Heterogeneous Catalysis and Catalytic Processes
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Lecture - 21

Good morning. In the last lecture I was talking about synthesis and characterization of zeolite and today again. I will cover some characterization part of the zeolite and then the application of zeolite especially in the catalytic industry.

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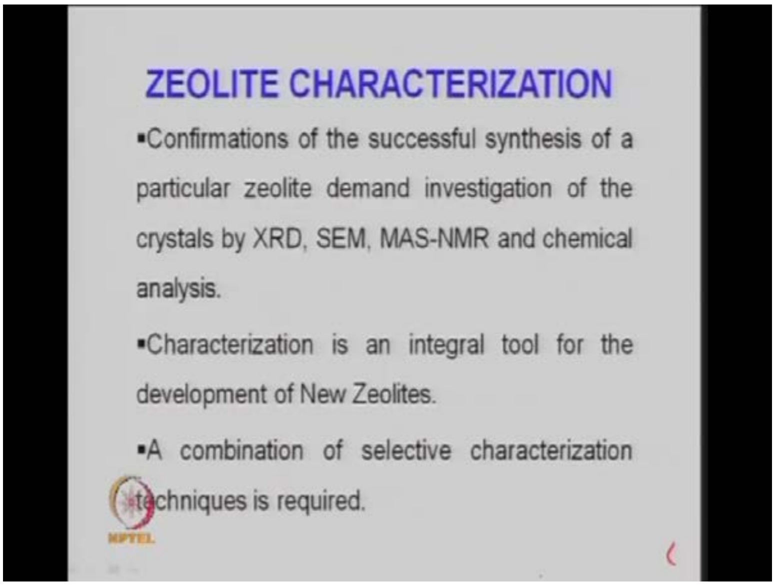

ZEOLITE CHARACTERIZATION

- Confirmations of the successful synthesis of a particular zeolite demand investigation of the crystals by XRD, SEM, MAS-NMR and chemical analysis.
- Characterization is an integral tool for the development of New Zeolites.
- A combination of selective characterization techniques is required.

So, the characterization part as I said because the zeolite contains a ratio of silicon to aluminum that is 1 which imparts the acidity to the zeolite so and the cage that is the type of the opening so pore structure of the zeolite then crystalanity of zeolite and the size of these crystals morphology all these things like in a usual amorphous catalysis or catalyst these things are desired in the zeolite also.

So, we need to find out the crystalanity, which is d 1 by x-ray diffraction scanning electron micrograph to find out the morphology size of that zeolite particle or crystals mass. Which is the spinning process for nuclear magnetic resonance? which is based on the shift chemical shift and the and 1 can determine the structure so mass-NMR, which is based on the magnetic angle the this thing the nuclear magnetic resonance so that is used for the again for the characterization of the zeolite because, you can get the silicon to aluminum ratio of a zeolite based on this and.

So, in fact when the new zeolites are prepared then also the characterization is important. So, we need to characterize the zeolite or a catalyst after preparation so a combination of the selective characterization technique is required. So, just 1 technique may not be enough to give you the idea about the type of zeolite so all details of this characterization are needed to confirm a definite type of zeolite and in order to use it for a particular catalysis process.

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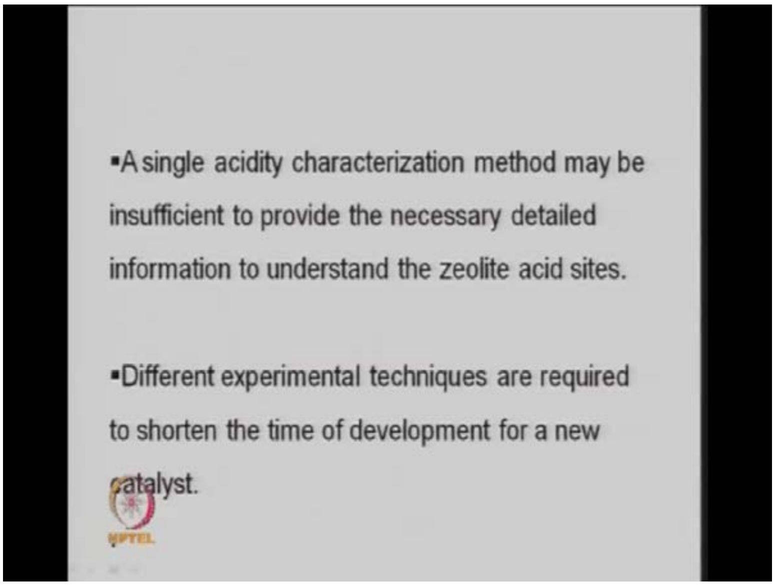

- A single acidity characterization method may be insufficient to provide the necessary detailed information to understand the zeolite acid sites.
- Different experimental techniques are required to shorten the time of development for a new catalyst.

So, as I said the acidity is 1 method. But, this may not be correct this may not be sufficient to determine the acid side because a concentration of acid is also to be determined because zeolite may contain the lewis type acidity and the bronsted type acidity.

So, concentration of these both type of the species that is required to confirm so just determine the acidity concentration which can be determined by acid based translation method that may not be sufficient. Then different experimental techniques are required to shor10 the time of development for a new catalyst so 1 need to identify the characterization technique in order to characterize a catalyst for a given process.

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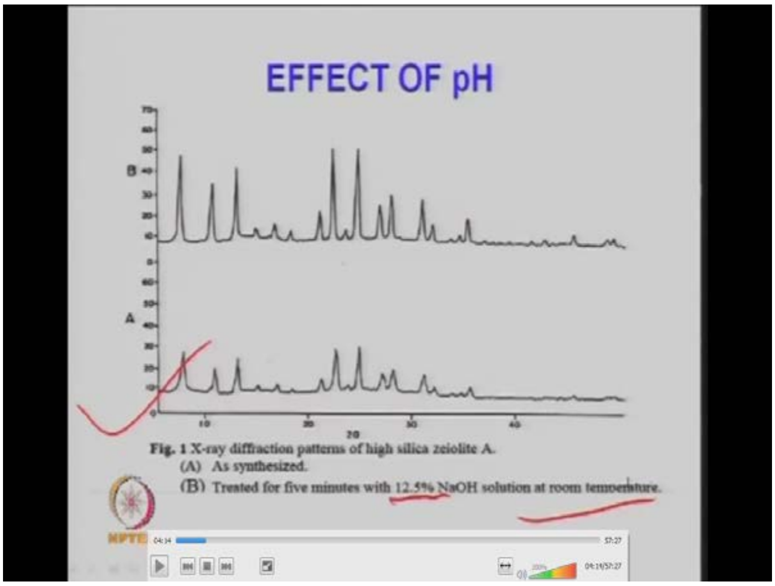

EFFECT OF pH

Fig. 1 X-ray diffraction patterns of high silica zeiolite A.
(A) As synthesized.
(B) Treated for five minutes with 12.5% NaOH solution at room temperature.

So, last time I was talking about this which is just how the crystalanty or degree of crystalanty of a zeolite matching depending upon the alkylic treatment.

Or depending upon the pores treatment method, so in zeolite crystal which is synthesized which has something like this a poor crystalanty to it is a it has shown some peak. Which indicates about the different the compositions of the depending upon the zeolite a material. So, silica alumina in the frame work of the zeoite but, the intensity should be poor and when it was treated for 5 minutes with this 12.5 percent any average it has provided some kind of hydroxyl lines in the zeolite.

So, the degree of crystalanity has been improved in this case it means the post synthesis also play a very important role and this is required sometimes in order to get the better crystalinity so crystalanity can be determined by x-ray diffraction pattern.

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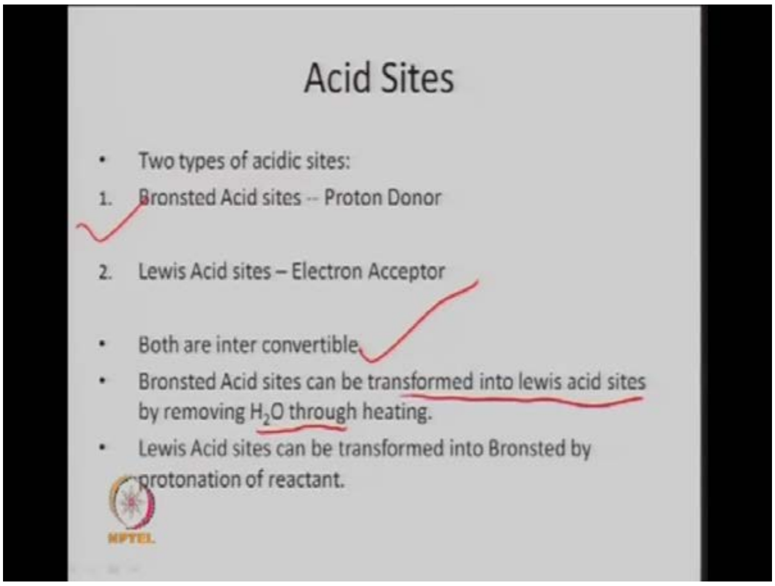

Acid Sites

- Two types of acidic sites:

1. Bronsted Acid sites -- Proton Donor
2. Lewis Acid sites – Electron Acceptor

- Both are inter convertible
- Bronsted Acid sites can be transformed into lewis acid sites by removing H_2O through heating.
- Lewis Acid sites can be transformed into Bronsted by protonation of reactant.

Acid sites as I said the acid site and the concentration. So, number of acid sites as well as the concentration of acid site that is very important and it depends on the silicon to aluminum ratio in the zeolite framework. So,depending upon the silicon or the aluminum in the framework the acid concentration may be high or low and same thing for the strength of the acidic site.

So, both phenomenons are very important in the case of zeolite material. So, basically 2 type of site bronsted acid site, which can donate a proton and lewis acid site, which can accept an electron. So, aluminum in the framework which has electro negativity that provides a kind of a lewis acidity in the catalyst and proton as positive which is present in the zeolite framework that is provide that provides the bronsted type acidity in a catalyst but, interchangeable these are interconvert table when you heat the bronsted site the water or evaporates or o h radicals removes from that which is h positive basically.

And your bronsted site gets converted to Lewis acidic site. So, this is transform into Lewis acid by removing water through heating and that has been discussed so Lewis acid sites can be transformed into the bronsted acid by protonation of the reaction so again you give some treatment with acids treatment with acid you can get certain kind of protonated site in the zeolite framework.

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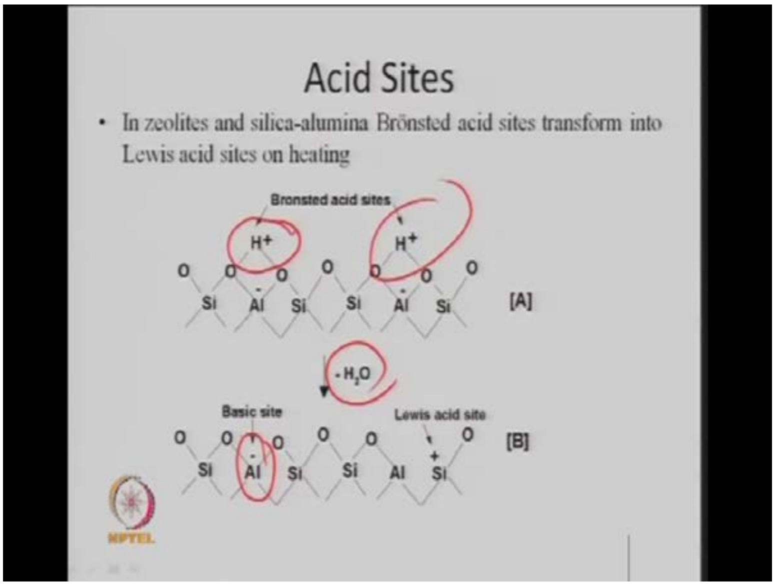

Acid Sites

- In zeolites and silica-alumina Brönsted acid sites transform into Lewis acid sites on heating

So, this has been discussed earlier that depending upon the silicon to aluminum a bronsted type acid.

So, which is because of this proton here and when you heat it the water gets out from this framework and ultimately it is a aluminum negative which provides the lewis acidity in the zeolite.

