Heterogonous Catalysis and Catalytic Processes

Prof. K K Pant

Department of Chemical Engineering

Indian Institute of Technology, Delhi

Module - 04

Lecture – 13

Good morning. So, last we were talking about the dispersion or chemisorptions technique for determination of the number of surface metal or active metals which are necessary for the catalytic reaction. So, we were talking dispersion, that is the some kind of percent dispersion, that is simply number of metals, which are available on the surface divide by the total number atoms or metal atoms, which may be determine from your atomic absorption a spectroscopy or maybe i c p some other technique and this is actually determined by titration method, which is a chemisorption here.

So, this technique is nothing but, a titration method and one can determine. So, the reactor system I told that, chemisorptions is very specific for temperature. So, you have to do that at different conditions of temperature and then, that can be used to define a turn over frequency, which is very important property for the characterization of the catalyst. So, number of active sites, which I am talking that can be reacted that number of molecules of the gas reactive gas chemisorbed per unit time and per unit active site, because was this percentage known number of sites are known.

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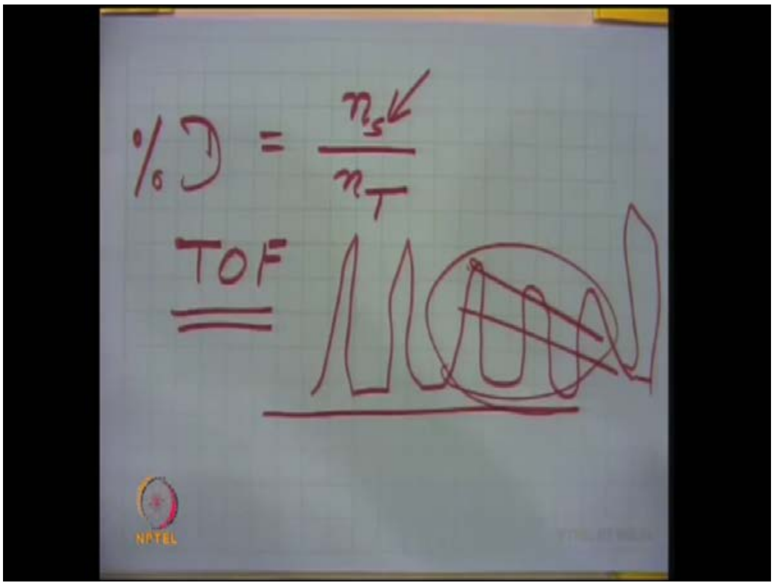

So, your rate in a reaction, when you compared different catalyst generally should be defined in terms of turn over frequency, because the metal completion may be different nodding may be different but, actually it is the active site or percent dispersion, which talks about the catalytic activity. So, this is just a typical graph, which a shown for platinum alumina catalyst 5 watt percent platinum on aluminum and carbon monoxide has been used as chemisorptive gas.

So, you can see here, that is depending up on the volume, because it is a kind of pulse volume. So, when you do the chemisorptions, you have identified a temperature and then, you have given pulses, say it may be just as I said ml but, it can be 1 ml or 100 micro liter. So, different volume of pulses can be given and then, you measure the amount of the gas chemisorbed till saturation. So, once you have the pulses will come like this if you have the some volumes. So, initially nothing is chemisorbing, it will come like this and finally, it will go like this, because this is just showing that, the chemisorptions has taken place and finally, it will come again like this. So, what about the decrement you are getting or you are just add the all these. So, you can find out the amount or the mille molecules of the carbon monoxide adsorbed on the surface and you can get the idea, because it is kind of Langmuir adsorption isotherm.

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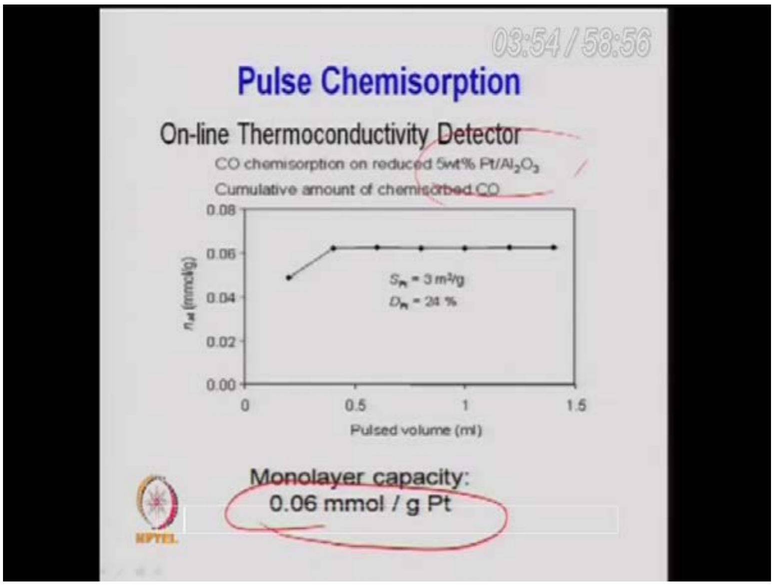

Pulse Chemisorption

On-line Thermoconductivity Detector

CO chemisorption on reduced 5wt% Pt/Al_2O_3

Cumulative amount of chemisorbed CO

Monolayer capacity:
0.06 mmol / g Pt

So, we are talking that is a monolayer coverage. So, v m is a kind of either, the volume of the carbon monoxide adsorbed on the active site or say for this case for carbon monoxide this is your number of molecules or gram moles of carbon monoxide adsorbed per gram of platinum. So, you can have the idea, which is related say this is we are saying suppose platinum is associatively adsorbed or sorry, carbon monoxide is associatively adsorbed on the platinum. So, you can get the idea about the number of atoms of platinum present on which the CO has been adsorbed. So, adsorption most of the time for hydrogen you consider a dissociative. So, stoichiometry should be known as a priory.

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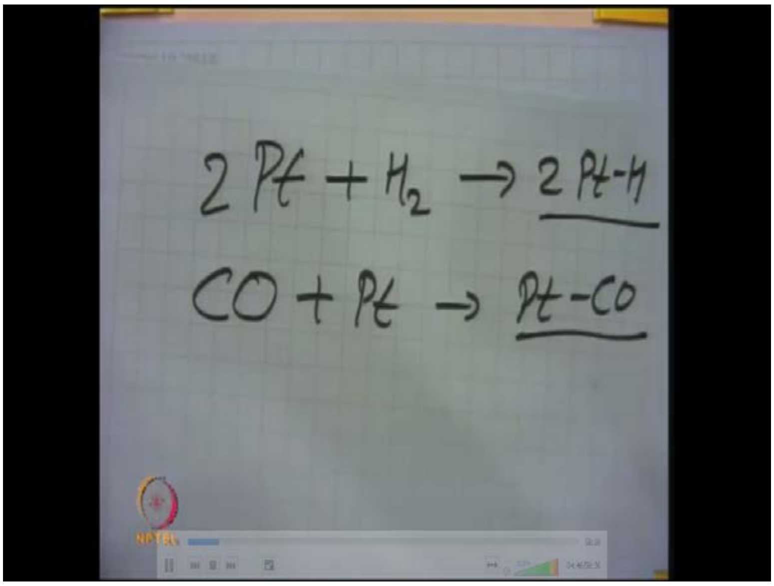

$$2\,Pt + H_2 \rightarrow \underline{2\,Pt\text{-}H}$$

$$CO + Pt \rightarrow \underline{Pt\text{-}CO}$$

So, when I am writing platinum adsorption then, it will be platinum which reacts with hydrogen. So, it will be 2 times platinum and this gives you P t H something like this, that a kind of chemical reaction is taking place here, same thing here, this can be associative this can be this associative. So, most of the time, this is associative here. So, this may be P t C o a chemisorptions. So, by knowing this, you can have the idea of the dispersion or percentage dispersion and also you can determine that crystal size also, what I said last time.

Because that is related to the monolayer depth and you can find out the atomic size and then, since monolayer is been formed. So, you can find out the size of the crystal also sometimes, because most you have the metal supported on the some alumina something like that silica. So, this is what I have discussed here is just a metal, you are not talked about the weaker chemisorptions of the gas on the support but, support may also have the chemisorptions property. So, you have to ensure that, there are no chemisorptions on the support, when you have a bimetallic catalyst or some metal on support. So, dispersion when you have platinum brenium or say, when you have a ruthenium along with some copper or molybdenum then, for bimetallic sometime you get total number of sites.

If you gone to get the individual number of sites or dispersion for given site then, you have to prepare two batch of the catalyst. So, first you prepare the rhodium on alumina then, prepare molybdenum on alumina and then take rhodium molybdenum on alumina and then, see the chemisorptions graph. So, this structure or curve is something based on to look at whether, there is chemisorptions of hydrogen on alumina or not. So, generally, the chemisorptions of hydrogen on alumina are very weak. So, we write here, the Henry law. So, v is proportional to k p. So, this for weaker adsorption as you increase the pressure, the volume of hydrogen adsorption like this and when you heat it will disrobe immediately.

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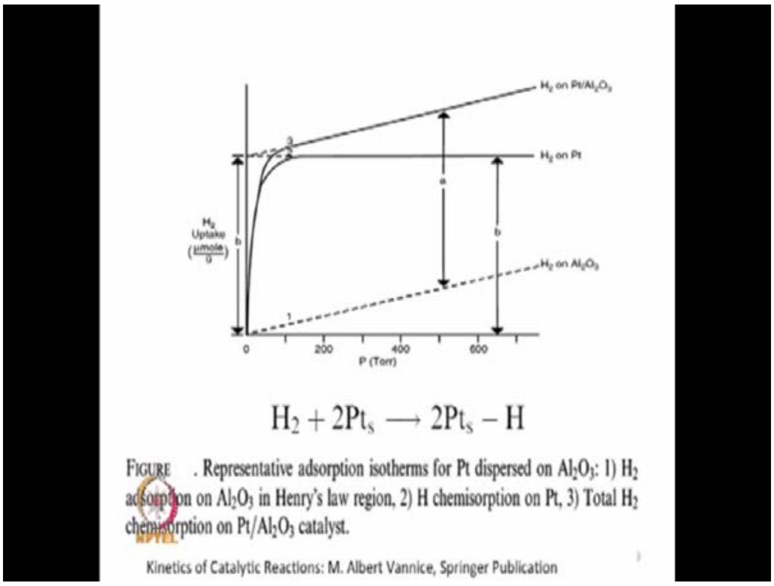


$$H_2 + 2Pt_s \longrightarrow 2Pt_s - H$$

FIGURE . Representative adsorption isotherms for Pt dispersed on Al_2O_3: 1) H_2 adsorption on Al_2O_3 in Henry's law region, 2) H chemisorption on Pt, 3) Total H_2 chemisorption on Pt/Al_2O_3 catalyst.

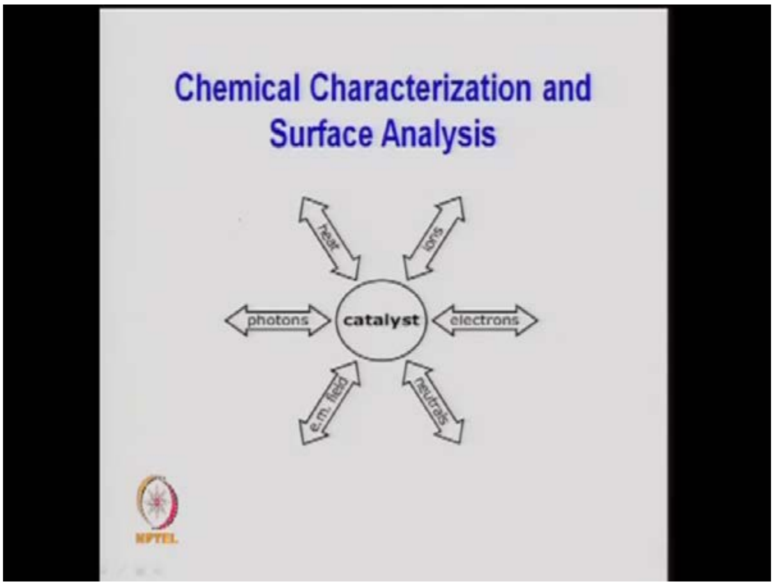
Kinetics of Catalytic Reactions: M. Albert Vannice, Springer Publication

So, you can check this just by taking the alumina and then, do the chemisorptions of that alumina. So, you can have the idea about the number of sites chemisorbed on alumina then, second if you have just platinum. So, the adsorption may be very strong, because platinum is strong adsorbed. So, this is a kind of strong chemisorptions or strong adsorption of hydrogen on platinum is metal support interaction or metal gas interaction adsorb it, if I talk hydrogen and it is adsorbing on the surface and this is your actual catalyst platinum alumina on which hydrogen is being adsorbed. So, this is a weak plus strong adsorption. So, on alumina it is weak, on platinum it is strong.

