to dimethyl either DME which can be a subscript for the diesel. So, in this oligopolization and you give your larger molecule.

So, this is a step in the formation of dimethyl ether but this can be used in the petrochemical industry also. Because ethylene is used widely in the petrochemical industry for high density poly ethylene, low density poly ethylene. So, many other remember step is that single step methane conversion 2 CNS 2 n s plus 2 paraffin and hydrogen. So, that is again very important step that conversion of methane into diesel or paraffin in a single step or hydrocarbon dimethyl ether that is again formation of dimethyl ether. And, then dehydrated get the ethanol hydro peroxide formation.

So, that is again where the catalyst is required some kind of catalyst are being developed for this process Knox removal. So, automatic exhaust catalyst so for that right. And, same thing for here nitrogen and formation of nitric oxide in simple step not the you get the nitric ammonia and oxygen get the nitric oxide. And, then you reacted Ostwald that is a H N O 3 formation by Ostwald method platinum catalyst.

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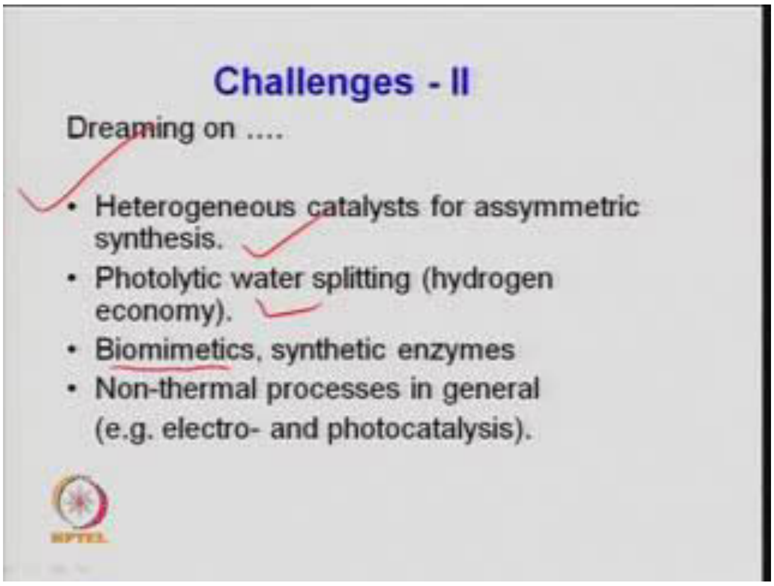

Challenges - II

Dreaming on ....

- Heterogeneous catalysts for assymmetric synthesis.
- Photolytic water splitting (hydrogen economy).
- Biomimetics, synthetic enzymes
- Non-thermal processes in general (e.g. electro- and photocatalysis).

So, this these are some challenge in the reactions. And, the development requires all these things that heterogeneous catalyst for asymmetric synthesis that is a paral catalyst what I was talking right a ligand based polymers. On a polymer matrix the metals are attached organo metallic complexes which are just formed during the co precipitation method; but do not draw it. And, directly use it for the process because the reason is that when you have a sol gel matrix the metal ions or metal particles are trapped in between that gel. And, they are in the form of nano particles when you try the gel the particles gets agglomerated; and then you have to support put it on support. So, these are the crucial steps.

Here, what I said earlier also a hetero homogeneous catalyst like Micro Milson. So, Micro Milson can be called something like hetero homogeneous; enzymes they are also the amino acids right large molecular weight. So, they are also the hetero homogenate type of catalyst; new trend is that look at this chiral catalyst system, asymmetric catalyst system which can have the particle in the well dispersed form. And, the activity will be very high, rate of reaction will be very high, turn over number will be very high. So, your conversion to a desired product that is selectivity will be very high in that case. So, these are the trends which need to be used to be in terms of R and D detail refine; same thing for photo catalytic react water splitting hydrogen product from water. And, nuclear forces are being used for that sulfide in psychology one on that.

So, you can have those type of process also where the catalyst may be developed sulfuric acid decomposition. So, although they are they require the large amount of energy initially. But once you produce them then the process the energy can be used in between during the process. And, there are simple enzymatic type catalyst synthetic are available; but these type of metals are not available Biomimetics and synthetic enzymes. So, these are some bio technology reaction where again the catalyst can be used; where non thermal process in general like electro and photo catalysis. So, electrochemistry is now a days for fuels replication widely being used where at low temperature you can convert them the product. And, the same funda is of the nano particle or nano catalysis in the reaction.

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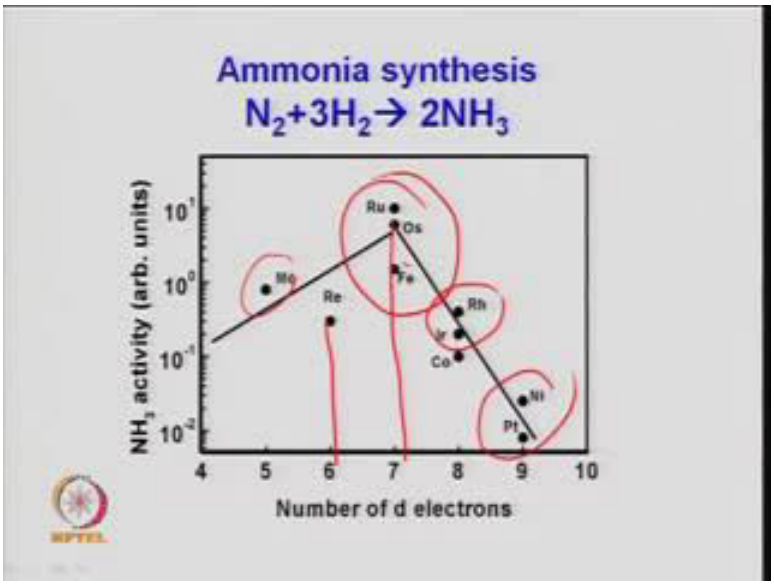

Ammonia synthesis

$N_2+3H_2 \rightarrow 2NH_3$

This is a just as example; if you look at that I said unpaired d electrons which are available that is giving you the catalytic activity. So, transition metal also whether just an example for ammonia synthesis which N 2 plus thrice H 2 B 2 twice NH 3. In this case we have defined the activity for ammonia production which can be called as a turned over number. But here it is just given the arbitrary unit; it is not the actual number and here it is the d electrons which are available. So, the number of d at electrons right of d atoms which are available per in the whatever the d orbital when I said that the available unpaired d electron; which provide the catalytic activity.

So, these are the atoms number of electrons d electrons available per atom; so for moly like this. And, this is for uranium, osmium, iron you can see here with these kind of metal the activity is very high. These have 7 number of d electrons. And, there if you look at Rhodium there that is also equally good, molybdenum is good; and within and platinum has low relatively low. So, it means when you look at Ruthenium type catalyst for these kind of reaction it may be more active; iron is equally active. So, that is why iron is used for that purpose.

So, Ruthenium is very costly. So, although the small concentration ruthenium may be active; but iron is better although it deactivates right agglomerates faster. But since the iron has also equally good activity for a certain period of time. So, generally iron may be considered for this. So, I stop here at this stage and we will continue it next time.

Thank you.