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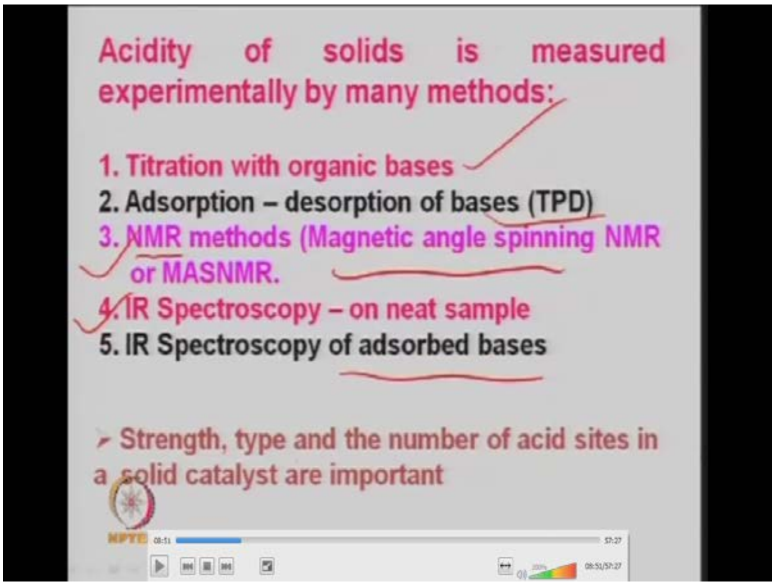

Acidity of solids is measured experimentally by many methods:

1. Titration with organic bases
2. Adsorption – desorption of bases (TPD)
3. NMR methods (Magnetic angle spinning NMR or MASNMR.
4. IR Spectroscopy – on neat sample
5. IR Spectroscopy of adsorbed bases

➢ Strength, type and the number of acid sites in a solid catalyst are important

So, method of determination of acidic site that is just basically, a titration if 1 look at the hammett acidity. So that is a titration with some base you titrade the acid with base and you can try or try to find out the concentration of those volume or mili equivalent of the base which has reacted with the acidic site.

That is very simple method and you call that titration with the organic bases then adsorption based process which are more common for the catalytic or especially solid catalyst material. This first 1 may be good for the liquid the solution based but, it may not give you the good result for the solid acid.

So, for solid substances like zeolite or any amorphous catalyst their's temperature program desorption method is the most promising 1. Then IR method infrared spectroscopy can again give you the concentration of bronsted and lweis type acidity so neat sample and the samples are adsorbed.

And then again say in adsorbed an. then look at the IR spectrum of that and at what concentration at what wavelength wave number it has been adsorbed and 1 can determine the bronsted or Lewis type acidity in the catalyst. Then nuclear magnetic resonance method, which is spinning basically because the depending upon the chemical shift comes because of the spin that is energy of that spin because the when the energy which is in the form of spinning or. So, that gives you kind of the magnetic resonance that can be measured in the form of shift and that is the principle of nuclear magnetic resonance.

So, this is can determine the concentration or composition, so and when you do it with magnetic angle spinning nuclear magnetic resonance then it is known as mass NMR. Which is very important for the zeolite type of material which can determines the silicon mass NMR. So, that can give you the crystalline crystalinity of the zeolite material it can also give you the information about silicon to aluminum ratio of the zeolite. So, suppose it can characterize the basisity or acidity of a zeolite so suppose it can very well characterize the silicon alumina phosphate type zeolite.

So, this is 1 of the very important method for the characterization of zeolite and again here it is based on the chemical shift. So, strength type and the number of acid sites in the zeolite , that is very important when you need a characterization of the zeolite.

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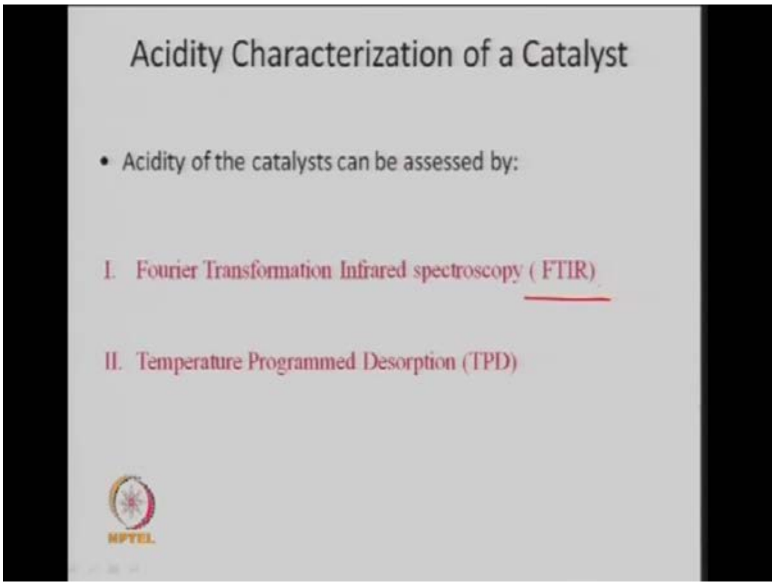

Acidity Characterization of a Catalyst

- Acidity of the catalysts can be assessed by:

I. Fourier Transformation Infrared spectroscopy (FTIR)

II. Temperature Programmed Desorption (TPD)

So, acidity of a zeolite can be determined as I said the IR or fourier transformed infrared spectroscopy , and T P D and we will talk these 2 in details.

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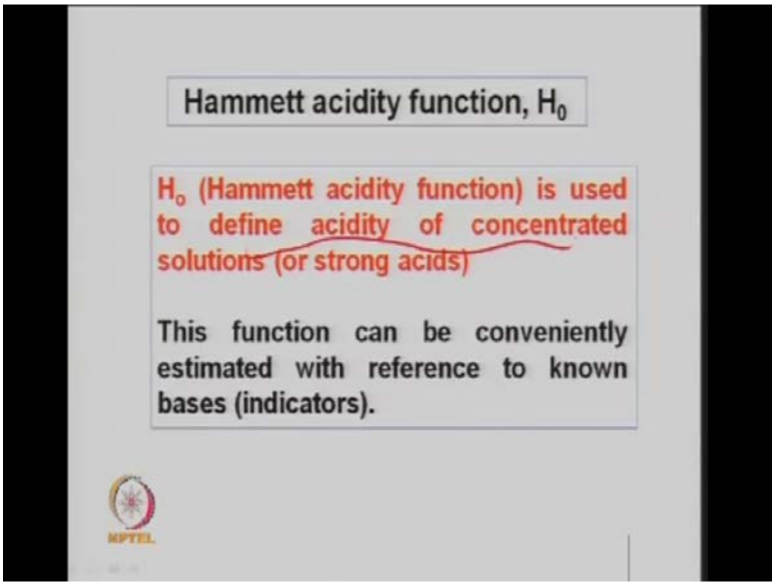

Hammett acidity function, H_0

H_0 (Hammett acidity function) is used to define acidity of concentrated solutions (or strong acids)

This function can be conveniently estimated with reference to known bases (indicators).

So, first thing is the hammett acidity all of you know that , it is basically the p h when you have a dilute solution it is nothing but, the acidity which is related to the p h ,.

So, it is used to define the acidity of a concentrated solution or strong acids strong acids so basically for solids very difficult but, for solutions it can be determined and this function can be conveniently estimated with the reference to known. Bases some indicators like pyridium can be 1 and any the liquid or solution type it can used for different acids this function will be different.

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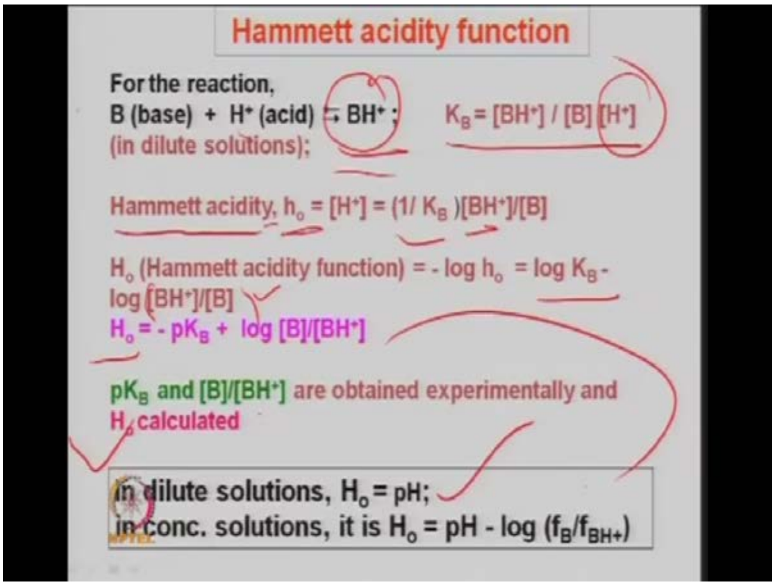

Hammett acidity function

For the reaction,

B (base) + H^+ (acid) $\rightleftharpoons$ BH^+ ; $K_B = [BH^+] / [B] [H^+]$

(in dilute solutions);

Hammett acidity, $h_o = [H^+] = (1/ K_B)[BH^+]/[B]$

H_o (Hammett acidity function) = $- \log h_o = \log K_B - \log [BH^+]/[B]$

$H_o = - pK_B + \log [B]/[BH^+]$

pK_B and $[B]/[BH^+]$ are obtained experimentally and H_o calculated

In dilute solutions, $H_o = pH$;

in conc. solutions, it is $H_o = pH - \log (f_B/f_{BH+})$

So, this is what you know that when base reacts with some acid and you get some it gets neutral. So, what concentration? What is the concentration of based? What is the concentration of acid?

Depending upon that you will your p H will change basically, so that is in dilutes also when it is at equilibrium you can very easily find out the equilibrium constant based on the concentration of this the total concentration of BH plus divide by the concentration of base and the concentration of the acid. So, this is acid this is base and basically it is a neutralization process. So, what is the concentration of acid or the base is present depending upon that you will have final p H of the solution?

And that is related to p H. So, what is known as hammett acidity small h 0 and represents the concentration of acid sites H positive so that is given by just from this equation you can calculate so 1 by k B times concentration of BH plus and divide by the concentration of B and these can be determined experimentally, all these are measured. You know the concentration what is the molecular concentration molar concentration of acid added base added soon can very easily use the titration equations.

So, once this is known then Hammett acidity which is just nothing but, the c you calculate the p h for the dilute solution as I said. So, Hammett acidity function which calculated based on minus log of this acidity h 0. Because; acidity related to hydrogen and concentration so, what I said that for dilute solution it become minus log of hydrogen and concentration.

So, this is simply if you just lie write it becomes log of k B which is equilibrium constant for this minus log of B H plus divide by the log of this. T hat is base so this old term is in the log like this. So, this is your Hammett acidity function defined as H 0 and this is known as p K B that is log of K B minus of p K B plus log of B divide by B H.

So, we just inverted this minus. So, this has been written in terms of minus plus log of H 0 and then calculated your Hammett acidity function. Which is something like minus k P B plus log of B divided by B H plus from this equation, so p K B and these 2 are experimentally measured or can be calculated so you can calculate the acidity function so for dilute solution as I said this hammett acidity function is equal to p H of that that is the once you know that p H is 5 p H is 6 you can very easily write the p H is equal to log of minus of hydrogen and concentration.

So, 1 can determine the acidity. So, this is what and for concentrated solution it is nothing but, p H minus log of f B divide by f B H plus 1. Which is same? What i have written here that is in terms of the concentration of this molar concentration of the base molar concentration of the final that is in terms of the morality when you calculate or in terms of the p hydrogen and concentration which can be determined from the solution.

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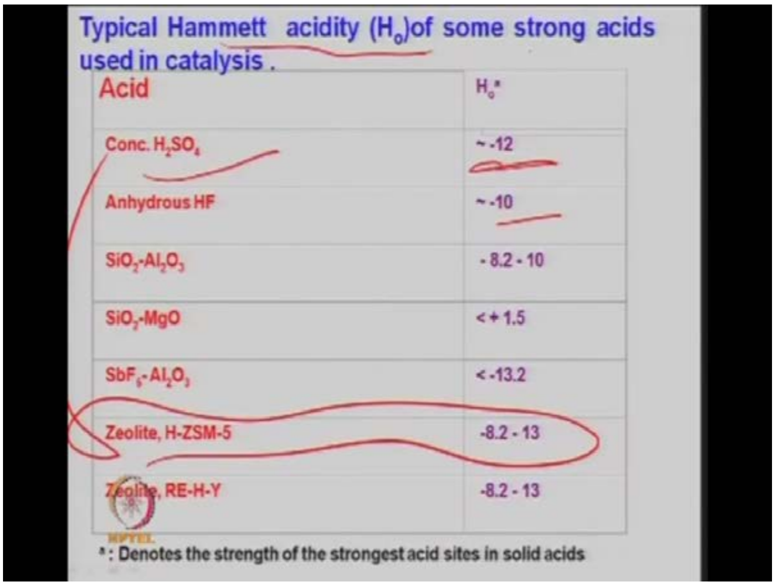

Typical Hammett acidity (H_0)of some strong acids used in catalysis.