So, what is the fraction of the platinum? Actually, on this catalyst, what is the metal dispersion? So, n s a, what you have to do, you have to just look at the Henry law here and this is the adsorption when, it is the platinum on alumina. So, basically this is only when, there is the alumina. So, difference of these two. So, this is your a, this is your b. So, b minus a, is nothing but, some kind of the molecules, which have adsorbed on platinum alumina so that is the dispersion. So, this will be used this information will be used in terms of uptake of hydrogen, which is actually adsorbed on the platinum catalyst, because the reaction is related to the platinum active site percent a dispersion of metal, we are talking not the support part.

So, hydrogen consumption for platinum sites is being measured in this case. So, v minus a can be calculated the difference or something like a minus b. I will say that here, so that is nothing but, a difference of this. So, which is mathematically look at here, this one is the actual adsorption of hydrogen, because after this we assume that nothing is changed here, this is the initial and then, this is the line which is just showing a tangent just draw a straight line. So, this is the value of b and this is the value of whatever here, which is 0 at low pressure.

So, this p can be written directly now and then, based on this because, 2 molecules of hydrogen will adsorb or hydrogen molecule will adsorb on 2 platinum sites. So, you can very easily find out the metal dispersion. So, when there is a bimetallic catalyst, multi metallic catalyst or metal support and support can also adsorbed the reactive gas or it has also the chemisorptions property. So, you have to do this study 2 time, first find out only for the support and then, for metal and then, take the difference.



Chemical Characterization and Surface Analysis

So, that was the chemisorptions part and the other characterization methods, which are generally based on the binding energy, because it is a core electron where, when you look at they are distributed in different shells in an atom. So, what you are some kinds of energy source some X-ray say so that will be primary beam of energy and that primary beam of energy if it strikes on the surface. So, this may be a primary beam of the energy when, it is strikes on a solid substrate, sub substance which has, which is metal basically and contains the atom. So, it gets activated and it will leave the different kind of energy.

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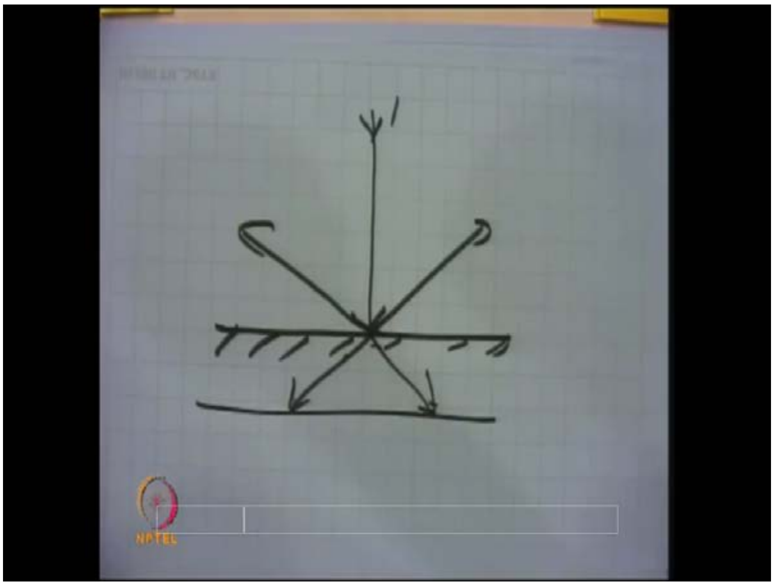

It may be for proton, it may be electron, it may be your X-rays and this can be a primary beam which is here and then, these are the secondary scattered beam and this can be some core kind of scattering here also to different depths. So, they may pass this defect, also this is diffraction and then, they may go to the other site and you can have the energy of these beams also, we will talk on that. So, basically, what I mean to say by giving some sub kind of energy source, which is strikes the substance or metal and then, you look at the response of that.

So, it can be 100 electrons, kilo electron volt and it can be 400 kilo electron volt and large amount of energy that is primary energy beam, which are strikes on the substrates. So, it will leave different kind of secondary beams X-ray protons, other electrons. So, their binding energy is this is whatever the kinetic energy of the beam, which is striking and what is the work function? So, work function is again the minimum amount, that what is required to take the electron out from a metal, because your catalytic activity what we have discussed earlier is, because of the d with d orbital's unpaired d electrons, which are present in the orbital's per atom number of d electrons. So, a larger number, it has the larger activity basically.

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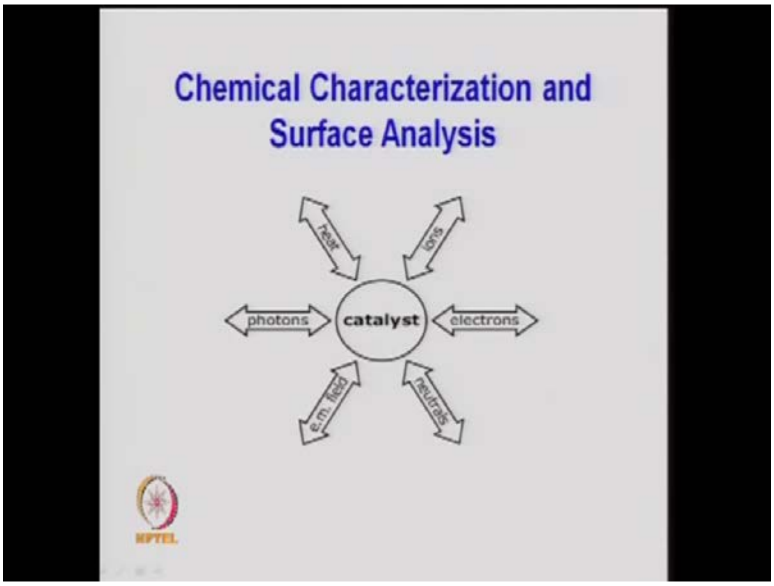

Chemical Characterization and Surface Analysis

heat

ions

photons

catalyst

electrons

e.m. field

neutrals

So, what we do this? We give the different kind of techniques. So, it can be based on heat like an your TPR, TPT, you do heat the sample and you see the response and it can be in the kind of ions beam of ions, which may be something like your ion electrons a spectroscopy and you can see the response of those ions, which comes from the catalyst surface, it can be some electrons. So, there can be different kind of techniques a standing electron transmission electron, it can be electromagnetic field. It can be photons extra spectroscopy. So, there are what I mean to say, there are different technique and then, decide that, there can be some other which are not based on this something like just titration methods or some other structural property of the catalyst crystallography study and. So, you can have those also characterize the surface.

So, the basic thing is that, we are looking a metal and we are looking at its electronic property. So, phase centered and the body centered and cubic centered. So, there are different kinds of crystals, which are available in a metal. So, crystal means, smallest grain and when you say particle, it is made of large number of many crystals so that may be a particle. So, when you do the X-ray diffraction, you are looking morphology of the crystal. So, there can be different crystal.

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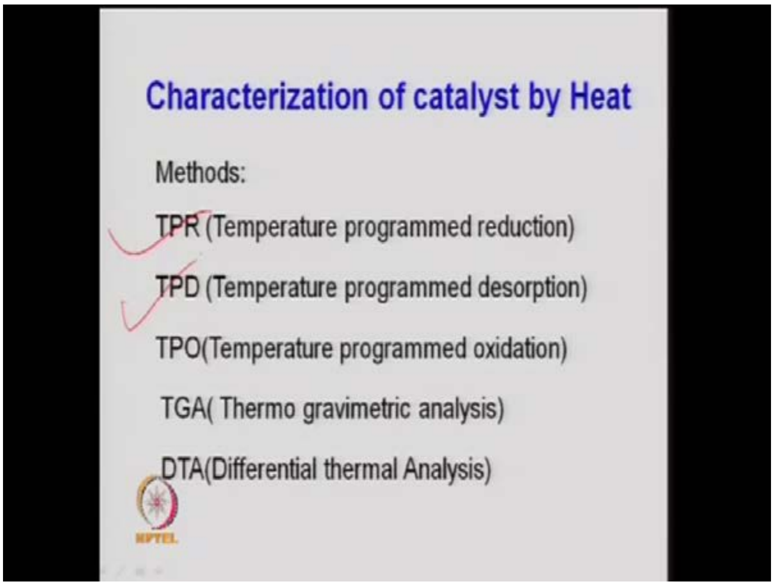

Characterization of catalyst by Heat

Methods:

TPR (Temperature programmed reduction)

TPD (Temperature programmed desorption)

TPO(Temperature programmed oxidation)

TGA(Thermo gravimetric analysis)

DTA(Differential thermal Analysis)

So, you see these techniques very quickly. So, characterization of the crystal by heat what I said first thing so that is your TPR temperature programmed reduction, you can see the phases, which are present in the catalyst and at what temperature, they reduce so that may be related to your metal and support interaction also type of oxide phase, which is formed on the surface and the reduction temperature may also depend on the second or metal or promote or which may be present on the catalyst.

Second is temperature programmed desorption like the, you do the ammonia TPD then, finds out the acidity and basisity of the catalyst so that may be a very good tool to find out the acidity or bonus typed acidity, Louis type acidity or same thing for preciosity of the catalyst temperature programmed oxidation at what temperature, the catalyst get oxidized. So, stability of the catalyst, this information can be obtained from temperature programmed oxidation.

So, here we are giving a kind of heating in this way, we are heating it to temperature of 1000 up to a temperature of 1000 degree centigrade or at the rate of 10 degree centigrade per minute or may be 20 degree centigrade per minute. So, you can do the kinetic based on that, also what is the kinetics of that adsorption desorption or reduction, you can do that same thing TGA also, you can have with the gas also, you can do the kinetic also, you can do a some reaction also by using the TGA. So, this is the thermo gravimetric analysis.

So that is the loss in weight, when you heat the sulphur to a different temperature range at a different rate. So, by using this you can find out the kinetics also and also on a catalyst surface you can find out, if this is a metal salt, you can find out what is the temperature required or calcinations if you pass hydrogen? It becomes something like TPR.

So, temperature required for reduction can be obtained for the oxide catalyst and since, in DTA which gives you the idea about the endothermicity, exothermicity and energy released during both the steps when, TGA has been done. So, TGA, DTA are jointly associative or can be done jointly. So, temperature programmed reduction as I said. So, basically, it is a characterization of oxide catalyst and may be other producible catalyst, which is producible. So, you can do the TPR study and qualitative information on oxidation state. So, there may be, when the oxide during the calcinations, you may have different kind of the freezers.

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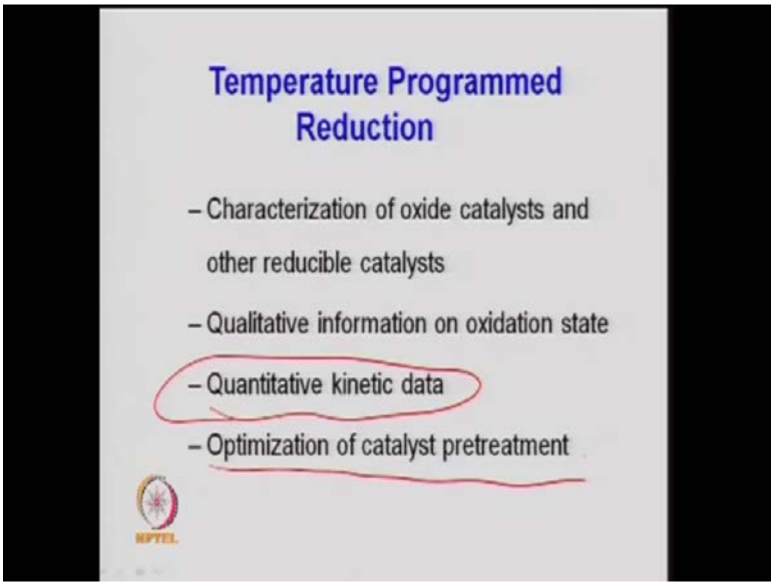

Temperature Programmed Reduction

- Characterization of oxide catalysts and other reducible catalysts
- Qualitative information on oxidation state
- Quantitative kinetic data
- Optimization of catalyst pretreatment

As I said calcium aluminates may be different phases of calcium will be present, same thing nickel oxide to represent different oxidation state cobalt may be present in different oxidation states same thing iron. So, all these metals may present in the different oxidation state. So, by doing this temperature programmed reduction, you can find out the temperature at the base, it can be reduced and also we can find out which phase may be present or how the reduction of these calcined catalyst takes place, this can talk on the kind quantitatively on the kinetic data also, because you know nor rate of change of temperature and simultaneously, you are by just if you are doing your reduction in hydrogen say.