Acid	H_0*
Conc. H_2SO_4	~ -12
Anhydrous HF	~ -10
SiO_2-Al_2O_3	- 8.2 - 10
SiO_2-MgO	< + 1.5
SbF_5-Al_2O_3	< -13.2
Zeolite, H-ZSM-5	-8.2 - 13
Zeolite, RE-H-Y	-8.2 - 13

*: Denotes the strength of the strongest acid sites in solid acids

So, if you just compare just a comparison that for concentrated sulfuric acid supposed this H function is minus 12 you.

So, when the very concentrated solution you cannot report just p H of that so it is reported in terms of the Hammett acidity. So, this is typical hammett acidity for some strong acid so H 2 S O 4 minus 12 anhydrous hydro floric acid minus 10 a silica alumina which is again minus point 8 2 to minus 10, silica magnesium oxide its plus less than plus 1.5 and so on so on.

So, zeolite material again you can see here because zeolites are similar; to something like strong acidic sites. So, Hammett acidity may be of the order of minus 8.2 to minus 13 very high values.

Depends on the silicon to aluminum ratio, so where as this again zeolite. Which is rare earth hydrogen wise zeolites ri are is known to representing the rare earth? Sometime, write we write u s y ultra stable zeolite these are different nomenclatures for the zeolite material so these just depend that is the strong acid sites which are for the different acid concentrations so 1 can calculate from that hammett acidity.

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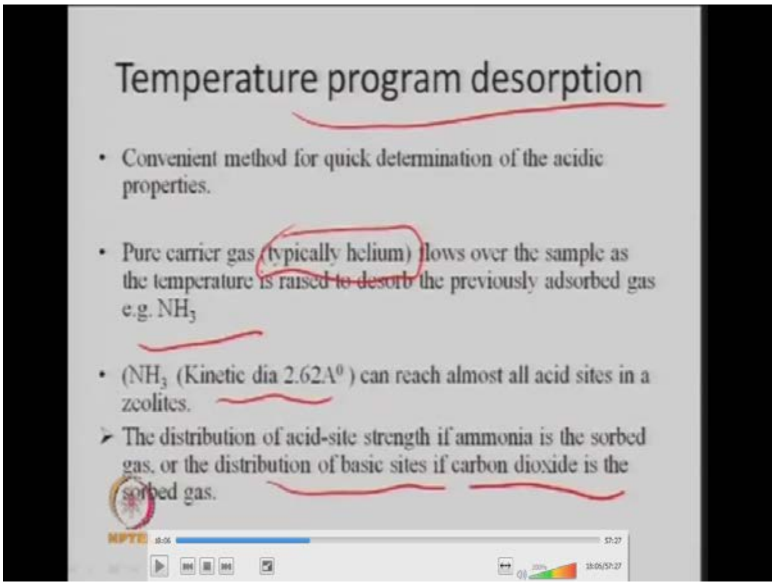

Temperature program desorption

- Convenient method for quick determination of the acidic properties.
- Pure carrier gas (typically helium) flows over the sample as the temperature is raised to desorb the previously adsorbed gas e.g. NH_3
- (NH_3 (Kinetic dia 2.62A^0) can reach almost all acid sites in a zeolites.

➢ The distribution of acid-site strength if ammonia is the sorbed gas, or the distribution of basic sites if carbon dioxide is the sorbed gas.

But, this is not a very correct method. This is just a titration method and nowadays the characterization by acidity by hammett acidity function, is not considered a sound method because; of the inapplicability of the concept to the solid.

Because for the solid the results may not be correct this cannot be used although you can take the solid and then titrate it with some bases but, the volume of the base which will be required to react with this is very very low. So, there will be always this kind of error so we need to find out the alternative methods so these instrumental methods like t p d ammonia t p d which we have already discussed in earlier lecture and that is 1 of the most promising method for determining the acidity of a solid substance.

Or solid material, so the basic fundamental thing is that you this something is being adsorbed on the surface of a solid a gas or vapor and then you are giving a heat treatment and then it is being desorbed , so x z at what temperature? which what concentration of that basic site or basic molecule comes that can be passed through a detector and that can be measured its concentration can be measured. So, with time course when you have given a definite heating rate and at that time, what is the mili molecule of the gas which have been desorbed or which had been desorbed from the surface that is reported?

So, depending upon this because the some of the gas may be adsorbed on the weaker acidic site, some may be adsorbed on the string acidic, so you can determine the acidity or the strength of the acidic site also. The concentration as well as the strength of the acid site can be determined. So, pyrydium can be used because it is a basic molecule and ammonia can be used to determine the acidity same thing if you want to determine some kind of basisity of that catalyst then it can be reacted with acidic gas.

So, carbon dioxide is 1 gas. Which can be used for this t p d and that can determine your give you the information about the basic site concentration. So, this is 1 of the most promising tool or 1 of the important tool for estimating the acid sites number of acid sites as well as the concentration strength of that acid site. So, the any carrier gas which is generally helium is used here flows over the sample ass the temperature is raised to desorbs the previously adsorbed gas for example, ammonia so you this is, when you are using ammonia? Then it is known as ammonia t p d.

So, that is the temperature program desorption studies of ammonia the similar; thing but, we have d1 earlier hydrogen t p r or hydrogen t p d and that information was used for determination of the chemisorption properties like the radius or size of the metal or the dispersion of the catalyst material on the support or to understand the metal support interaction the principle is same here also. So, ammonia has generally a kinetic diameter of 2.6 2 angstrom so it means it can go a throughout the micro pores of the zeolite so this is the advantage so it can reach almost all acid sites in a zeolite.

So, complete acidity of the zeolite can be determined when your ammonia the distribution of acid site strength if ammonia is the desorbed gas or the distribution of basic sites if carbon dioxide is the sorbed gas can be estimated by the t p d method or from the t p d method.

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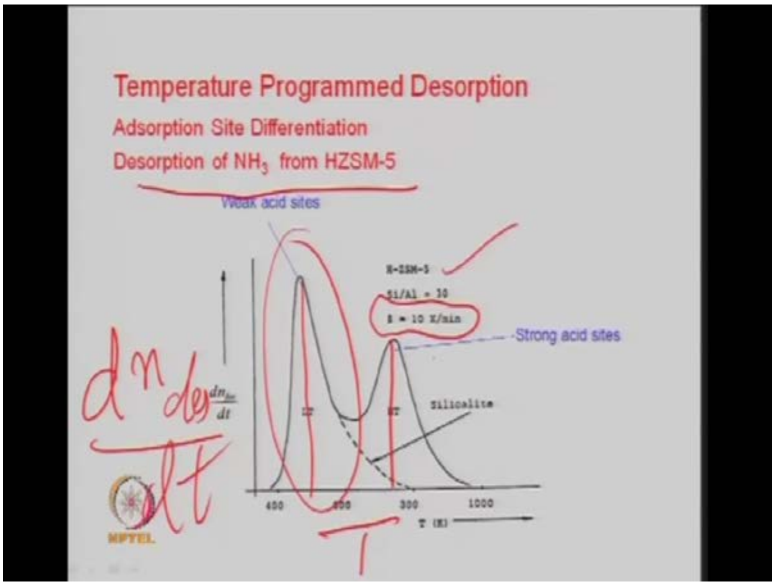

Temperature Programmed Desorption

Adsorption Site Differentiation

Desorption of NH_3 from HZSM-5

So, this is just a typical graph to get during the T P D. So, this is the desorption of ammonia from the H Z S M 5 catalyst, so generally first you have allowed the ammonia to adsorb under a given condition and then you have just flux with some inert gas so that superficial ammonia should be removed.

And then give a heat treatment to the sample. So, it can be in the form of pulses also you give a pulse and then at heat sample now. Once adsorption is over then heat it and that different temperature you will see the peak which is coming out in the detector. So, here see it is just shown here that the heating rate is 10^0 Kelvin per minute or 10 Kelvin per minute.

A zeolite which is H Z S M 5 having silicon to aluminum ratio 13. So, you can see here that the molecules desorbed per unit time which is reported here d n desorbs divide by d t. So this side is molecule of ammonia which has been desorbed per unit time and this side, it is as a function of temperature.

You can see there are 2 peaks basically these can be deconulated to study in details, so this is the first peaks which have been observed at lower temperature around say this is approximately your 450^0 Kelvin. whereas the second peak which has come here at around say 700 8eyer or 790^0 Kelvin, you can see that there is a difference , so the first the ammonia has chemisorbed basically; thus if you look at the chemisorptions fundamental the ammonia gas has strongly or weakly chemisorbed on the acid sites , depending upon the acid concentration or the strength of the acid site.

So, this 1 which has desorbed at a lower temperature is representing a weaker acid site , and our second 1 which is at a higher temperature that is representing the stronger acid site so you can measure the area under these curves and you can find out the mili moles of ammonia consumed desorbed form here and mili moles of ammonia desorbed some of these will be reported in terms of the total acidity in terms of mili mole of ammonia per gram of catalyst , and the separate individual you can provide the information these are the weaker acid sites and this is the number of the strong acid sites.

So, a very useful information about the catalytic activity which can be correlated finally, for the reaction , especially when you have a cracking type of reaction where the acidity plays a very important role 1 can inform the catalytic acidic sites.

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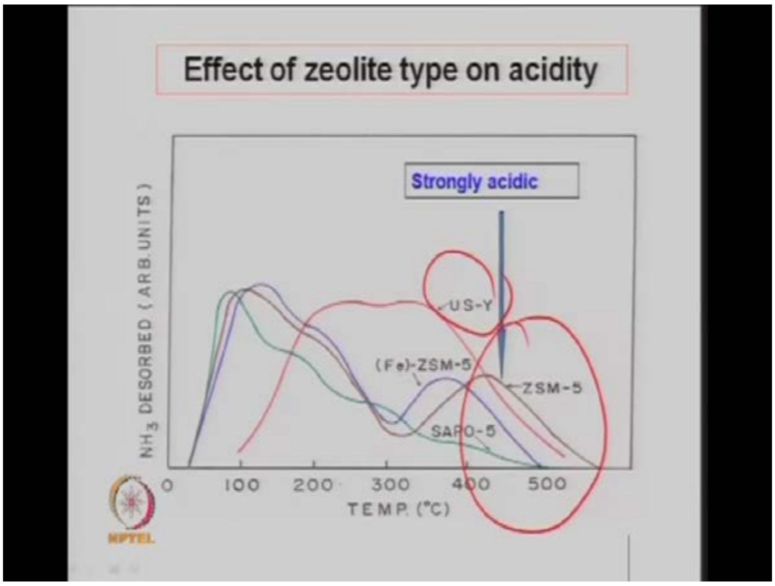

Effect of zeolite type on acidity

So, again this as I discussed earlier also that depending upon the type of zeolite the acidity will change. So, this is your ultra stable y type zeolite this is for iron Z S M 5 that is the H Z S M 5 has been h has been replaced by iron this is a silica alumina phosphate type zeolite. Which is again supposed are the weaker type acids? This is our Z S M 5 which is stronger basically. So, this just talks here that these are the stronger sites, which have been obtained here at higher temperature so you can see here that 1 2 3 if you deconulate in different type of zeolite material different peaks have been reported, and these are just report representing the concentration of these acid sites.

So, 1 can get the idea that total concentration is nothing but, area under the curve or if you want to divide them into different temperature z1 that say between 200 and 200 200 to 400 so what is the mili equivalent of ammonia? Which has been desorbed from the surface and 1 can correlate it with the acidity of the zeolite. So, this is good in terms of the comparison a comparative study can be obtained that this mush this are these are the number of sites in the temperature range over different catalyst.

So, which catalyst size higher number of acid sites and which catalyst has higher strength of the acid site both information can be provided if you have the ammonia t p d for these.

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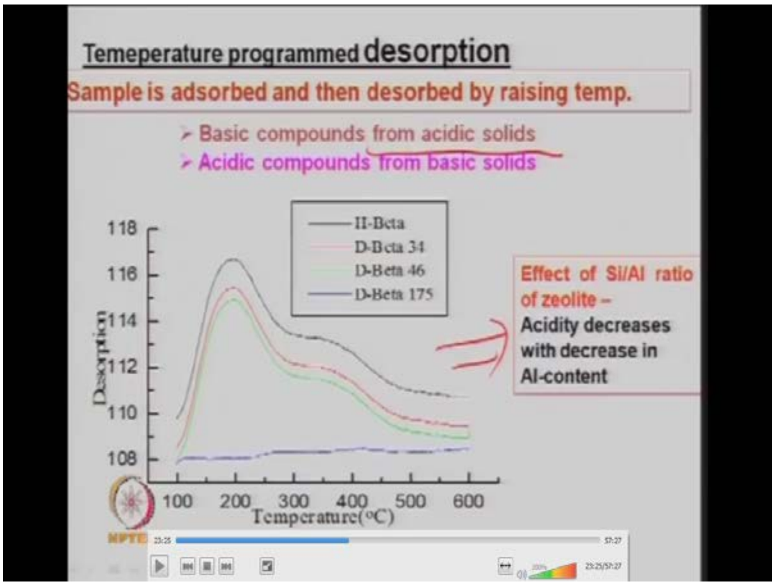

Temeperature programmed **desorption**

Sample is adsorbed and then desorbed by raising temp.