So, how many molecules of hydrogen consumed can be determined by measuring the area under the carbon. So, molecules of hydrogen reacted basically, at a given condition of temperature so that is nothing but, d alpha by d t e if I do and if I know that T is changing the temperature. So, I can co relate T as a function of temperature and then, very easily one can, because k is equal to k 0 e to the power minus e by r t, it is from erroneous equation. So, you can co relate all these and you can find out the kinetics for this reduction.

And this is also helpful in optimizing the catalyst rate pretreatment, that at what condition you need to reduce the catalyst whether, reduction with hydrogen reduction with carbon monoxide is desired you can check that by making different phases and test the catalyst or do the kinetics institute. So, calcinations temperature, the question may be asked, how did you select this calcinations temperature. How did you select the reduction temperature? So, this information's can be or provided by doing these studies.

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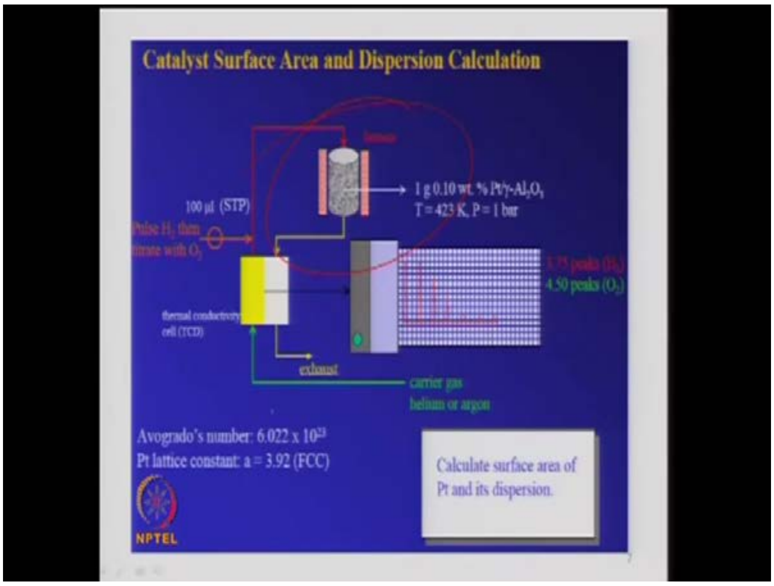

Catalyst Surface Area and Dispersion Calculation

Avogrado's number: 6.022×10^{23}
Pt lattice constant: a = 3.92 (FCC)

Calculate surface area of Pt and its dispersion.

So, the reactive system is similar, you need not to have a very specific set up these thing can be done in your micro reacted suppose, you put a given mass of the catalyst and then, reduce it at different conditions and then, do the just measure the phases absorbing phases and that can give you the idea, that at what temperature, which phase have been reduced so that temperature time both are important, when you give the heat treatment doing the calcinations, doing the reduction. So, a simple reactive system again as I have discussed last time also, that a simple reactor system where you put a known mass of the catalyst and then, the do the reduction intuitive in the presence of hydrogen. So, this is the setup is same.

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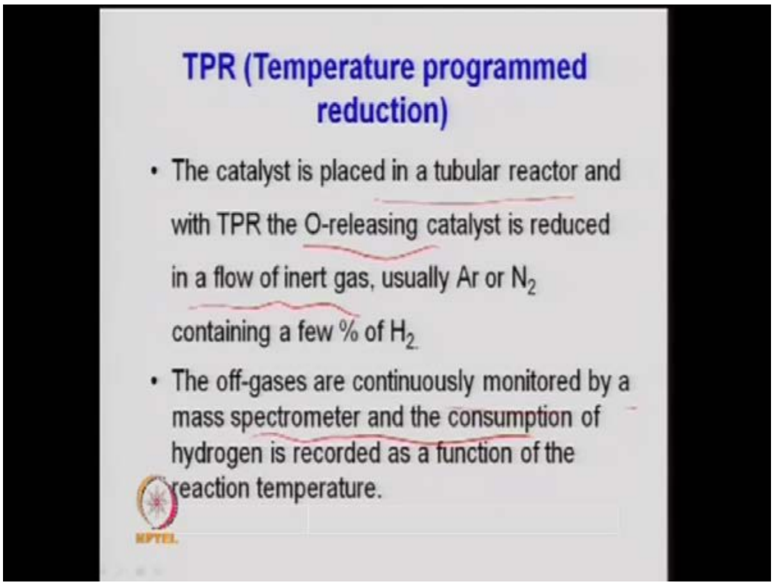

TPR (Temperature programmed reduction)

- The catalyst is placed in a tubular reactor and with TPR the O-releasing catalyst is reduced in a flow of inert gas, usually Ar or N_2 containing a few % of H_2
- The off-gases are continuously monitored by a mass spectrometer and the consumption of hydrogen is recorded as a function of the reaction temperature.

Which are generally used for measurement of dispersions? So, when you do the chemisorptions study, first you reduce the catalyst. So, anyhow a metal type catalyst. So, you reduced and then, that chemisorptions. So, the same thing, what we have discussed last time, so that set up is used for doing the TPR also. So, the catalyst generally, the steps are methodology, you place the catalyst in the reactor and place the TPR the oxygen releasing catalyst is reduced in a flow of the inert gas.

So, you are passing argon, nitrogen in presence of a small concentration of hydrogen. So, hydrogen will react with the oxide sites. So, you can have the idea about the temperature, which is equal to reduce that oxide catalyst. So, of gases are continuously monitored by a mass spectrometer or a detector and the consumption of hydrogen is recorded as a function of the reaction temperature. So, you can give the different heating rate. So, temperature versus time plot is available with you and the hydrogen consumption is monitored. So, you can find out how many molecules of hydrogen consumed at a given condition of temperature and you can co relate the physical or the chemical property of the catalyst with the reduction temperature.

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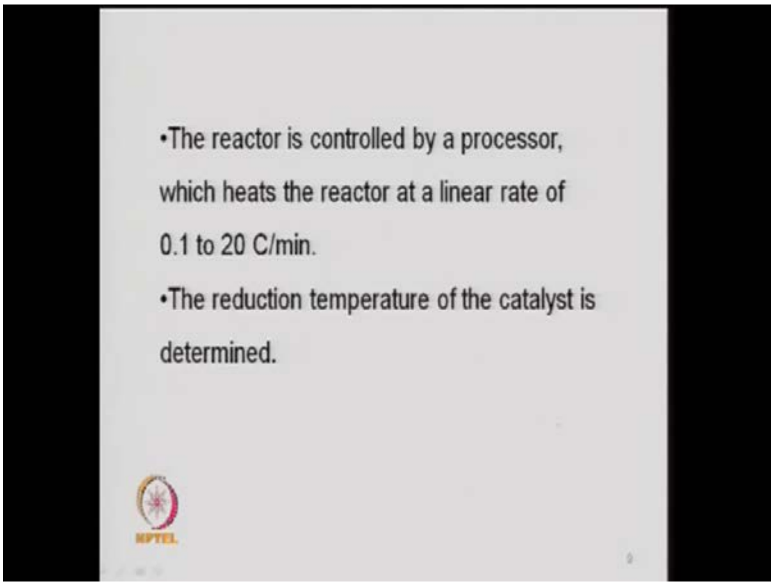

- The reactor is controlled by a processor, which heats the reactor at a linear rate of 0.1 to 20 C/min.
- The reduction temperature of the catalyst is determined.

So, the reactor is controlled by processors, you have the temperature control in the flow control and obviously. So, control a processor, which heats the reactor at a linear rate of 0.1 to 20 degree centigrade per minute. So, depending up on the type of the operators, the heating rate can be changed in your PID controller and then, you can have the fast heating rate, slow heating rate because that is also equally important, when you do the reduction in catalytic reactor system. So, for calcinations also for reduction also, the rate of heating is also equally important, because it is a kind of reaction a chemical reaction between the solid particles or between a metal and a support a particles between two metals, two different metals or similar metal. So, this is the, you know our kinetics depends on the temperature rate of change of temperature also.

So, all these information can be obtained if you do this kind of analysis. So, reduction temperature of the catalyst can be determined and you can have the kinetics also if you used. So, why TPR is done, that you have not seen, that oxides of the some of the catalyst, which are formed during the preparation step of the catalyst and may be undesirable so that can be reduced, so that is the first important part and you can determine the temperature required for the reduction.

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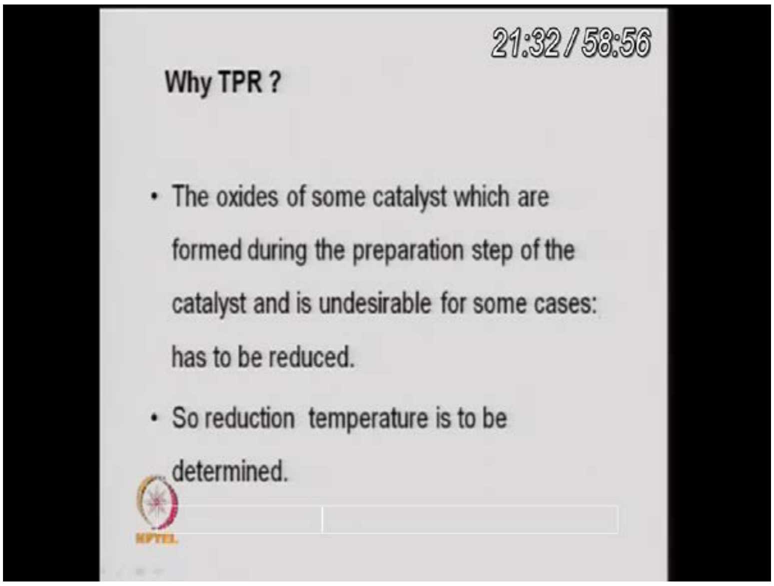

Why TPR ?

- The oxides of some catalyst which are formed during the preparation step of the catalyst and is undesirable for some cases: has to be reduced.
- So reduction temperature is to be determined.

So, if you see that, your nickel oxide catalyst nickel oxide is prepared during the calcinations and your actual catalyst is nickel. So, you have to reduce it. So, most of the catalyst are in metal state. So, you are most of time they are in metallic or the all the hydrogenation reaction dehydrogenation reaction. So, you need to reduce them. So, metal can exist in more than one oxide form that, you know when your calcine. So, different phases will form, because you are giving a certain kind of heating grade and at a given oxygen concentration. So, just like in the case of cobalt, it can be cobalt oxide or Co3O4 also, same thing f u t o 3 also, fe3o4.

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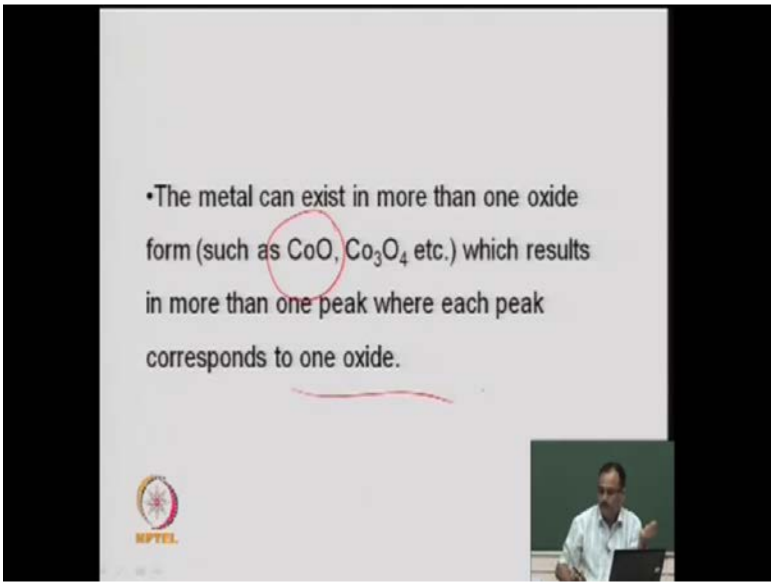

- The metal can exist in more than one oxide form (such as CoO, Co_3O_4 etc.) which results in more than one peak where each peak corresponds to one oxide.