- Basic compounds from acidic solids
- Acidic compounds from basic solids

Effect of Si/Al ratio of zeolite – Acidity decreases with decrease in Al-content

So, similarly; there can be just for hydrogen beta D beta 34 beta 46 beta 175 different kind of zeolite and just to get the idea about this silica too alumina ratio also, 1 can have again the information in terms of the desorption versus temperature and you can get the information so basic compounds can be obtained from acidic solids acidic compound from basics.

So, 1 can get the concentration of acid and basic sites so this is just effect of silicon to alumina ratio of zeolite you know that acidity decrease with the decrease in aluminum content from framework. So, if you have more aluminum it will have a aluminum negative, so this is providing a kind of Lewis acidity in the sample, when it is protonated such as high silicon so, it will have higher strength to the acid site.

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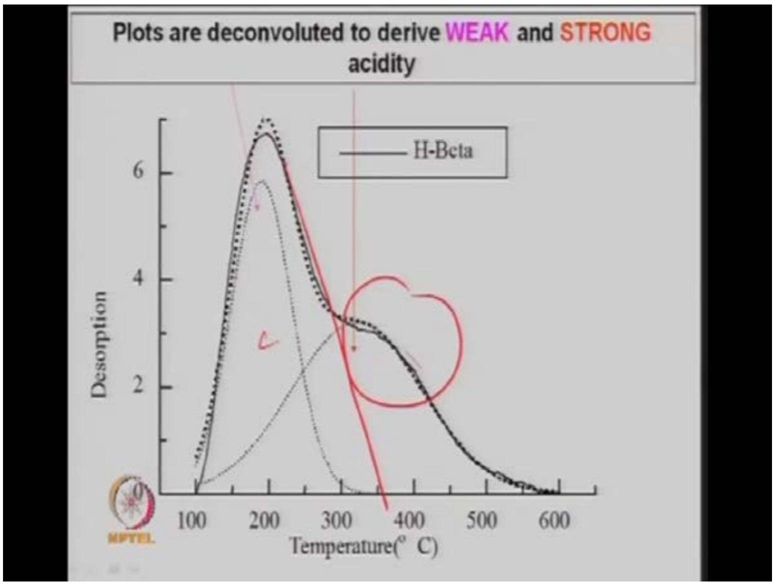

Plots are deconvoluted to derive WEAK and STRONG acidity

So, you can deconulate the peaks also for different say just for hydrogen beta. So, 1 peak at this and another peak has been which is reported like a peak curves you can see here.

So, 1 goes like the other so these have been separated 1 this and another like this , so that can be done and 1 can get the idea about the 2 peaks so 1 peak here another peak here and in between they are merged. So, 1 can deconnulate and find out the weak acid and strong acid. So, there are different methods and this same principle can be used to find out heat of adsorption, heat of desorption also , just measure the slope at different heating rates you can find out the rate of desorption of ammonia and that can be used to find out the heat of adsorption or heat of desorption. So, that has been discussed during the t p d.

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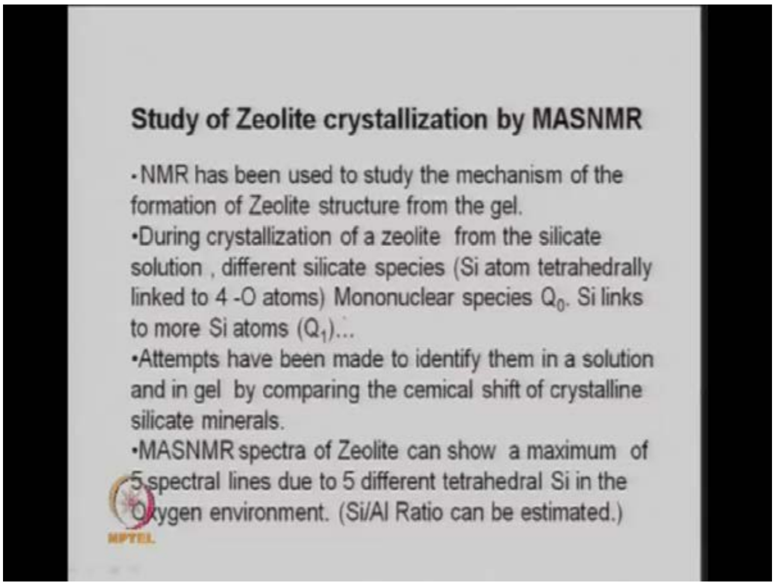

Study of Zeolite crystallization by MASNMR

- NMR has been used to study the mechanism of the formation of Zeolite structure from the gel.
- During crystallization of a zeolite from the silicate solution , different silicate species (Si atom tetrahedrally linked to 4 -O atoms) Mononuclear species Q_0. Si links to more Si atoms (Q_1)...
- Attempts have been made to identify them in a solution and in gel by comparing the cemical shift of crystalline silicate minerals.
- MASNMR spectra of Zeolite can show a maximum of 5 spectral lines due to 5 different tetrahedral Si in the Oxygen environment. (Si/Al Ratio can be estimated.)

Another what i said that? you can get the crystal linty or crystallization by using this mass n m r. So, this is just very important information which you can get in terms of structure of the zeolite in terms of silicon to aluminum ratio , in terms of the acidity and acid concentration. So, it is also 1 of the important tool for characterization of the zeolite material especially so n m r has been used to study the mechanism of the formation of zeolite structure from the gel.

So, during preparation also 1 can get the information because if you look at your silicon which is attached to aluminum. So, s i o 4 and then aluminums are attached to the group, that is t o t what we discussed the earlier. So, if i just look show you the briefly here the different arrangement which can be possible like here they are 5 types of arrangements if this is your silicon here these are oxygen atom if you just look at .

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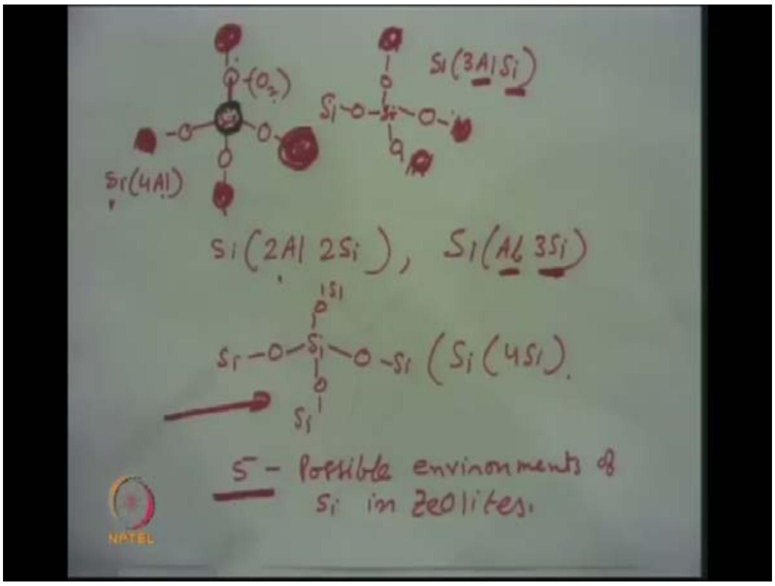

So, silicon connected to oxygen and then aluminum here. So, this is 1 possible and 1, 2, 3, 4 so these are your aluminum atoms. Which can be made like this? So, 4 aluminum, and we report it s i 4A l, so it means a 1 t o t or 1 tetrahedron which has 4 aluminum atom, and silicon at the center if you look at second combination can be 1 aluminum is again replaced by the silicon. So, silicon here at the centre and then this is s i and others are aluminum i so 3 aluminum 1 s i, another combination can be again 1 more this this aluminum can be replaced by silica ,.

So, there are now 2 aluminum 2 silica third combination , this can again we replaced so 1 aluminum and 3 silica only 1 aluminum left 3 silica and finally, if all are replace then you can have a structure like this. So, different type of tetrahedron silicon tetrahedron can be made but, you can see that 5 possible environments are available and all this 5 environments can be detected by mass NMR, so this is the application of the mass NMR that it can talk about all these type of pi environment which is possible in the case of a silica zeolite material. So, this happens when the gel is forming, so you have the oxygen member drings and they are connected to the bridge, condensation. What i said the secondary building unit?

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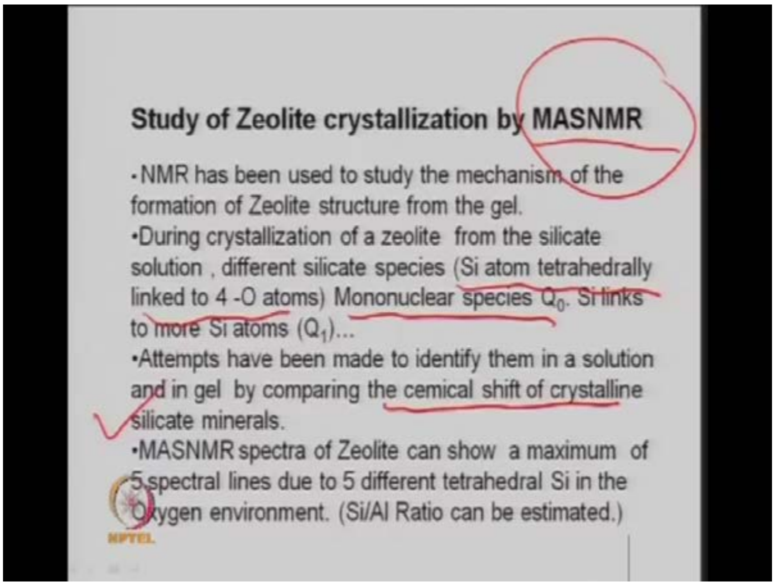

Study of Zeolite crystallization by MASNMR

- NMR has been used to study the mechanism of the formation of Zeolite structure from the gel.
- During crystallization of a zeolite from the silicate solution , different silicate species (Si atom tetrahedrally linked to 4 -O atoms) Mononuclear species Q_0. Si links to more Si atoms (Q_1)...
- Attempts have been made to identify them in a solution and in gel by comparing the cemical shift of crystalline silicate minerals.
- MASNMR spectra of Zeolite can show a maximum of 5 spectral lines due to 5 different tetrahedral Si in the Oxygen environment. (Si/Al Ratio can be estimated.)

So, during crystallization of a zeolite from the silicate solution different silicate specie which i’m talking say they they just the silicon atom tetrahedral linked to 4 oxygen atom that is what you call 2 0 so basically this is silicon atom tetrahedral linked to 4 oxygen atom and we call it monomolecular specie s 0, now s i links to more silicon atoms so Q1 Q2 Q3 like that,.

If bridging may t o t and there is bridge of that, so oxygen then again silicon then again oxygen then silicon like that, a cage forms of that. So, attempts have been made to identify them in a solution and in gel by comparing the chemical shift of crystalline silicate material so otherwise it is a very difficult, the technique has not been utilized so far in commercial success but, has been tested to find out the change in structure of the gel, when it we say that time raising time is important raising temperature is important. So, what happens during that? When we say that the a type zeolite converse to a y type zeolite.

When the you have given the edging as we discussed in our last lecture1! now how does it change because, basically this is happening thus aluminums are been replaced silica type zeolite, so it means gel structure is changing. So, these information can be obtained if you know the spill energy and with some reference, so and this spill energy change is nothing but, the chemical shift, and that what you are measuring in the terms of 80 to 100 p p m or different region.

So, that information can give you about the crystalline type of the zeolite and the structure of the zeolite, so this is a very important tool because this gel by comparing the chemical shift of crystalline silicate material you can compare the change in the structure change in the gel with time course, just like as i said when you prepare a zeolite you do the check the crystalline t x r d but, this is another main by which 1 can look at the mechanism of this gel formation.

So, MASNMR spectra of zeolite can show a maximum of 5 spectral lines due to 5different tetrahedral silicon in the oxygen environment so silicon to aluminum ratio can be estimated. Which what I said here? If you know these things that these are 5 possible environment.