So, different forms of the oxidation states may be available and when you reduce them then, you will find out that what concentration of which phase is present, because the area under the curve as I said, can better give you the idea bat the mole moles of the hydrogen consumed for a given phase. So, if you have two phases. So, you will get two p's, because both will reduce at different condition of temperature. So, you can find out the concentration of that phase.

So, if there is some promoter on the then, there may be also the interference of that sometimes the reduction temperature may change in the presence of the promoter. It is not like that, if you are iron oxide catalyst, the reduction temperature will be same if you have some promoter it may, because by adding the promoter, the dispersion may be improved if crystal sizes are low, they will react faster so that is the nano catalysis. So, it is a kind of electronic configuration will change, when you are reducing the size of the catalyst. So, reduction of the size is not related to the physical sometime it changes the chemical structure also.

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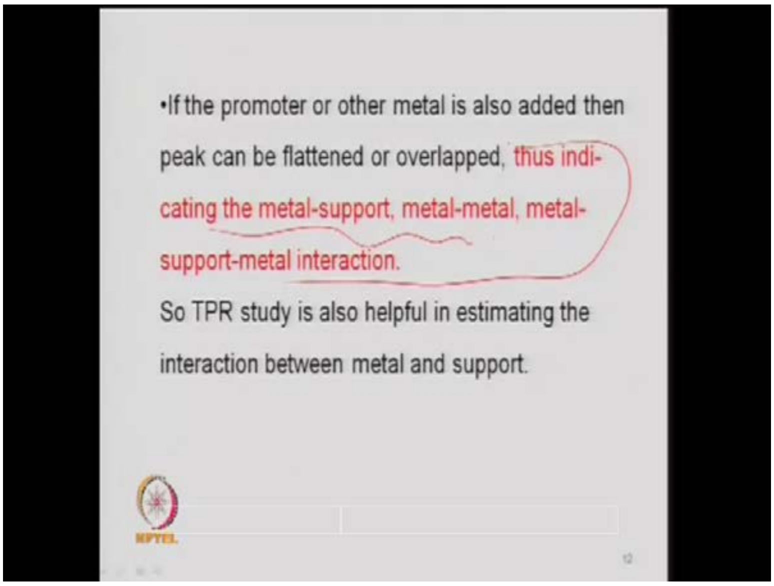

- If the promoter or other metal is also added then peak can be flattened or overlapped, thus indicating the metal-support, metal-metal, metal-support-metal interaction.

So TPR study is also helpful in estimating the interaction between metal and support.

Shape changes. So, its reducibility may be easier, so that happens sometime your promoter also to improve the dispersion and sometime they may have the negative effects also, in the presence of these, you can get the idea about the metal support, interaction metal interaction and metal support interaction. So, these are also equally important for understanding or diversifying the property of the catalyst, so that gives you the idea about that whether, the metals support instruction interaction is strong.

So, your reduction will be difficult and once your reduction is difficult it means, you need a higher temperature for reduction, that is one thing and same thing for the catalytic activity the gas molecule will have difficulty to chemosorb on that site, because the metal has the affinity towards the support rather with the gas molecule so that is what I said earlier, that we do not need a very strong metal support interaction and at the same time, we do not need very weak metal support interaction.

A definite kind of metal support interaction is desired for a given catalytic activity so that is becomes very important, just as an example. So, once you, when you do the TPR, you get curves like this at different temperatures. So, these are the nickel base catalyst basically and just I am talking one example of the nickel alumina, say and this is the hydrogen consumed, which is here in orbit unit then, one can be measured in terms of the mille molecules or mille moles of hydrogen consume per gram of the catalyst and as a function of temperature.

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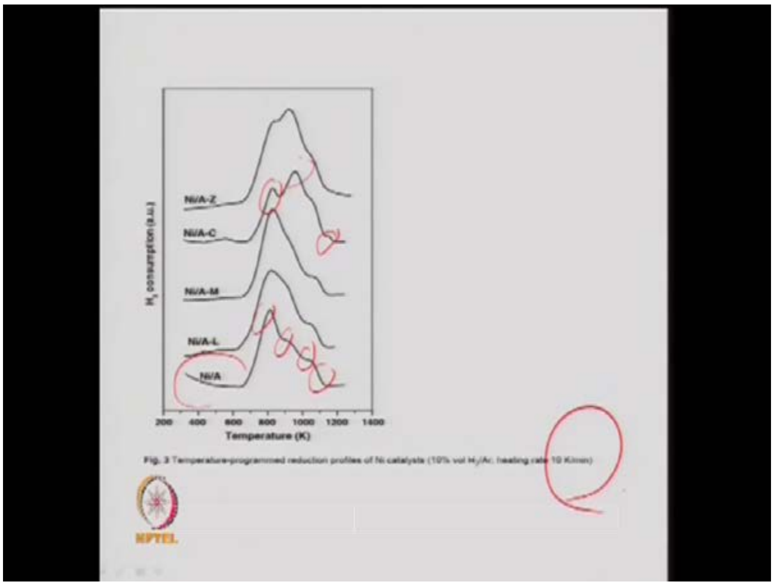

Fig. 3 Temperature-programmed reduction profiles of Ni catalysts (10% vol H_2/Ar, heating rate 10 K/min)

So, you can see here is that, this is one peak, another peak here then, again some peak here and some peak here. So, different peaks and this peak are nothing but, this is peaks are related to the reduction temperature and why this temperature, this reduction temperatures are different, because different phases are formed, same thing here you can see one peak here, another peak here, then here is some kind of change here and then again here. So, you can see that, there is a kind of diffraction or change in the measure of the peak, it just indicates that, these are another peak, which is because of the some other component may be impurities, some other component suppose, you have a copper oxide also then, this will also reduce along with an iron oxide.

So, like that. So but, we can just make it as large, that you can de convolute by changing this rate of heating temperature. So, if you just say this is just what heating rate, say 10 degree Kelvin per minute. So, if you change the heating rate then, these p 2 peaks makes get separated. So, you can just measure them by changing this, heating rates adjusting the heating rate, adjusting the temperature so that can be differentiated. So, this is an example, what are shown the graph, the catalyst supported on pure alumina this exhibits a broad reduction peak at 850 and 1150 Kelvin.

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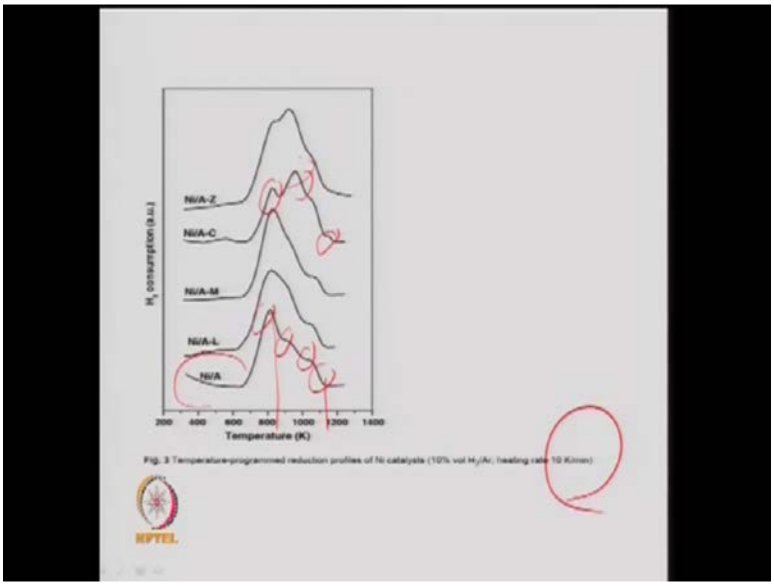

Fig. 3 Temperature-programmed reduction profiles of Ni catalysts (10% vol H_2/Ar, heating rate 10 K/min)

So that is for nickel I am talking and which is here something like 1 here and another here at 1150, this is the broader peak if you look at for different in all cases basically. So, this is nickel on alumina and nickel on different metal support. So, which could be de convoluted into three components at reduction temperatures of 818,942 and 1041. So, the peaks, what I said. So, there in total 1, 2, 3, 4 and 5 peaks. So, this can be just 1, 2 and 3 at different temperatures we have. So, one peak here, another peak is here. So, you can identify the peaks at different temperature if you just look at the picture carefully.

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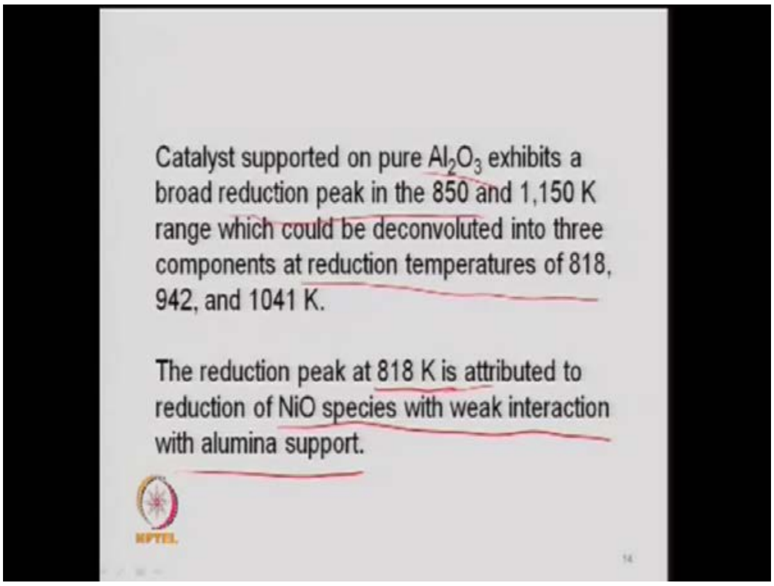

Catalyst supported on pure Al_2O_3 exhibits a broad reduction peak in the 850 and 1,150 K range which could be deconvoluted into three components at reduction temperatures of 818, 942, and 1041 K.

The reduction peak at 818 K is attributed to reduction of NiO species with weak interaction with alumina support.

The reduction peak at 818 just is an example but, you can do this by and confirm to your X-ray diffraction pattern, the X-ray diffraction pattern will give you the peak intensity base on your Bragg’s law, lambda is 2-d sin of theta and at different 2 theta values, you will have the different peaks which may be related your inter planar distance, what you call d value so that is the distance between two crystal planes and that is very specific for one phase. So, calcium oxide will have one Col23, will have another one nickel oxide, will another d value so that is very specific and the database software’s are available by which one can identify those components.

So, by comparing that X-ray diffraction results with this TPR result, you can very easily confirm that these are the phases formed and the temperature required for reduction of these phases is this one for a given is this one and also, because the same conditions are here, because reduction on nickel oxide species with weak interaction with alumina. So, if this is only nickel oxide supports. So, at the peak obtained, because of nickel oxide, if it is 2 temperatures, it means the part of the nickel oxide is strongly banded with the support. So, it means for reduction, it will require a larger temperature. If the peak comes at an earlier temperature it means, the temperature is lower for reduction. So, it may be weaker adsorption.

So that is what, it is mentioned here 818 Kelvin, which may be somewhere here and that is it says that for same alumina nickel alumina. So, one peak here, another here same thing here also here and here at same oxide phase so that is because of the strong metal support interaction or weaker metal support interaction. So, that is for same phase if you are getting that, the X-ray diffraction pattern says just that there are only one phase present and here you are getting a 21 or 2 different peaks for one phase only, so that could be because of the metal support interaction.

So, by doing this TPR study, you can get the information about the phases, which can be confirmed from X-ray diffraction and also you can get the idea about the amount of the hydrogen required to reduce the catalyst, because area under the curve you can get the molecules of the hydrogen consumed and that will be required in final catalytic reduction also. So, reduction peaks which appear at higher temperature in this case, they are related to the reduction of highly dispersed non stoichiometric amorphous nickel aluminates spinals.