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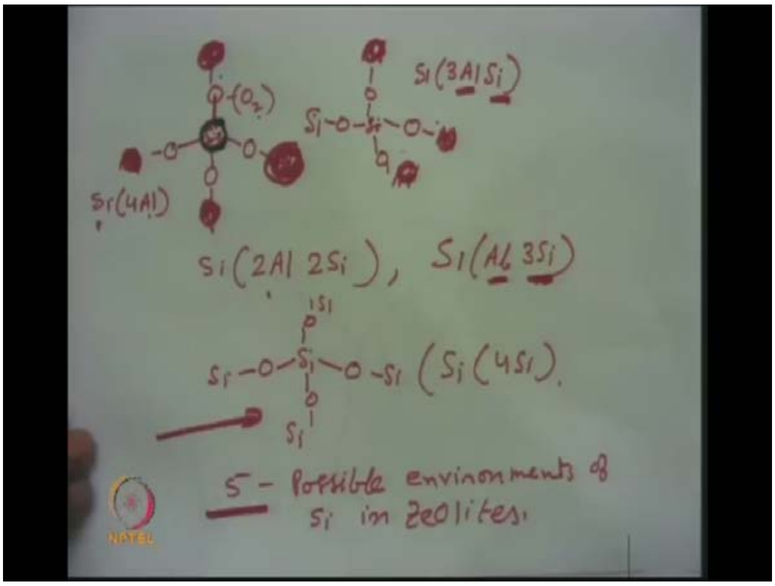

So these are nothing but, how many silicon to and aluminum are attached to the frame work of the zeolite, so 1 can very easily find out the silicon to aluminum ratio of the zeolite.

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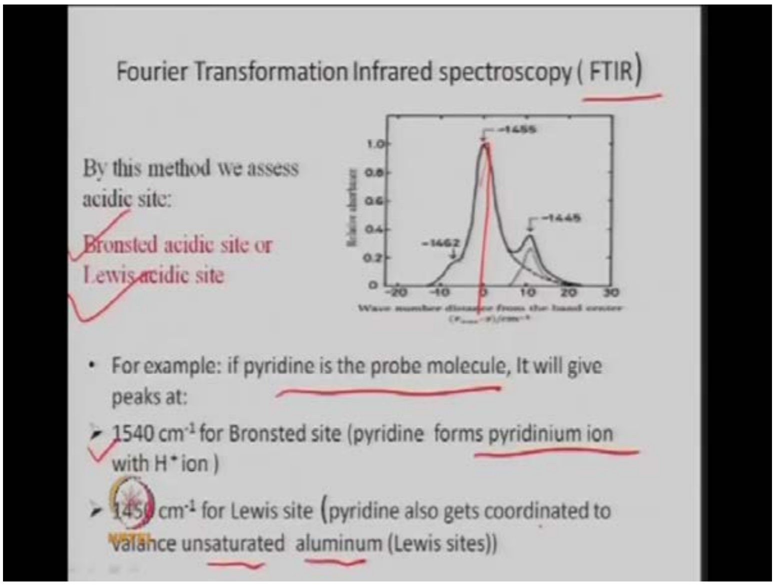

Fourier Transformation Infrared spectroscopy (FTIR)

By this method we assess acidic site:

Bronsted acidic site or Lewis acidic site

- For example: if pyridine is the probe molecule, It will give peaks at:
  - 1540 cm^{-1} for Bronsted site (pyridine forms pyridinium ion with H^+ ion)
  - 1450 cm^{-1} for Lewis site (pyridine also gets coordinated to valance unsaturated aluminum (Lewis sites))

And again in the tool for determining the acidity is FTIR, IR spectra or FTIR and that again have discussed earlier also, by this method we can find out the bronstead type acidity or Lewis type acidity.

So, FTIR also gives you the information or the acidity of a zeolite , so you can see here that the wave number which is distansive wave number distansive from the band center, which is measured here these are the wave number it can be negative also because it is a relative. So, 1 can see the peak at different wave numbers so 1 4 5 5, 1 4 minus 1 4 6 2, minus 1 4 5 5 and so on so on, so these are the wave numbers which are here , in terms of frequency , so and this is also related to the distance of the band.

So, that information is also provided here! And this is just a relative adsorbents when you have the FTIR of the catalyst, so depending upon the acidity the adsorption band will be different as I said in the IR, so pyridine absorb with you have just catalyst which is absorb with pyridine so 1 you 1 is with the need sample another is with the adsorb samples so pyridine is allowed to adsorbed on the catalyst and then do the IR of that. So, where you can find out the positions or locations where the pyridine has been adsorbed?

Because it will have a kind of bonding, and 1 can measure those bondings and get the idea about the concentration of pyridine, which has been at absorb on the catalytic surface. So, by absorption 1 can find out the concentration of the acidity so just for example; here if the pyridine is the probe molecule it will give peak at 1540cm, inverse for the bronsted site, so 1 can that at what phase number the pyridine has adsorbed on the catalyst sample so the adsorption is this and 1 can measure the concentration because it forms pyridinium ion with hydrogen ion.

A stronger acid site it has a positive ion, so pyridine will adsorb on that and will form a pyridinium ion, so the adsorb concentration of pyridinium can be measured and if it is a Lewis type then at 1450cm, inverse the pyridine gets coordinated to the valance unsaturated aluminum, which is Lewis site? So, Lewis site is because of a l negative, so pyridine coordinates with that a l negative and gives you a kind of Lewis acidity.

So, the concentration of Lewis acid can be related with the mili molecule of the pyridine adsorb on the catalysts, so by this info also 1 can determine the different kind of acids, or acidity present in a zeolite material.

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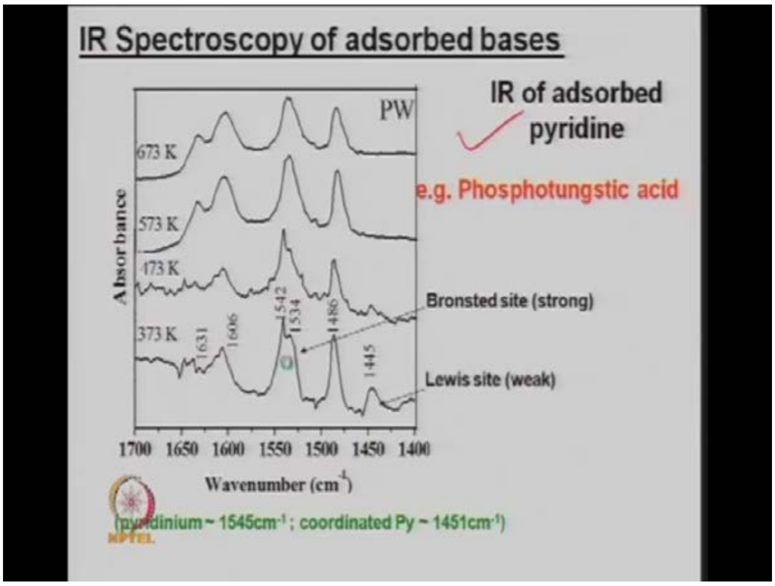

IR Spectroscopy of adsorbed bases

IR of adsorbed pyridine

e.g. Phosphotungstic acid

Bronsted site (strong)

Lewis site (weak)

(pyridinium ~ 1545cm^{-1}; coordinated Py ~ 1451cm^{-1})

So, this is again an IR of the adsorbed bases just as I neat sample or adsorb let us say so, me pyridine is adsorbed here, and you can see that at for different phosphotungstic acid has been just used here so different wave number, the adsorption is different.

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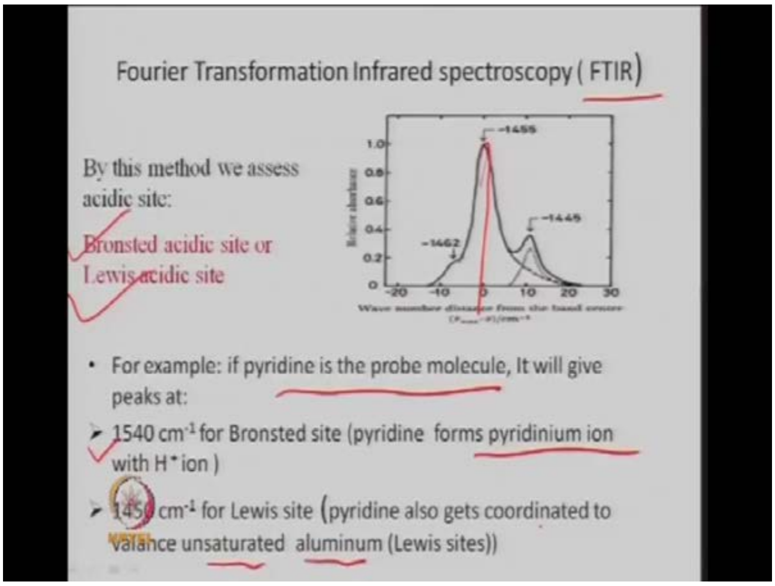

Fourier Transformation Infrared spectroscopy (FTIR)

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So, here the bronsted acid site because as I said here1 5 4 0 1 4 5 0.

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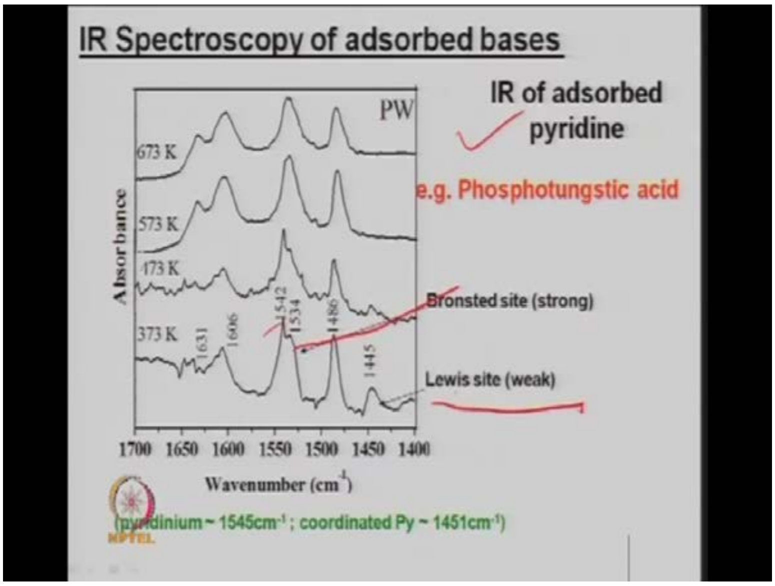

IR Spectroscopy of adsorbed bases

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e.g. Phosphotungstic acid

Bronsted site (strong)

Lewis site (weak)

(pyridinium ~ 1545cm^{-1} ; coordinated Py ~ 1451cm^{-1})

So, these two and at these wave numbers 1 can find out the concentration of the acid sites, so this is representing a bronsted type acid. This is representing kind of Lewis type so 1 can see and find out in a different catalyst and will be a function of temperature also, at different temperature 1 can see these kind of adsorbents, and 1 can identify the acid. So, IR method is again important tool to characterize a zeolite for its acidity that is concentration as well as the strength of acid sites.

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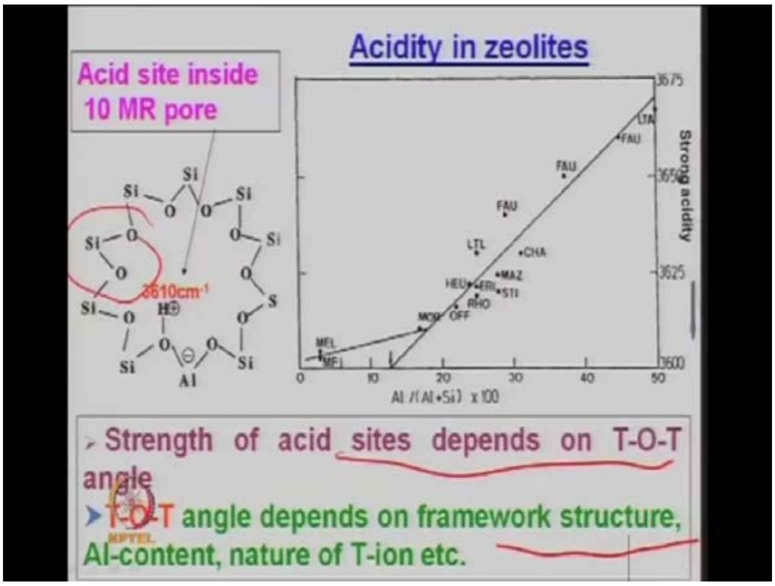

Acidity in zeolites

Acid site inside 10 MR pore

- Strength of acid sites depends on T-O-T angle
- T-O-T angle depends on framework structure, Al-content, nature of T-ion etc.

So, the rings depending upon the membrane membered rings as here, you can see that c 6 1 0 the proton has been here shown. So, the acid sites inside a zeolite will depend on these kind of orientation also angle is also important that is how the stream has been found and how this silicon and aluminum are connected so, that also provides a kind of acidity inside a zeolite pore so, strength of acid site depends on t o t angle silicon oxygen aluminum and in what way they have been oriented? That is what I said earlier also the orientation towards a plane crystal plane. So, that is important T O T angle depends on the framework structure aluminum content.

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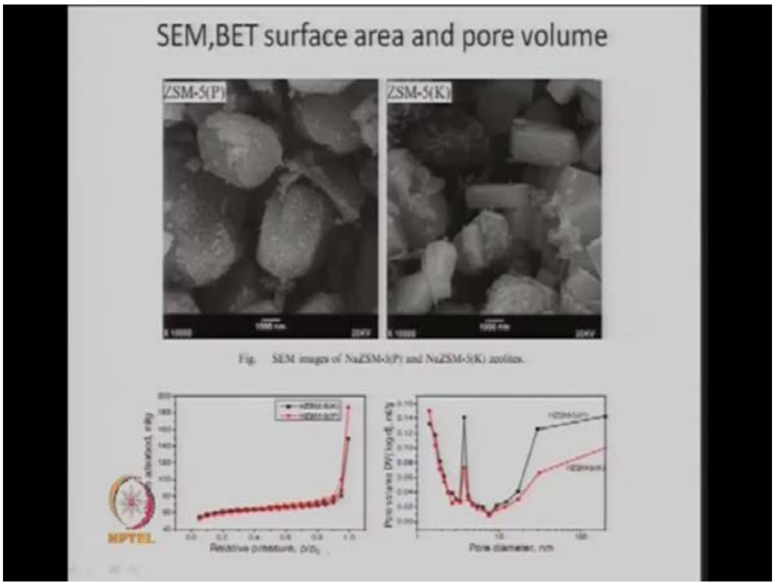

SEM,BET surface area and pore volume

Fig. SEM images of NaZSM-5(P) and NaZSM-5(K) zeolites.

And nature of the T-ion.

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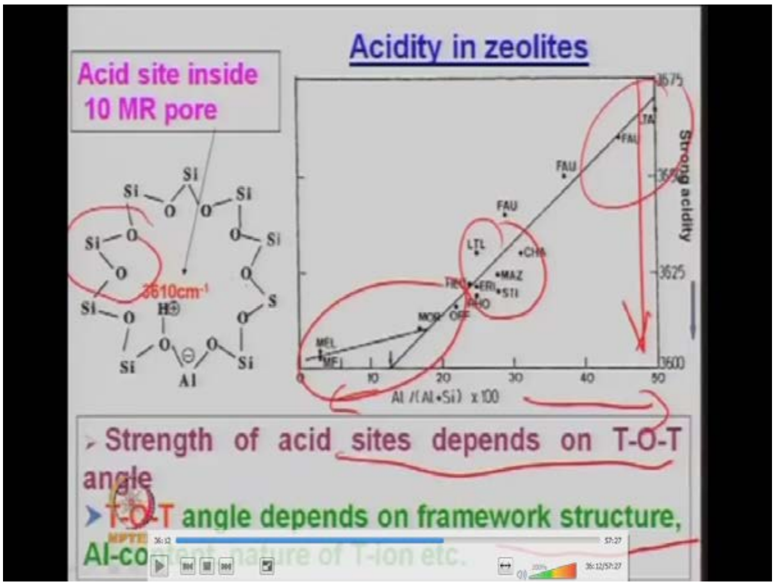

Acidity in zeolites

Acid site inside 10 MR pore

- Strength of acid sites depends on T-O-T angle
- T-O-T angle depends on framework structure, Al-content, nature of T-ion etc.

So, all these factor that is what is concentration of silicon in the framework. What is the concentration of aluminum? or if, some third component like the boron is added gallium is added, so depending upon these then there will be a change or shift, so T O T angle will depends on the framework structure which is during the gel formation, as I said earlier it depends on the aluminum content and it depends on the nature of the T-ion so you can see here the e s acidity increasing in this side you know that basically.

And this is representing the aluminum divide by aluminum plus silica in the zeolite, so this side the aluminum is more, and aluminum is decreasing in this side so aluminum is decreasing means silicon is increasing, so higher is that the acidity will be higher for these kind of zeolite which is your M F I type zeolite say Z S M phi, mobile phi zeolite, mordinite also has equally good acidity strength in terms of acidity and if you look at here the L T A fauzasite , cohabite irionite.

So, the they have some kind of mild acidity in the zeolite and these are the weaker type of acid sites, that is lewis type of acidity maybe present here in these kind of zeolite. Because the aluminum is more in the framework of the zeolite, so this is depending upon this structure of the O-ring you will have different kind of acidity in the zeolite.

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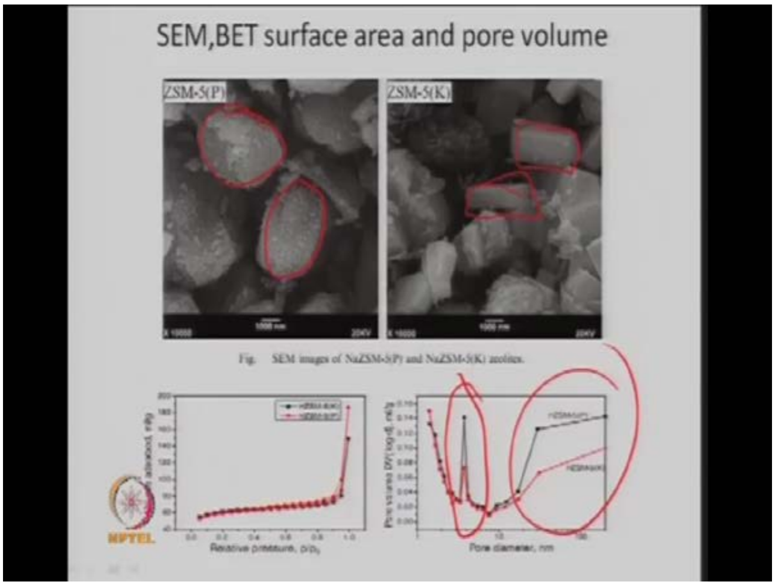

SEM,BET surface area and pore volume

Fig. SEM images of NaZSM-5(P) and NaZSM-5(K) zeolites.

The another method as we discussed earlier is by using the scanning electron micrograph, transfer electron micrograph you can look at the crystal size shape morphology, at different angis magnification 1 can find out so you can see here the magnification this is a there is some 5 type zeolite ,.

So, this is your the size you can see here , so at 1000 nano meter so 1 can measure this size and that is the average particle size of a zeolite , crystal size and here you can see the particles are somewhere they are in the longitude shape not the spherical geometry , they are length wise like if you look at your rectangular or real type structure can be seen here in this and same thing for pore size distribution can be measured or determined from the b g h plot.

So, your mercury porosimiton can be used or nitrogen adsorption desorption method which is a physical adsorption here and then the pore size distribution of a zeolite can be determined and you can see that these are the micro pore or mesho-pores, in the zeolite material, a narrower pore size distribution in a zeolite so because this angle is this you can see gap all. So, it is a kind of narrower pore size distribution and there some macro pores in this z1, of the zeolite and this is what you can see the hysteresis also almost negligible hysteresis, because all pores are the same size.

So, 1 can have the idea about the pore structure of the zeolite the porosity, all these can be determined just like a usual characterization method which we have already discussed.

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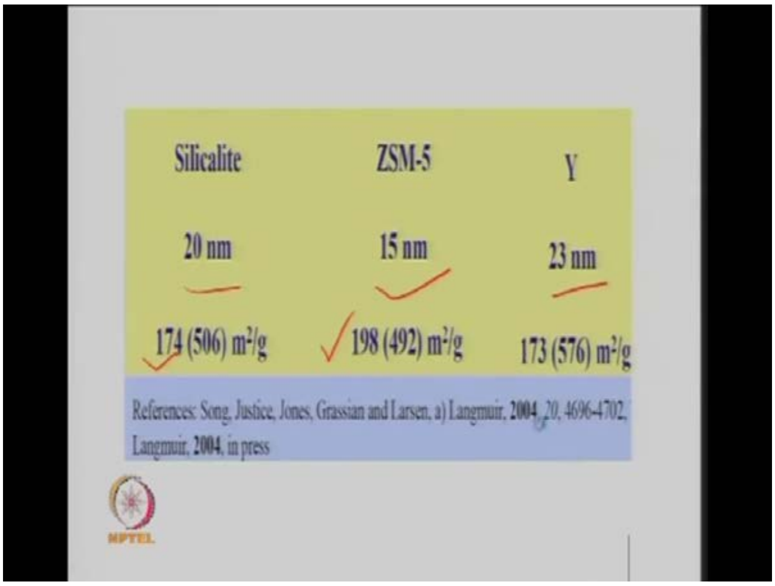

Silicalite	ZSM-5	Y
20 nm	15 nm	23 nm
174 (506) m^2/g	198 (492) m^2/g	173 (576) m^2/g

References: Song, Justice, Jones, Grassian and Larsen, a) Langmuir, 2004, 20, 4696-4702, Langmuir, 2004, in press

so different size can be determines say silicalite here it is 20nm ZSM-5 the size is 15 nano meter y type it is 23nm, so these are nothing but, there pore size so zeolites or particle size of the zeolite so area b e t area 174, which is for this kind of material meter square per gram 194 8 meter square per gram.

So, these are just kind of these pore size, at total surface area can also be determined from the b e t method which is written there in the bracket, so different kind of so isotherm can be used for the determination of the surface area and pore volume of the zeolite so this is just for information I shown here.

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SYNTHESIS OF NANOCRYSTALLINE ZEOLITES

Nanocrystal zeolites now because for these hydro isomerization reaction or for most of the refindive operation your nano zeolite may have the good catalytic property, because they they particle size is very very small, so then they have good catalytic activity for the some catalytic reactions in the hydro carbon industry.

So, these are the kind of nano synthesis zeolite and you can see this particle size they are smaller and all are uniform in size , and they have been shown at different magnification say here this is shown this distance say hundred nano meter here , just from here to here and in this case again it is your magnified 1000 times here so this is 1000 times larger the particles which have been so 1 can very easily measure the particle size here. So, distance or the geometry of the crystal can be seen clearly by looking at the these different morphology of the that is these pictures of the zeolite, scanning electron micrograph. So, one can see at different magnification and check the morphology and even you can count a number of particle if your transmission electron micrographs of that zeolite.

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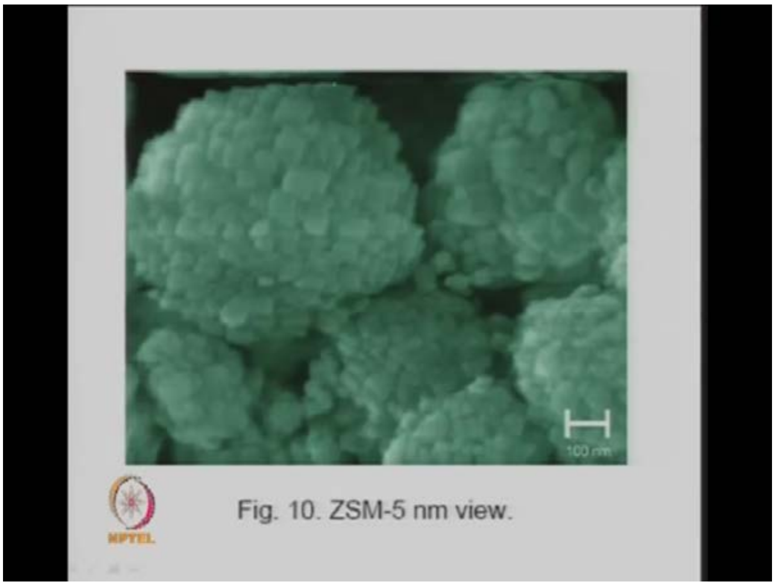

Fig. 10. ZSM-5 nm view.

So, this is again the shown the nano zeolite material , the some 5 nano metrics view so this distance in now hundred nano meter again here. So, this you can see very easily the crystals of the zeolite shape of the zeolite particle can be easily detected here.