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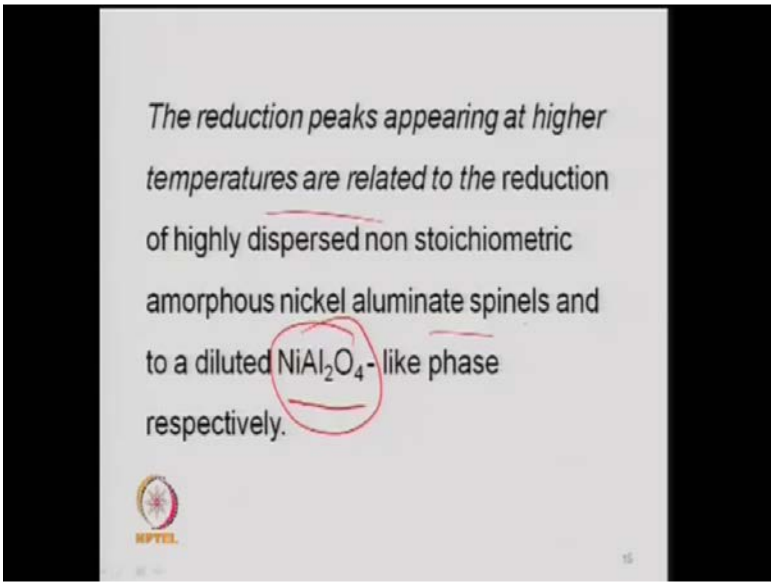

The reduction peaks appearing at higher temperatures are related to the reduction of highly dispersed non stoichiometric amorphous nickel aluminate spinels and to a diluted $NiAl_2O_4$- like phase respectively.

So, there may be another phase, which forms like this one is nickel oxide but, when you have done the calcinations as I said earlier also, that temperature and time is very crucial. So, it may happen, that part of the nickel reacts with the aluminum oxide or nickel oxide reacts with the aluminum oxide and forms a structure, which is another phase nickel aluminates NiAl2O4. So, this will require a higher temperature.

Because now it is a metal which has reacted with the support aluminum, much more strongly binded with that, so that will require a still higher temperature. So, 1100 or above ,that what we were showing in that, that is because of this amorphous nickel which has reacted or the formation of this non crystalline, that is amorphous nickel aluminates spinal and this is because of this phase. So, there can be other phases also in nickel aluminates itself, as I said in calcium aluminates 12CO7O23 is one size CO7123, another one or Cal23. So, these all are the reacted component reaction between calcium oxide and alumina oxide and forming different phase. So, they will have different peaks during XRD same thing here, nickel oxide reacts with alumina oxide and different phases may form.

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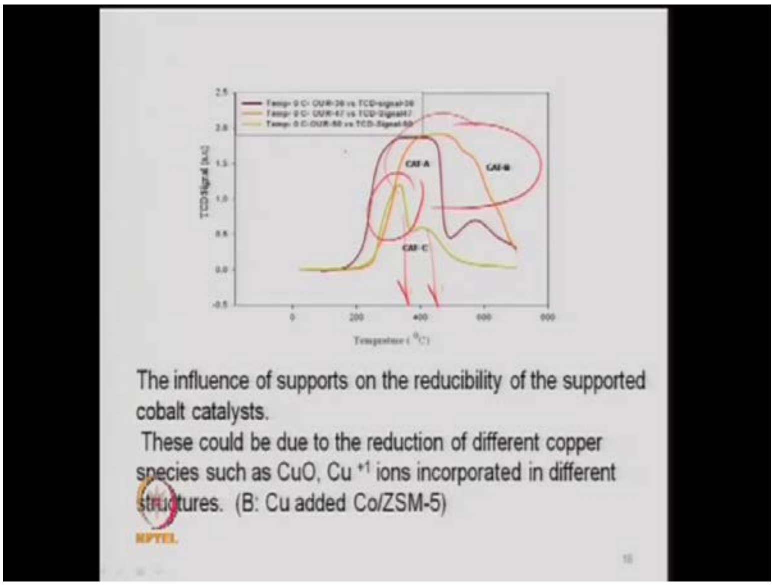

The influence of supports on the reducibility of the supported cobalt catalysts.

These could be due to the reduction of different copper species such as CuO, Cu $^{+1}$ ions incorporated in different structures. (B: Cu added Co/ZSM-5)

L24 is one just one and this is again I have just shown for cobalt catalyst supported on ZSM-5 and added with copper promoter. So, this is the study, which has been carried out in our lab. So, the basic idea here, again this 2 to show you that, if you have a different metal then, peak structure or the peak nature may change something what you see here in one catalyst, we have already changed just cobalt. So, you have say looking one peak here one peak here, when you added copper then, peak has conversed together. It has gone to single peak something like there.

So, it means if you want to separate these two peaks, your heating rate should be changed, that one heating rate at identical condition. So, copper oxide and the cobalt oxide, both have just because the large amount of suppose copper is therein cobalt is the there. So, both will show the peak or both will show the consumption of hydrogen and these two peaks will club together. So, you may have a wider peak. So, when you have a bimetallic component. So, again to confirm these, you should go first with the just a cobalt on ZSM-5 then, at prepare by H of copper on ZSM-5 or from literature just find out, what is the oxidation state temperature required or reduction temperature is required for copper oxide.

Then, you can distinguish the atom, because copper oxide may also reduced then, cobalt oxide is also reducing and then accordingly. So, cobalt oxide again, it can have Co3O4, it can have Co. So, these are phase will reduce and finally, you get metallic cobalt from that. So, there may be a different peak or the complex nature of the peak or TPR structure may be observed. So, you have to just analyze that carefully, here just again I have just discussed that a minimum of two peaks could be observed in the all the catalyst, that is because cobalt has two phase oxidation stability state.

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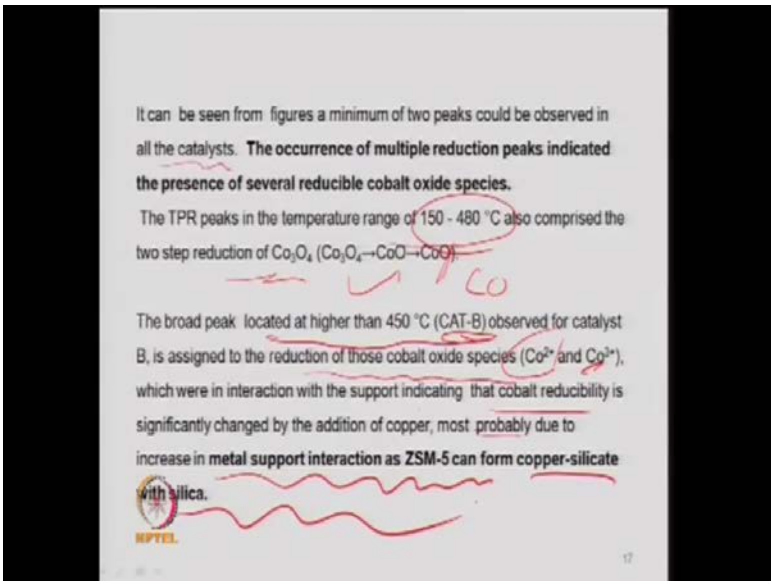

It can be seen from figures a minimum of two peaks could be observed in all the catalysts. **The occurrence of multiple reduction peaks indicated the presence of several reducible cobalt oxide species.**

The TPR peaks in the temperature range of 150 - 480 °C also comprised the two step reduction of Co_3O_4 ($Co_3O_4 \rightarrow CoO \rightarrow CoO$).

The broad peak located at higher than 450 °C (CAT-B) observed for catalyst B, is assigned to the reduction of those cobalt oxide species (Co^{2+} and Co^{3+}), which were in interaction with the support indicating that cobalt reducibility is significantly changed by the addition of copper, most probably due to increase in **metal support interaction as ZSM-5 can form copper-silicate with silica.**

The occurrence of multiple reduction peaks indicated the presence of several reducible cobalt oxide species. So, c o three o four c o like that what I am saying c o 2 3. So, the t p r peaks in the temperature range of this is comprised of c o 3 o 4. So, c o 3o 4 generally reduces like this it goes to cobalt oxide and that goes to metallic cobalt basically, here or c o 3 o 4, c o 2 o 3 then c o o and then cobalt metal. So, it means if you have c o o peak that will come at a later end if you have Co3O4.

So, first it will reduce to cobalt oxide and then, to cobalt metal. So, the plot that is the reason that may be another reason that you may see a broader peak if the phase all phases are present and then, one is reducing. So, hydrogen is consuming then, second phase is also reducing cobalt is going to metallic cobalt. So, again there will be a peak. So, the broad peak located at high temperature, which is for copper integrated is observed for catalyst b which I have written there it assigned to the reduction of those cobalt oxide, which is Co2 plus and Co3 plus, which were in interaction with the support indicating that cobalt reducibility is significantly changed by the addition of copper.

So, I have, I do not want to go in detail of this at this state, because this is a part of different results but, what I mean to say if you have a promoter then, that TPR structure changes at a temperature required for reduction may increase or decrees also sometimes. We add a promoter to improve the dispersion. So, once you see that is the dispersion is improved it means, that temperature required for reduction should also be reduced, because size is reduced crystal size is reduced so that is also related to the crystal size, sometime promoter may have a role to reduce the reduction temperature so that is what the addition of copper in this increase the metal support interaction at ZSM-5 can form copper silicate. So, here it is negative effect in one, because it has more metal support interaction.

So, you got a peak something like this a single peak and the reduction temperature has gone a higher site. So, it means the nature of the metal promoter and the support their tendency to react tendency to interact during calcinations can also be understand through TPR study, you can get some idea by doing the TPR, how this promoter has behaved or what kind of phases have formed or may have formed which can further be confirmed by X-ray diffraction.

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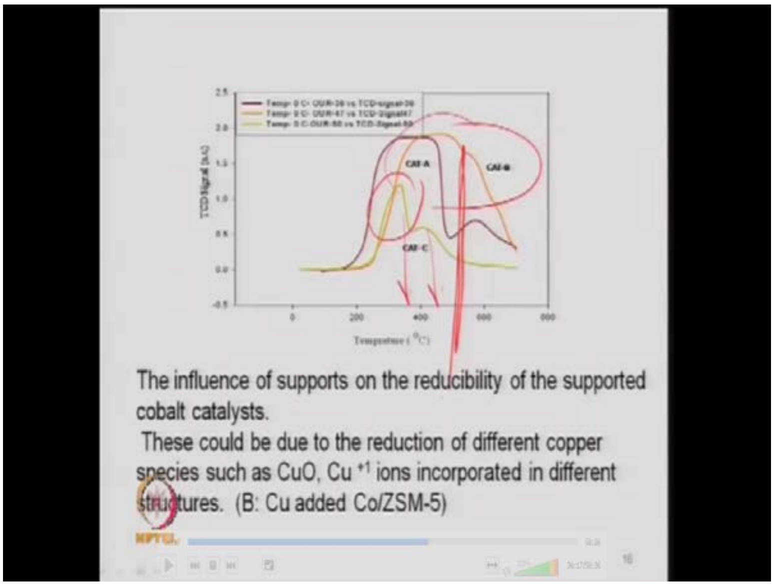

The influence of supports on the reducibility of the supported cobalt catalysts.

These could be due to the reduction of different copper species such as CuO, Cu^{+1} ions incorporated in different structures. (B: Cu added Co/ZSM-5)

So, TPR gives a very useful information mainly in terms of the reducibility but, one can look at in terms of the metal support interaction or analyze the data at least qualitatively if not quantitatively sometime qualitative information is very difficult to interpret from this kind of result, because this will depend on the loading of copper loading of cobalt and then, concentration of the species present in different phases.

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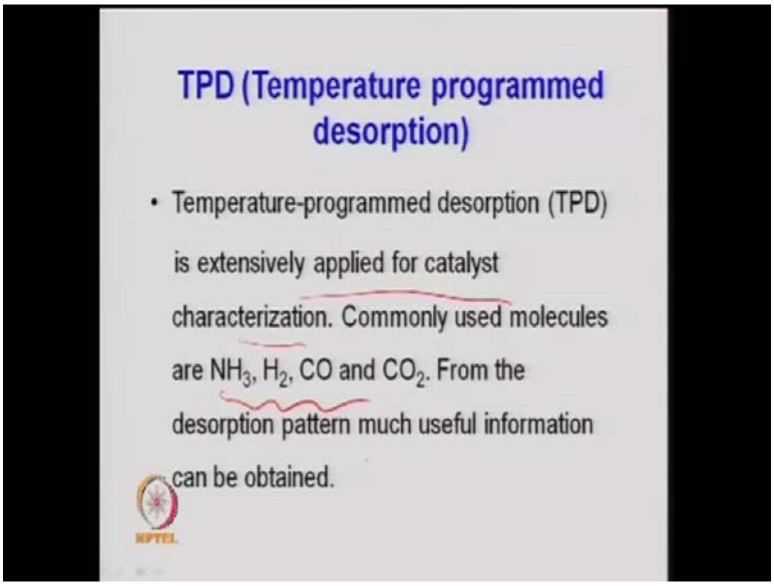

TPD (Temperature programmed desorption)

- Temperature-programmed desorption (TPD) is extensively applied for catalyst characterization. Commonly used molecules are NH_3, H_2, CO and CO_2. From the desorption pattern much useful information can be obtained.

So, similar to TPR as I said temperature programmed reduction you are reducing the catalyst and getting the idea in terms of reduction temperature, this temperature programmed desorption is another important tool to get the active sites or acidity and basicity of the catalyst. So, this is applied for a catalyst characterization and something like ammonia, which is a basic gas. So, it will give the acidic site hydrogen again talks on the chemisorptions. So, this can uses for dispersion percentage dispersion, when you kind of pulse chemisorptions.

So, carbon monoxide can give you again, the type as I said the reduction in the presence of carbon monoxide and also you can look at the active sites, which are adsorbed and what temperature they do disrobe, because to have the reaction the metal site should be free from that is catalytic adsorbed site should be free from the reactant specious or the production species.

So, you can get the idea about desorption and same thing carbon dioxide, again carbon dioxide is an acidic gas. So, this will give you the basic site of the catalyst. So, these information and decide the perioding can be used. So, any basic gas to find out the acidity and this type velocity type acidity can be calculated and same thing in terms of the basicity if you take different concentration of weaker acid gas or weaker basic gas. So, you can get the idea about the mille equivalent of these gases reacted and which is adsorbing on the sites. So, they provide sometime very useful information in terms of the catalytic concentration of these sites active sites.

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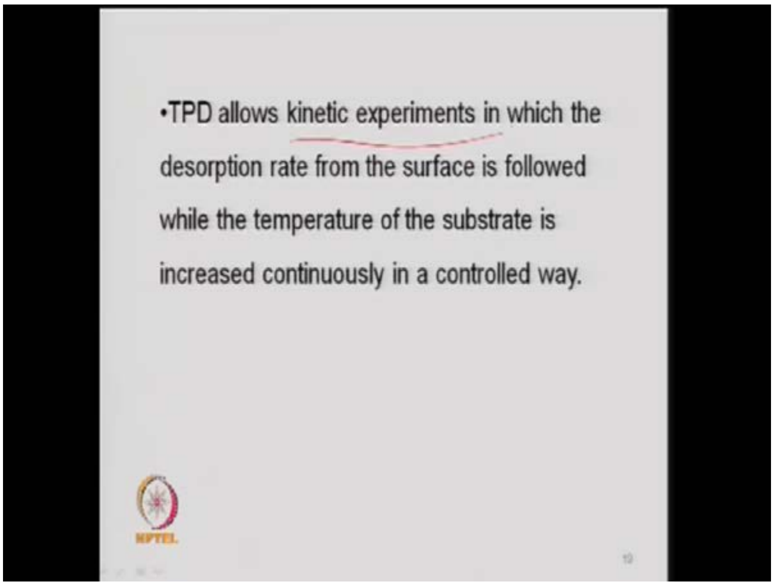

- TPD allows kinetic experiments in which the desorption rate from the surface is followed while the temperature of the substrate is increased continuously in a controlled way.

So, TPD allows kinetic experiment. So, again here, in terms of Co chemisorptions and adsorption and desorption basically, when I say chemisorptions so that carbon give you the idea about the kinetics of the reaction, because it may be function of temperature at different you do and then, you report the activation energy or chemisorptions same thing is what I said turn over frequency, turn over number. So, for how many times, the catalyst can be released again and again the satellite in the system.

So, because the catalyst is stable or not by doing this, because once carbon monoxide chemisorbed and does not dissolve form the surface usually, it means the site is damaged or deactivated. So, you can get some information from that also, desorption rate can be measured from the surface at different rate of temperature and then, you can calculate the rate of desorption.

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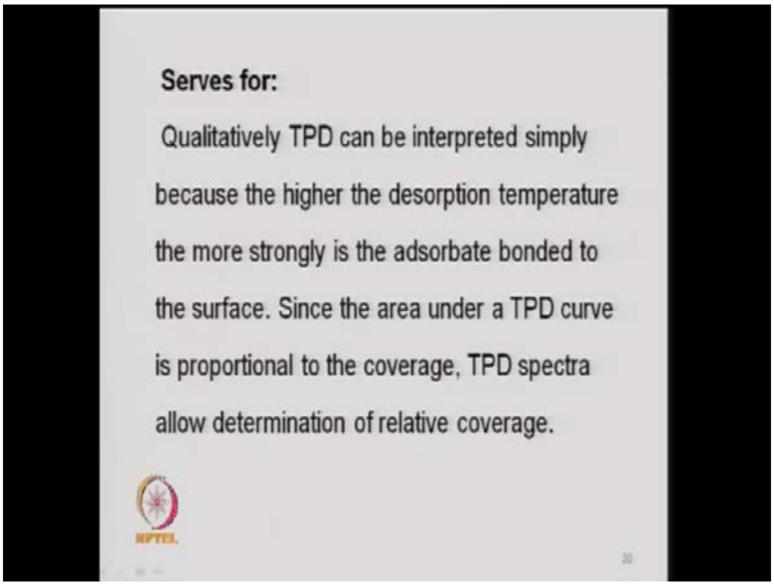

Serves for:

Qualitatively TPD can be interpreted simply because the higher the desorption temperature the more strongly is the adsorbate bonded to the surface. Since the area under a TPD curve is proportional to the coverage, TPD spectra allow determination of relative coverage.

So, qualitatively TPD can be interpreted simply, because the higher that desorption temperature the more strongly the adsorbed bounded to the surface. Just like in the TPR hydrogen chemisorptions you are doing, when you have hydrogen, it is nothing but, the hydrogen TPR or hydrogen temperature adsorption, desorption is study which is similar to once you reduce the catalyst. So, these are desorption or when you are determining the concentration of the metal sites chemisorptions. So, you are reducing the catalyst first. So, after TPR you are doing this, chemisorptions hydrogen chemisorptions or pulse chemisorptions, which I discussed earlier so that is again TPD hydrogen TPD basically.

So, when you use this or when you do this. So, the temperature required for adsorption desorption is high, it means the metal and support are strongly binded. So, again a strong chemisorptions, when I say that the metal is strongly binded, so that adsorption of that gas will require a higher temperature and if it is a weaker then, it will be a lower temperature. So, you can get this idea desorption temperature, the more strongly is the adsorbed bounded to the surface strong metal support interaction can be seen here.

Since, the area under the TPD curve is proportional to the coverage. So, how many molecules of that gas adsorbed on the surface just like in a physical adsorption and here it is a monolayer. So, TPD spectra allow the determination of relative coverage. So, this used for dispersion basically, because we had done it for hydrogen Co earlier, in our earlier study what we have discussed, this is an example here, again that when you do the TPD. So, there can, this is your just your titanium TiO2 and this is your silica Sio2.

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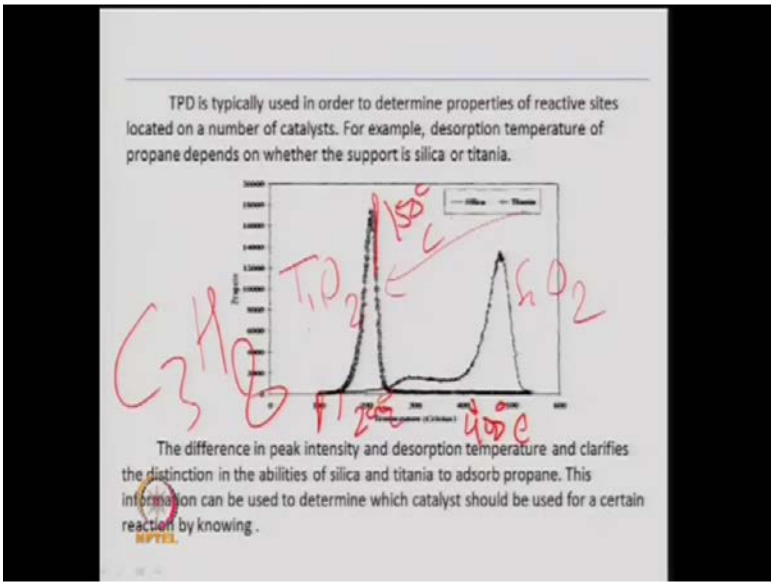

TPD is typically used in order to determine properties of reactive sites located on a number of catalysts. For example, desorption temperature of propane depends on whether the support is silica or titania.

The difference in peak intensity and desorption temperature and clarifies the distinction in the abilities of silica and titania to adsorb propane. This information can be used to determine which catalyst should be used for a certain reaction by knowing .

So, TPD is typically used in order to determine the properties of the reactive sites located on a different catalysts just for example, here the desorption temperature of propane depends on whether, the support is silica or titian. So, this is used for propane. So, any reactive gas can be used here, this can used during reaction suppose you want to look at some reaction propane dehydrogenation, propane oxidation you want to do that study, which support is good selection of the support. So, the just the experiments have been carried out on two support. So, one is silica support and other is titanium support, you can see here, that is on the titanium support, the propane chemisorptions at a lower temperature 300 degree centigrade where as on silica, it is around between 400 and 500 degrees centigrade.

So, this is here, 400 degree centigrade, this one and this is your 100, this is 100 degrees and this temperature mentioned here is 200 centigrade here. So, I will say that this peak may be around at around 150 degree centigrade or. So, what I want to say here, if you are different support silica or titanium same gas propane will chemisorbed at two different temperature, it means something which is related to the acidic sites or the property of the support, it may be some kind of pores structure also but, since we are talking on chemisorptions so that time that is less related.

So, the difference in peak intensity and desorption temperature and clarify the distinction in the abilities of silica and titanium to adsorb propane. So, you can just distinguish the whether this is better or this is better. So, now I will say that since, we have a propane adsorption is faster on titanium support. So, titanium gives better support, that you have to check other things also simultaneously it may disrobe the surface if it is weaker then, this may not be suitable adsorbs and does not react and leaves the surface propane, adsorbs and also disrobe faster so that is also equally important but, this says that, here it is wreaker adsorption, here it is a strong adsorption.

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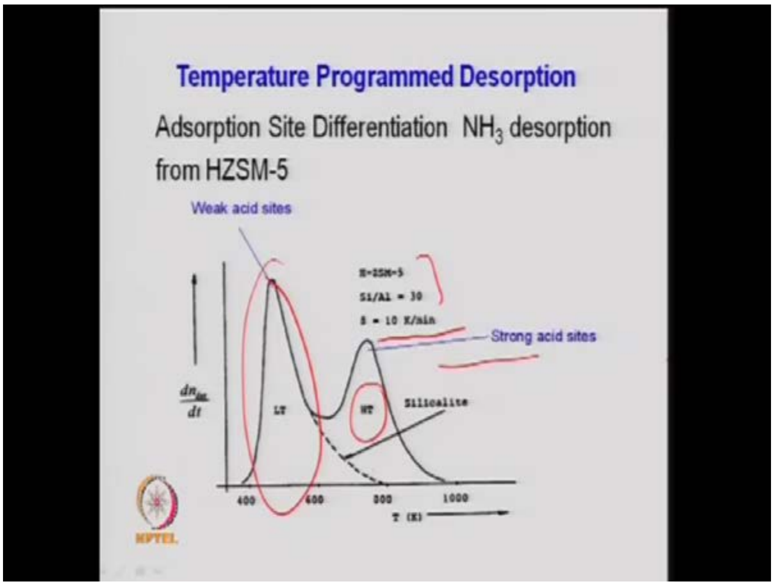

Temperature Programmed Desorption

Adsorption Site Differentiation NH_3 desorption from HZSM-5

So, this information can be used to determine, which catalyst should be used for a certain reaction by knowing the chemisorptions property. So, this is just an example, that information you can get from the TPD this is again to find out the acidity or of the catalyst, that same thing can be used if you have different gas you can talk the basicity also and also it talks about the stronger or weaker acidic sites also, here it is ammonia desorption and at Where as on silica. It is around between 400 and 500 degrees centigrade. Which is silica alumina material so that has been used as a adsorbent so, if you look at here, that is the molecules of ammonia adsorbed.