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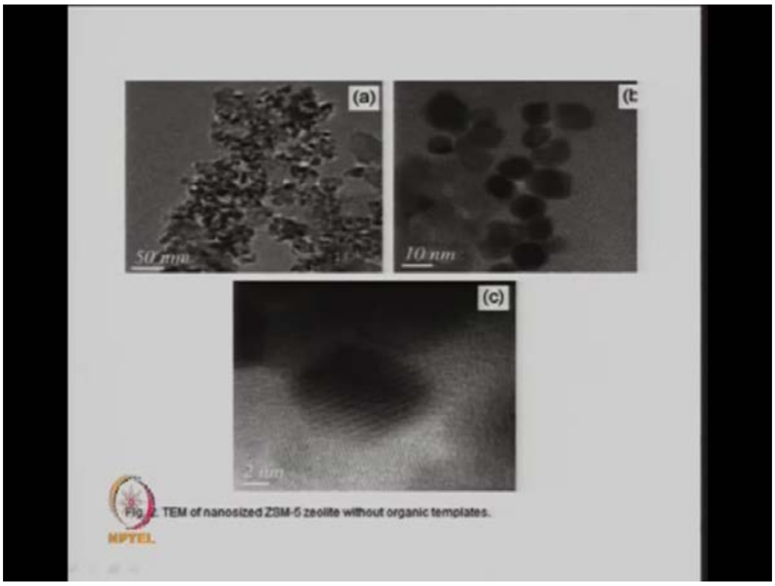

Fig. 2. TEM of nanosized ZSM-5 zeolite without organic templates.

So, this is transmission electron micrograph of the zeolite 50 milli nano 50 nano meter then 10 nano meter and this is 2 nano meter. So, same particle has been now shown in a this way the morphology complete morphology of a picture of the particle can be seen by looking at the transmission electron micrograph. So, 1 can count these number of particles also a 1 can determine the size of these crystals, very carefully by measuring and that is related to if you metal on this then 1 can correlated with the dispersion also metal dispersion. So, these you can see here the they are well dispersed here no enumeration, if you look at this picture, and this is just a 1 particle of that which has been shown.

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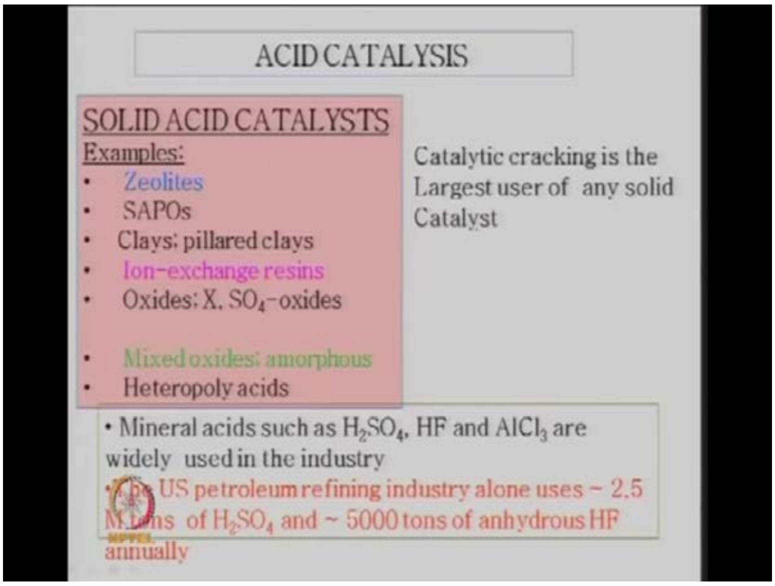

ACID CATALYSIS

SOLID ACID CATALYSTS

Examples:

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

Catalytic cracking is the Largest user of any solid Catalyst

- 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 anhydrous HF annually

So, these are some characterization tools for the zeolite, so there so the basic idea is that the silicon to aluminum ratio in the zeolite is very important acidity of a zeolite is very important strength is important that is concentration and number of acid sides then degree of crystalenty is important the concentration means Lewis type or bronsted type acidity is desired.

So, all these information's are required the micro pore macro pore size distribution of a zeolite is again very important because sometime they act just based on a molecular sieve. So, the kinetic diameter of the gas molecule what I just discussed earlier for the ammonia t p d so, the kinetic diameter of a molecule and the pore diameter of zeolite so, these 2 should be looked into when you look a catalytic reaction.

So, you have to select the material or the pores of a zeolite accordingly depending upon the pore size or the kinetic diameter of a reactant molecule. So, that is important so when you look at application because we say zeolites and its application for the catalytic industry , and it is the important in terms of the acidity of a zeolite so they are known as; acid catalytic basically.

So, wherever in the industry where the liquid catalyst has been used they can be replacing by the zeolite material. Because it is easy to handle the solid catalyst or solid acid material so in this case if you have the information here that solid acid catalyst they can be zeolite they can be silicon indo phosphate they can be clay type materials that is pillared pillared clays, they can be ion exchange resins oxides. So, all these kind of materials can be used as a catalyst in the various reaction acid concentrations or proton is desired.

So, catalytic cracking is if you look at just 1 example the largest user of this catalyst because cracking rapture of large molecular weight compound into small molecular weight compound, and that depends on the acidity of the zeolite. Because generally the acid sites are desired and during cracking the series of the reaction state it is not just 1 reaction , the its not rapture of a large molecular compound or carbon hydrogen bond breakage but, the isomerization be also take place it may be the hydro isomerization also if the conditions are severe it can be just like the polygomerization which is the kind of polymerization so, small olefins can be assembled together and joined together they make a larger olefin of the gasoline range of hydrocarbon.

So, objective of the cracking reaction is to produce the gasoline range of hydrocarbon from the naptad type of feed stop or atmospheric gas oil feed stop vacuum gas oil and now a day’s vacuum residue also. the larger or heavier feed stock can be used and you can get the desired product which is the need of that is the energy products. So, sulfuric acid hydrofluoric acid aluminum chloride like that whatI said sulfuric acid alkylation hydrofluoric acid alkylation can be done? Because these presently the commercial process for alkylation either h f alkylation.

Similarly; for if you look at your alkylation or polymerization sulfuric acid and h 3 p o 4 phosphoric acid are also used , so it means these can be used but, they are very strong acid so the metal of construction may be an issue the separation because the emulsion which you get the mixing of the reactant materials have isobutene isobutene and you get isooctane , that is a kind of polymerization reaction in the ah this refinery industry polymer gasoline what you call , same thing alkylation also you get alkylated gasoline , and h f alkylation is used for that purpose.

So, which is strong acid , so polymerization alkylation , all these are used in the industry and similarly, a l c l 3 is kind of lewis acidity , so this can be used for feudal craft generally aluminum chloride is used for feudal craft reaction if you look at the chemistry part which i am not discussing here , so these are widely used in a industry so if you just look at scenario by u s petroleum refinery industry al1 it used 2 point 5 million tons of sulfuric acid , and 5 thousand tons of anhydrate hydrofluoric acid for this catalytic industry.

Just for catalytic industry as a catalyst this amount is being used so it is a huge business means; if 1 can replace these acid catalyst by some zeolite type material it is a new trend, and any silica alumina ratio by adjusting or by taking z s m 5 catalyst 1 can do these reactions alkylation via zeolite catalyst which is now days being practiced.

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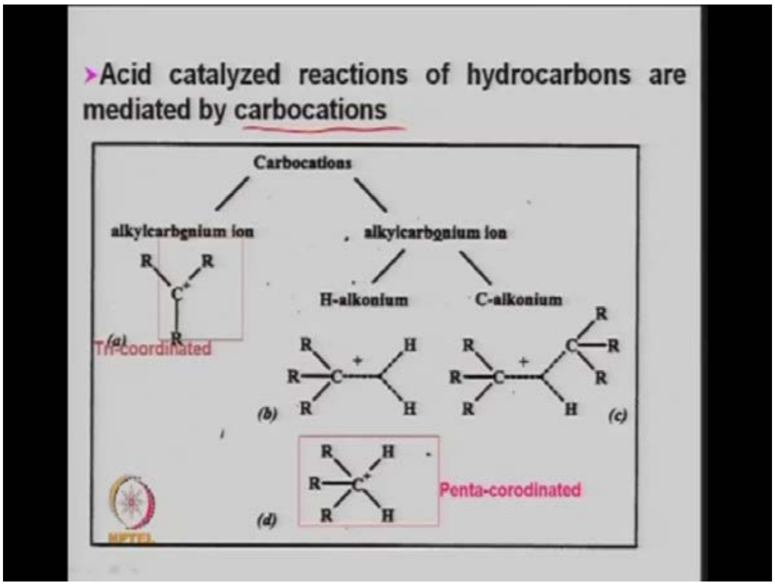

- Acid catalyzed reactions of hydrocarbons are mediated by carbocations

And fundamental thing for any acid reaction is nothing but, you know that carbonium ion carbanium ion formation. So, a action that is the proton which is in the catalyst, and the any alkyl carbonium which forms here in the presence of acid catalyst. So, h positive which is provided say like in cracking reaction Iam saying the z s m pipe provides the h positive. So and this is a kind of tri coordinated alkyl carbenium ion, and there can be different carbon this penta type say here. So, any carbo action which can be alkyl carbonium ion? So h alkonium carbon alkonium so they are different type of carbonium ion can form so, which is the primary reaction basically.

The formation of this carbonium ion. Now depending upon the stability because they can isomerizes primary will go to secondary secondary can go to tertiary. But, depending upon the stability of these carbonium ions because these are kind of intermediate, they will transform into some product. So, tertiary is stable then secondary then primary so you will more tertiary. So, like that is the you got more and more isho compounds so that is the principle of these zeolite reaction.

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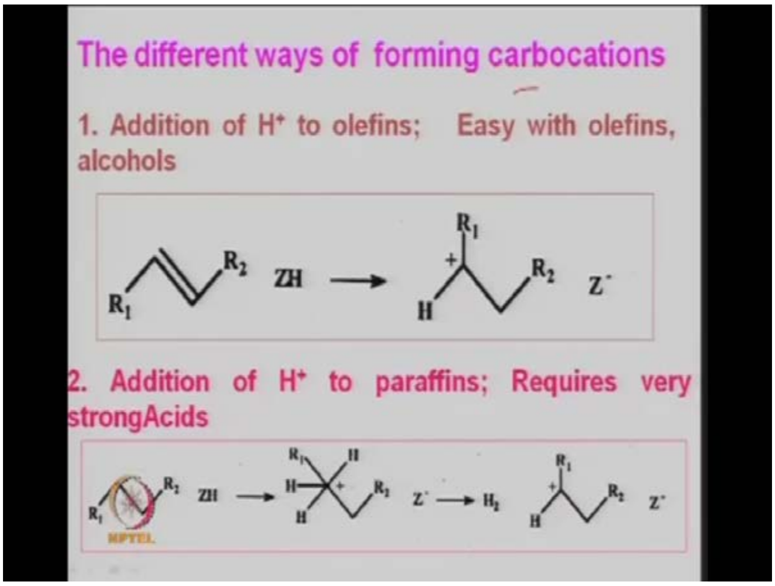

The different ways of forming carbocations

1. Addition of H^+ to olefins; Easy with olefins, alcohols

2. Addition of H^+ to paraffins; Requires very strongAcids

So, just different ways if you look at to form carbocations or carbonium ion a just addition of h plus to olefins this can be used in the alkylation reaction what i said or polymer gasoline. So, alkylated gasoline so that that is what so easy with poly olefins alcohols so this is 1 and this is zeolite material which has the h positive.

So, this reacts with this olefins r 1, r 2 the double bond so here you derive r 1 plus h n r 2 like this. So, this is your primary carbonium ion and then this carbonium ion can be converted into other so addition of h plus to paraffin’s and that requires the stronger acid site that is paraffins is there hydrocarbons are there then you have this something like that again this catalyst zeolite.

And then this r 1 r 2 and this is another paraffin carbonium ion and you get again the reaction and that gives you hydrogen give you the another carbonium ion. So, which means something like suppose? If I say heptanes so heptane adsorbs that is the it takes the proton and it forms some say heptine carbonium ion. And now this is further convert it can rapture into 2 molecules so 1 olefins 1 paraffin so most of the time when you see in the cracking industry.