So, area of this curve if you take this is simply talking the number of acidic site of the catalyst, because ammonia is a basic gas. So, it will chemisorb on acid sites. So, by knowing this, that is between 400 and 600 degree Kelvin temperatures, this is the mille equivalent of the ammonia which is adsorbed.

And if you have some information of rate of change also, suppose I have temperature verses time and if I have the rate of adsorption of ammonia on this, I can use this information for kinetics also, desorption kinetics adsorption kinetics same thing in the second case if you look at this is ZSM-5, the silica alumina is 30 and heating rate is here 10 degree Kelvin per minute 10 Kelvin per minute rather so that is also equally important, because the higher heating rate means, the same temperature will come at a lower end and that is also important at what rate, the heating has been done and that will come when you do the kinetic, because K is equal to KoT power minus T by RT.

So, you have to take care that how K is changing with time also, because that time when you change this. So, you have write T verses time profile also, this is at high temperature HT. So, high temperature and again you can get some information on the strong acid sites. So, weaker acid sites, stronger acid side this information’s can be obtain if you do the ammonia TPD.

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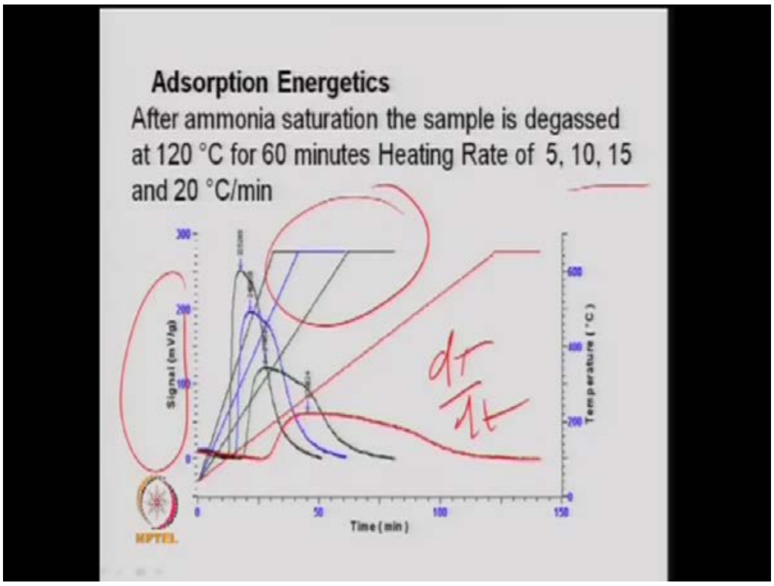

Adsorption Energetics

After ammonia saturation the sample is degassed at 120 °C for 60 minutes Heating Rate of 5, 10, 15 and 20 °C/min

So, like that, this is the ammonia saturation, the sample is degassed on 120 degree centigrade. So, you have to spilt it, the sample for 1 hour and heating rate 5, 10, 15, 20. So, as I said that effect of heating rate is also equally important. So, heating rate verses time and this is here in terms of the signal mille volt. So, basically mille volt, signal per gram of the catalyst, which is related to the volume of the ammonia which is injected. So, basically ammonia is being passed.

So, pulse chemisorptions, you are given a pulse of ammonia suppose or through syringe you have given 100 micro liter of ammonia and then, you are response. So, what will happen, when ammonia will adsorbed your heating is been done. So, ammonia will adsorbed and once everything is adsorbed then, at the end all your ammonia what if you are injecting continuously, it will come same saturation and then, you are heating the sample.

So, just remove, just pass it with certain concentration of helium for some time so that, the superficial gas removes and now whatever the chemisorbed gas, when you heat it now and then, that will start disrobed. So, you can have the information on desorption. So, this is just given here at different temperatures. So, you can see that, these are the peak intensities at different conditions. So, I am not going in details but, basically this slope which has been shown here, to find out the activation energy for chemisorptions, because for this curve, blue line this is the line for black line, this is third line. So, we have some idea on the rates of the adsorption chemisorptions and desorption as a function of temperature.

So, this information can be used, because this is temperature verses time profile. So, d t by d t will be calculated from that at different temperature. So, these are different linear rate 5, 10, 15, 20 centigrade per minute. So, by calculating this d t by d t you can find out. You are in equation, you can find T as a function of time a linear rate here and that will be use for kinetic study and these are the signals. We just talks that at this temperature.

So, here you can see the area under the curve you can find out the mille equivalent of the ammonia, which is disrobed or when you look at adsorption adsorbed. So, in general we talk desorption of the ammonia and molecules over ammonia, which have been disrobed from the surface in this case. So, when you change the heating rate, you can see that this nature of the curve is changing.

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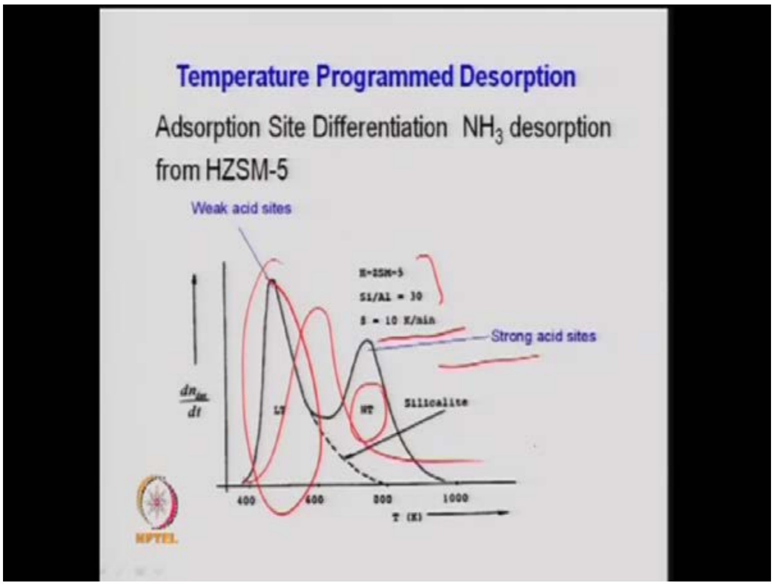

Temperature Programmed Desorption

Adsorption Site Differentiation NH_3 desorption from HZSM-5

So, theoretically if you have because with the all the ammonia has been adsorbed on a stronger or weaker sites, whatever the rate of temperature, the total mille equivalent of minus should be same, the only thing is that, what I am saying that, when the heating rate is different then, it may happen at higher temperature, when there are two peaks. So, the peak may merge together when, the heating rate is very high.

So, when you have a peak like this thing. So, if you are heating rate is very high. So, these two may also merge like this a silly peak will come, you have to de convolute that. So that heating rate is also equally important, to look at or to analyze the results quantitatively as well as qualitatively for the different molecules of the gas which have been adsorbed at different temperature? So, this information, which is generated from this, because you have a temperature verses time profile, you have the mille volt signals, which can be in arbitrative way but, one can very easily find out the molecules of the gas consumed by knowing the area under the curve.

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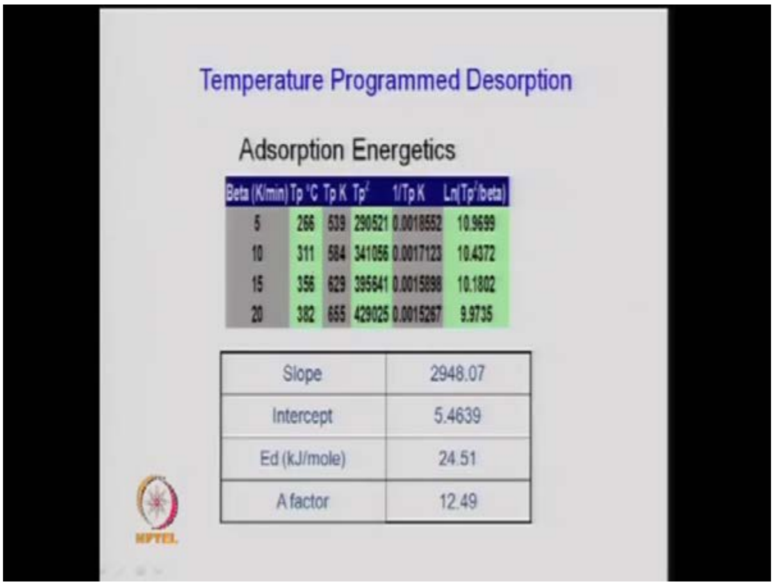

Temperature Programmed Desorption

Adsorption Energetics

Beta (K/min)	Tp °C	Tp K	Tp^2	1/Tp K	$Ln(Tp^2/beta)$
5	266	539	290521	0.0018552	10.9699
10	311	584	341056	0.0017123	10.4372
15	356	629	395641	0.0015898	10.1802
20	382	655	429025	0.0015267	9.9735

Slope	2948.07
Intercept	5.4639
Ed (kJ/mole)	24.51
A factor	12.49

So, that can be used to find out, because at different time heating rate you have that temperature at which. So, you can just very easily linearize the equation d alpha by d t, if I write which is rate of adsorption or desorption of ammonia per gram of catalyst per unit time kinetics basically. So, by doing the kinetic, it can be first order kinetics second order. So, I can write it just some constant times, the concentration to the power n.

So, there is lost, if it is loss I will write it just in TGA, you write 1 minus alpha to power n d alpha by d t is equal to T time minus alpha to the power n. So, you can very easily and that is weight, which is lost same thing here, I can find out the molecules of the ammonia adsorbed as a function of time and that is a function of temperature at what temperature it is adsorbed or chemisorbed.

So, you can very easily solve this equation and you can do the kinetic like in Arrhenius equation. So, you can find out the activation energy for chemisorptions and the reaction in a factor like this from the slope and interception. So, the just an information, that is what, you can get from this graph, what I have shown here and mathematical equation which I have not shown here but, may be it later, when I will talk the kinetics I will show you but, basically it is nothing but, the change in the number of moles per gram catalyst per unit time, which is rate of chemisorptions as a function of K times e to the power n, when you write and K is a function of temperature. So, K is related with T verse time data. And if you just take a log plot l and K verses one by T you will get a straight line. So, find out slope find out interception. So, slope is your e up on r something like that. So, calculate that activation energy.

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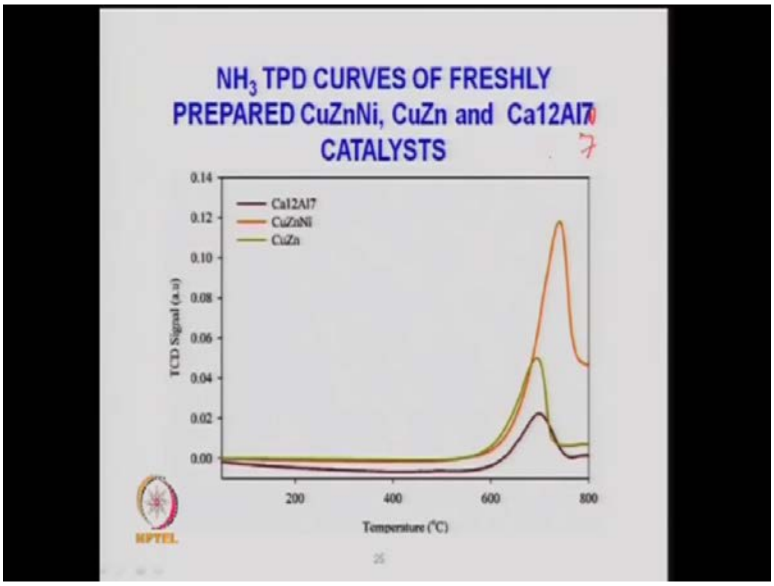

NH_3 TPD CURVES OF FRESHLY PREPARED CuZnNi, CuZn and Ca12Al7 CATALYSTS

7

So, this is again a typical curve what is from our lab data. So, we have different catalyst, copper, zinc, nickel copper, zinc calcium, aluminates as I said earlier, Ca 12, Alo 17 sorry AloAl7. So, this is something like this.