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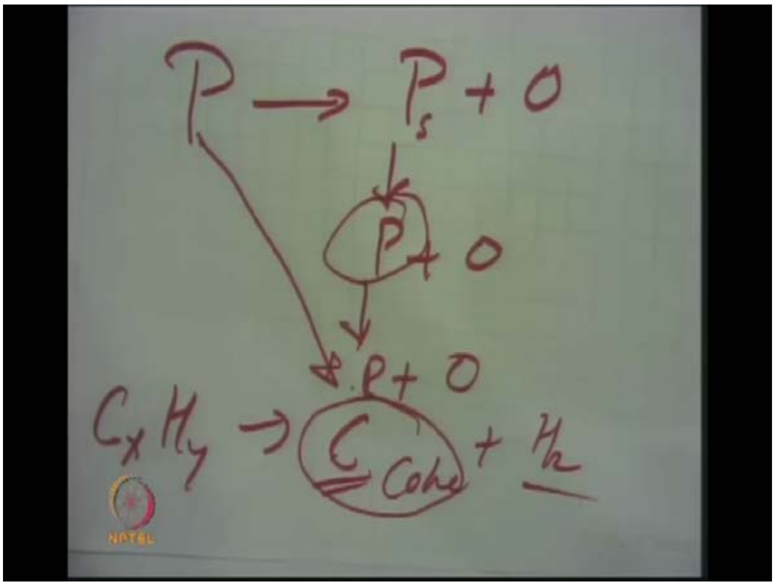

So, a large paraffin it gives you a paraffin small paraffin plus 1 olefin, so suppose this is heptane so this can give you the hep j n it can give you pentane it can give you butane like that and then this paraffin because this is nothing but, a primary carbonium ion formed and that gives you the secondary reactions. So, this again goes to pro paraffin and another olefin this will again go to another paraffin plus another olefin and chain continues so you need to terminate that reaction again.

So, depending upon the condition and finally, if you do not terminate it so ultimately any carbon hydrogen or c x h y can give you just a carbon coke and that is just to hydrogen and whatever. So, this is undesired now in the crack line so if you very strong acid site then the chances are that will give you this carbon where as your desired product is some kind of intermediate parathions iso-parafins. so that alpines are not desired so generally these alphins reacts during the secondary reactions , so the mechanism of cracking if you look at its a very complex reaction.

So, depending upon say atmospheric gasoil cracking or just a simple hydro carbon acid the propane heptane butane ethyl eths you must have heard the gas crackers propane is being cracked so that purpose is to get the alphins there petrochemical industry they need they crack these hydrocarbons say ethylene is produced which is your raw material for the petrochemical industry to produce high density poly ethylene low density poly ethylene ethyle poxides.

So, various poxides same thing butane butyl gives you butine buteene and that is used for a stirine butadiene rubber and so many hydrocarbons. So, the these are the petrochemical industry they produce this olefins from these hydrocarbons cracking that is basically known as pyrolysis of that hydrocarbon in refinery the objective is to get a gasoline range of hydrocarbon.

So, the catalyst will be different, when you have same raw material? But, in 1 case you need the olefins more smaller olefins basically other case you need a tuned desired product of gasoline range of hydrocarbon which may be iso-parafins and a small concentration of a parametric hydrocarbon so the the depending upon these you need tune the catalytic activity and beside these catalytic activity you need to tune the reaction conditions also operating condition for reaction with the combination of this will be d1 to get a desired product.

So, so mechanism understanding the mechanism of reaction becomes very important when conversize the process or look at a larger scale reactor design so kylog is doing something u p is doing on the top so is doing so they are looking process in terms of development that is design a reactor depending upon the mechanism which is available for a given gas cracker whatever so different kind of reactor designs may be possible under by using these kind of catalyst because you need to optimize the reaction conditions for that so this can happen.

So, here again bimolecular hydride transfer reaction so again in this say tertiary kind of carbon this r 3 z zeolite materials and r 1 r 2 section hydrocarbon so 2 molecules are thus associated to this framework and then you have zeolite material and another is r 3 h so r is any alkyl group , of any change carbon number so say ethyl propyl butyl anything a r 1 r 2 can be different it can be same also same thing a condensation reaction.

So, this is to form an aromatic hydrocarbon larger molecular rate of hydrocarbon so all these steps are possible in the presence of some acid catalyst because basically a primary carbonium formed and then it converts to the secondary secondary and tertiary so depending upon the stability , you get a stable product. so, tertiary is more stable.

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Applications of Zeolites

Ion-exchange

- Water pollutants (Natural zeolites)
- Clinoptilolite is successfully employed for removing Ammonium from municipal sewages
- Ammonia is air stripped in regeneration and absorbed by sulphuric acid to give ammonium sulphate, a kind of fertilizer

So, zeolites can also be used as an as tilled told earlier water purification so are widely used and this natural zeolite what i discussed earlier also clinoptilolite is successfully employed for removing ammonium from the municipal sewage.

So, that is used for the treatment of the waste water ammonia air stripped in regeneration and absorbed by sulfuric acid to ammonium sulfate a kind of fertilizer so in the sewage treatment you get large amount of ammonia r because the nitrogen the biomass material contains lot of nitrogen so you get ammoniac nitrogen and this ammonia can be used over this zeolite material and again you can desorbs that and that can be used for the fertilizer industry.

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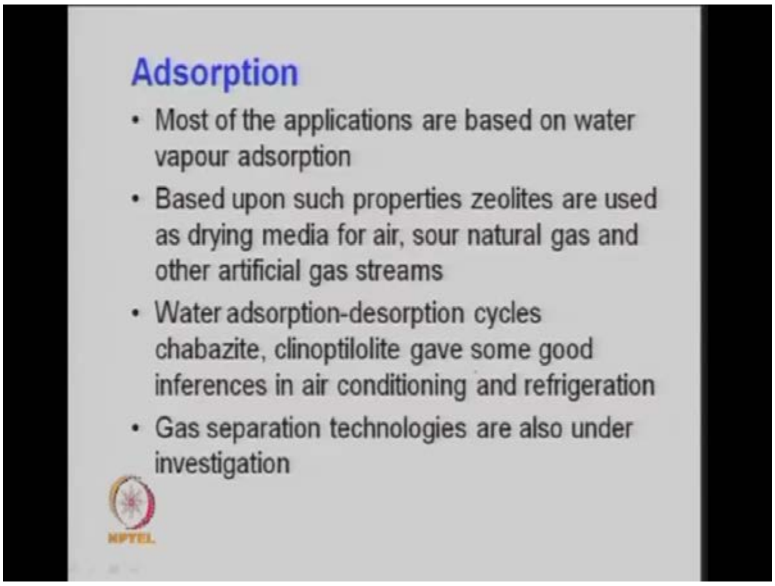

Adsorption

- Most of the applications are based on water vapour adsorption
- Based upon such properties zeolites are used as drying media for air, sour natural gas and other artificial gas streams
- Water adsorption-desorption cycles chabazite, clinoptilolite gave some good inferences in air conditioning and refrigeration
- Gas separation technologies are also under investigation

So, these are some applications zeolite in sewage treatment or treatment of the waste water adsorption again i said they are molecular sea materials. So, again for water pure vapor adsorption the zeolite materials are used even dehydration of alcohol the zeolite materials are used. So, based upon the properties of zeolites are used or drying media for air because they have dehydrating 10dencies they can absorb water they can absorb water for natural gas and other artificial gas steam. So, zeolites can be used for the purification of the gases also. So, zeolite activated charcoal is also another material but, zeolites have been.

Because; they have very specific pore size very specific molecular dimension or kinetic diameter of the molecule can be compared to the channel size of the zeolite and then then suppose you have a mixture of the gases say hydrogen sulphide can be removed from natural gas by using the zeolite material So, these can be used then water adsorption-desorption cycle like chabazite clinoptilolite they gave good inference in air conditioning and refrigeration.

So, different type of materials can be used clay type materials or because here you need a high surface area that is 1 thing and from i r 1 can confirm because this is a kind of bonding also a definite bonding is required with the material or adsorb ate material, which is to be removed from the gas mixture.

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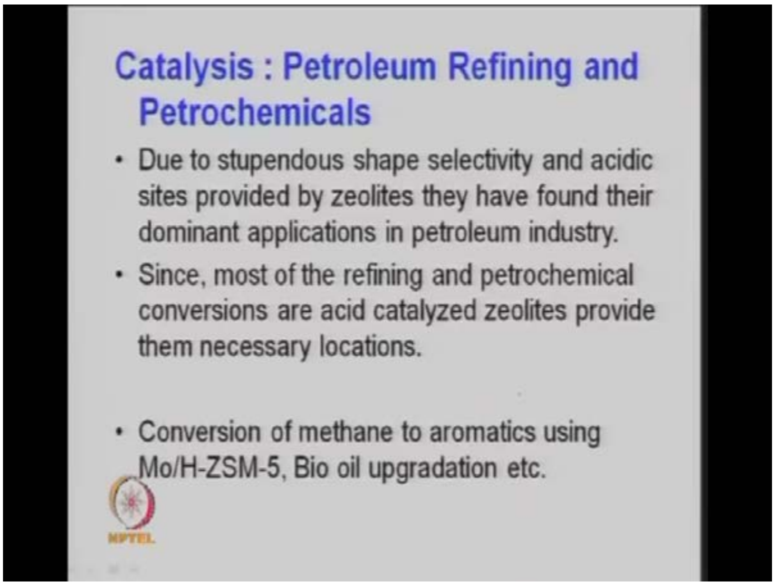

Catalysis : Petroleum Refining and Petrochemicals

- Due to stupendous shape selectivity and acidic sites provided by zeolites they have found their dominant applications in petroleum industry.
- Since, most of the refining and petrochemical conversions are acid catalyzed zeolites provide them necessary locations.
- Conversion of methane to aromatics using Mo/H-ZSM-5, Bio oil upgradation etc.

So, that is to be adsorbed on the surface so 1 can look at that catalysis that is petroleum refinery petrochemicals it is a wide application of zeolite and they are widely used in the refinery and petrochemicals which I have already discussed. so molybdenum h z s m 5 say used for methane range to aromatic range of hydrocarbon. So, l p g aromtism over gallium h z s m 5 so, these are wide application of zeolite and these have been commercialized also especially say l p g aromatization.

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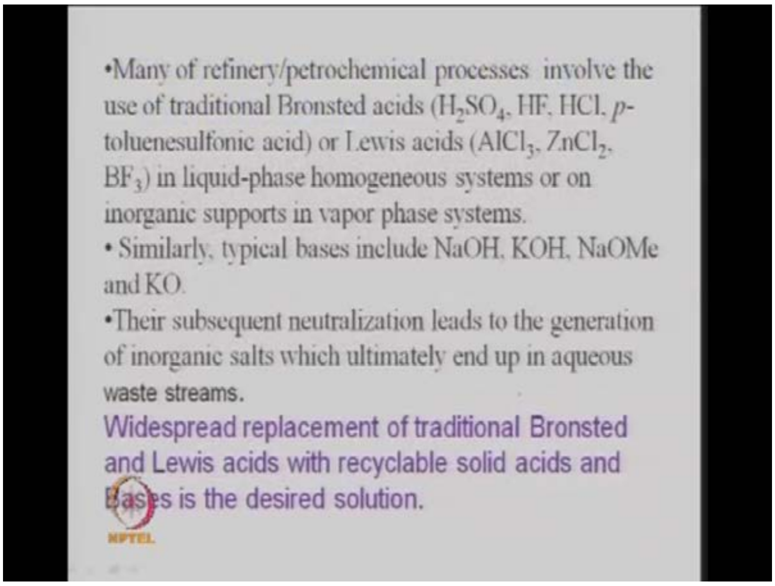

- Many of refinery/petrochemical processes involve the use of traditional Bronsted acids (H_2SO_4, HF, HCl, *p*-toluenesulfonic acid) or Lewis acids ($AlCl_3$, $ZnCl_2$, BF_3) in liquid-phase homogeneous systems or on inorganic supports in vapor phase systems.
- Similarly, typical bases include NaOH, KOH, NaOMe and KO.
- Their subsequent neutralization leads to the generation of inorganic salts which ultimately end up in aqueous waste streams.

Widespread replacement of traditional Bronsted and Lewis acids with recyclable solid acids and Bases is the desired solution.

So, refineries as I said earlier that they use the traditional bronsted sites earlier sulfuric acid hydrofluoric acid hydrochloride toline sulphonic acid Lewis type aluminum chloride zinc chloride.

So, all these are used as a acid stronger or Lewis type acidity weaker type relatively weaker so they have been tested similarly. The bases are also being used but, if you can replace them. Because, the problem is in terms of the utilization of these catalyst although it is a homogenous systems. so, liquid phase may be better. But, separation is the problem there you need a some huge amount of energy to separate the catalyst from the mixture.

So, that or the product so that is an issue so that is why the heterogeneous catalysts are widely used for this purpose. So, this is what written here the neutralization leads to generation of inorganic salts which ultimately end up in aqueous waste streams.

So, treatment of that waste is another issue. If that transfers into the waste water so wide spread replacement of traditional bronsted and Lewis acids with recyclable solid acids and bases is the desired option. So, this is that is why the petroleum or petrochemical industry is looking for solid catalyst like zeolite materials.

So, various types of zeolites have been used in the process catalytic cracking a crude oil fauzasite type zeolite the products are gasoline heating oil by cracking of the gasoline material so I will continue it next time.