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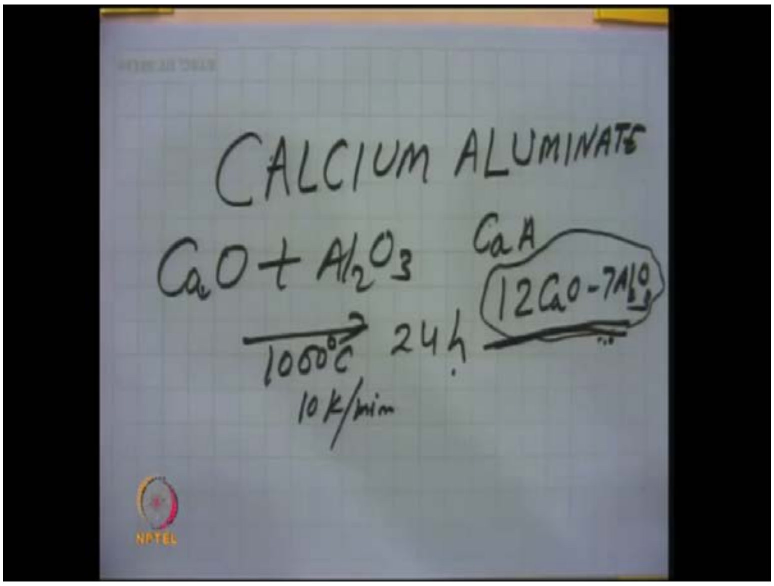

CALCIUM ALUMINATE

$CaO + Al_2O_3 \xrightarrow[1000^\circ C]{} 24h$

$10 K/min$

CaA

$\boxed{12CaO-7Al_2O_3}$

So, I will write it here, if I just look at this is Ca calcium aluminates, what I am saying. So, I told you that is prepared by mixing calcium oxide and aluminum oxide and then, it was entered to a temperature of 100 degree centigrade in one typical run where, the heating rate was again 10 degree Kelvin per minute and for a period of 24 hour, the n form XRD, we observed, that has different phase. So, this is calcium aluminates. So, just like Caa, I will write where, calcium oxide aluminum oxide binded together.

It was another phase 12Cao-7Al2o3 which. So, this is basically desired phase, because this has excess oxygen in the lattice structure and basically good when, you have a reforming type reaction. So, or even for the paranosis reaction, this catalyst have been tested or these catalysts have been tested. So, what I mean to say here. So, we have prepared different catalyst and this is one support on Ca121l7, which is written, which is something like 12Cao7al2o3 and these are nothing but, copper, zinc, nickel, copper, zinc and the supported on these catalyst.

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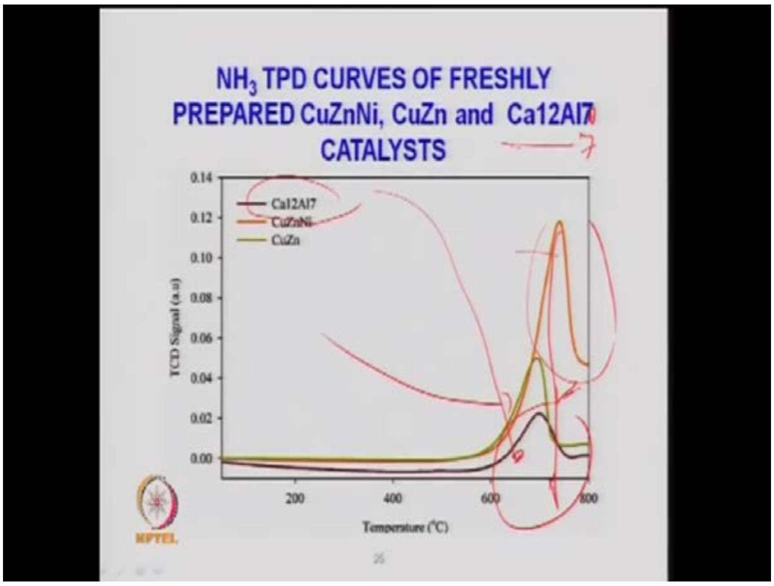

NH$_3$ TPD CURVES OF FRESHLY PREPARED CuZnNi, CuZn and Ca12Al7 CATALYSTS

So, you can see here, that is the just a support, which is just line and this one is your copper zinc nickel and this is your third line which is copper zinc here. So, this is copper zinc, this is your support is lower one. So, the basic idea here, what I am saying that basicity is mainly because of the support, because this 12Co7al2o3, it is basic in nature calcium oxide alumina oxide. So, you can find out the signals in terms of ammonia TPD but, So, since it is basic catalyst ammonia will not give any T, because ammonia will not chemisorbs on that but, when your copper zinc alumina then, it may have certain kind of because aluminum have some kind of amphoteric property something called as acid acidity also.

So, 12Co7al2o3, when I am saying it does not mean that, it is a totally basic. It has some kind of acidic side also but, we have reduced the acidic side by reacting it with calcium oxide. So, basically it has certain kind of basic property also, basicity will be determined in this case but, acidity can be determined. So, this is nothing but, area under the curve if you look at so that will talk on the concentration of that acidic side and when you have the copper zinc nickel. So, this is the concentration now. So, there is slight variation in the temperature also desorption, because the metal support interaction is dominating.

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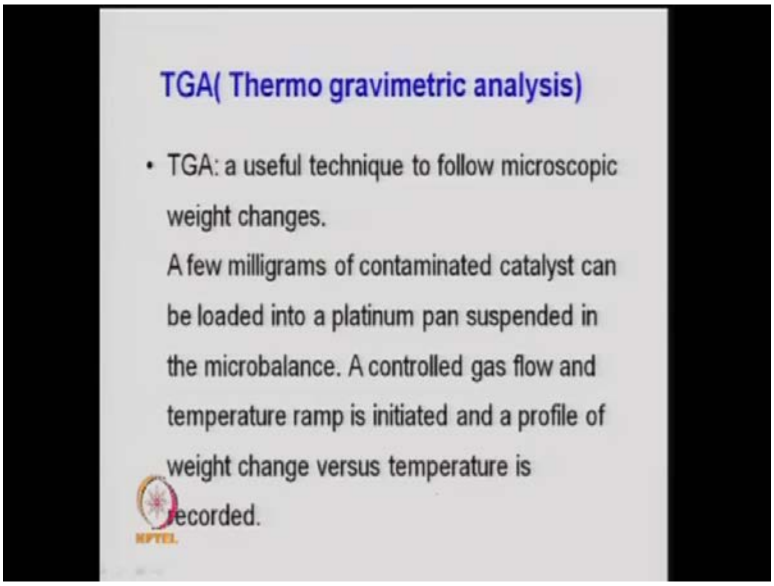

TGA(Thermo gravimetric analysis)

- TGA: a useful technique to follow microscopic weight changes.
  A few milligrams of contaminated catalyst can be loaded into a platinum pan suspended in the microbalance. A controlled gas flow and temperature ramp is initiated and a profile of weight change versus temperature is recorded.

The copper zinc it binded with the support part. So, because of that your reduction temperature is different, which I have not shown here but, it is different and also the TPPD curve shifts to a slightly to a hand side so that type of information you can get, when you have the TPD with different support and different metal integrated catalyst same thing another technique which is your TGA.

So, as I said that, it talks about the loss in weight when you heat the sample. So, basically when you have a catalyst, which is something, say calcium carbonate just like a solid material and you heat it. So, it will decompose. So, you can do the kinetics for the non catalytic reaction also just if you want to see the decomposition of calcium carbonates that can be done through this.

So, generally here in this, the small amount of the catalyst is kept in a pan weighing, just weighed amount which is a platinum pan here and you just heat it at a different heating rate and you find out the loss in weight or change in the mass as a function of time and again heating rate will important here. So, temperature verses time is one profile and w verses time is another profile. So, how mass is decreasing with the time and how temperature is changing with time.

So, you can very easily do the kinetics from this is TGA operators and also, you can get the idea about the catalyst property that is at what, temperature it will decompose, basically calcinations temperature, what temperature is required for calcinations, you get the information from this and if you put in the same operator, some reactive gas like hydrogen is similar to TPR.

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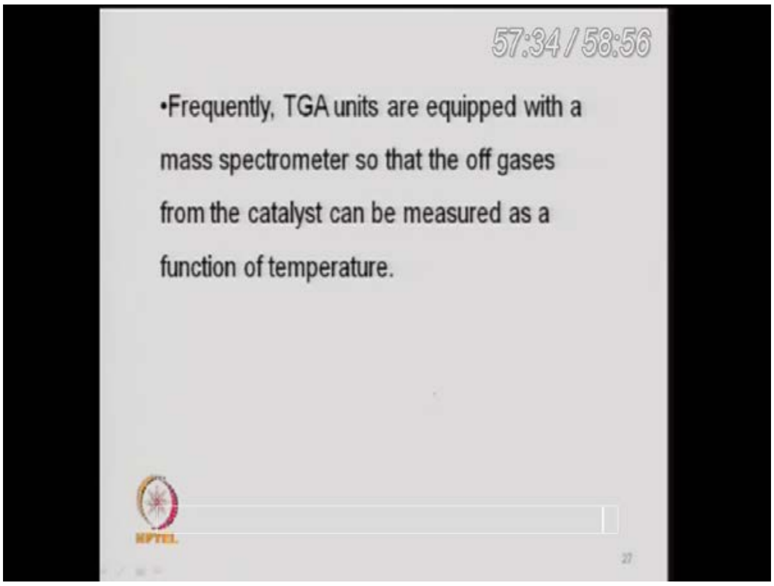

- Frequently, TGA units are equipped with a mass spectrometer so that the off gases from the catalyst can be measured as a function of temperature.

Because you already seen the catalyst if the presence of hydrogen. So, TPR study can be done. So, TGA units are generally connected to a mass spectrometer also, whatever the gas decompose then, you have a biomass material and you want to do the kinetics of the biomass then, you connect this TGA to a mass spectrophotometer. So, you can find out the composition of the product also.

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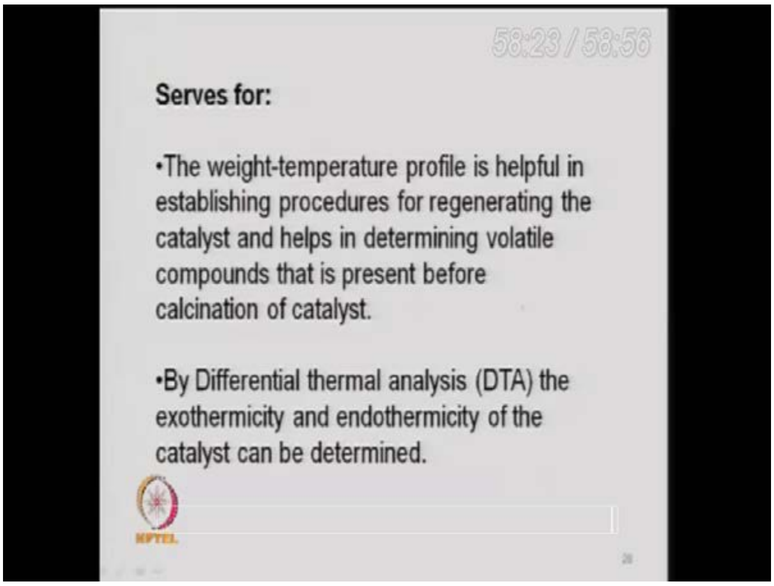

Serves for:

- The weight-temperature profile is helpful in establishing procedures for regenerating the catalyst and helps in determining volatile compounds that is present before calcination of catalyst.
- By Differential thermal analysis (DTA) the exothermicity and endothermicity of the catalyst can be determined.

So, complete characterization of the oil or product can also be done through kind of reactor system. So, the off gases form the catalyst can be measure as a function of temperature and you can very easily do the kinetics and simplify the product distribution as well as using a catalyst, you can do the reaction also. So, TGA generally serves as a weight temperature profiles, which is helpful for regenerating the catalyst and helps in determining the volatile components that is present before calcinations, sometime TGA used to remove the carbon from the catalyst, the spent catalyst give the TGA and you can find out what is the temperature required for removing the carbonaceous material or impurity form the reacted catalyst. So, I will continue at next time.

Thank you.