Heterogeneous Catalysis and Catalytic Processes
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Lecture - 17
Introduction to Zeolites

Good morning. So, let us talk about zeolite today which is also a type of crystalline material and very porous in structure but, can have a mesoporous or macrospores structure.

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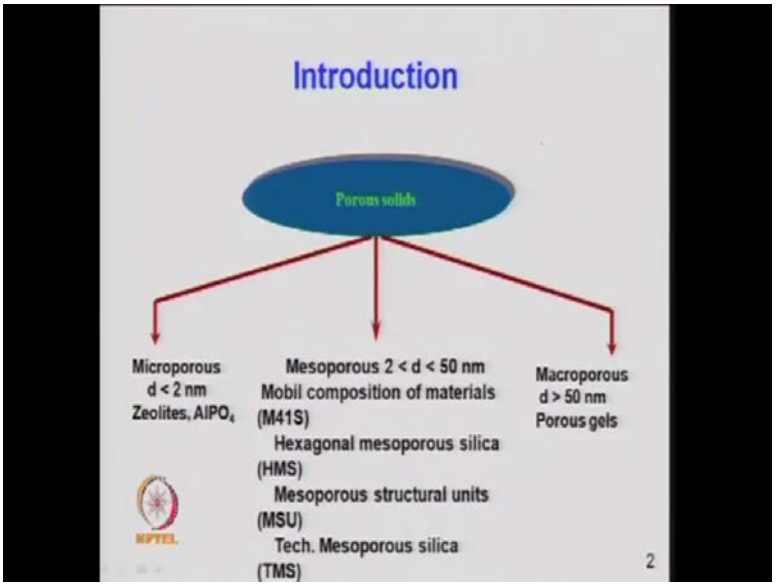

So, when you look at a catalytic activity you look at a porous material we just porosity is 1 of the property of the material acidity is another property, so the catalyst and the crystanality where you have the crystalline structure or a definite phase, which may be desired for a catalytic activity. So, zeolite is also a kind of say natural clay material if, you look at they are already available in the form of silicates silica materials or calcium aluminum silicates. So, these all are natural clay materials but, they are not crystalline in nature, if you look at catalytic activity we just characterize the micro-porous material which may have the pore side less than 20 arm strong or 2 nanometer which can be silico alumino phosphate material calcium aluminates silicate so, aluminum silicate material, where alumina silica t atoms these can be attached then most mesoporous which is also

micro crystalline material your m c m type material or other kind of zeolites, that is some 5 materials.

The pore size is between 2 and 50 nanometer so mobile composition materials like different coded materials between materials m 41 s hexagonal mesoporous silica materials which is known as h m s and then mesoporous structure units m s u, so these kind of which is technical mesoporous silica.

So, these kind of patent materials are available in the wide range and this can act as a molecular sea material which can act as an absorbent also for removal of the or purification of the gases also and macro porous which is the range of pore size more than this 50 nanometer or 500 arms strong.

So, these are your traditional alumina materials. When you have in palletized date and meet certain, so between the pore ,you can have the micro pores, the particles between the particles and. So, here we are talking a kind of a mesoporous material now and these are known as a zeolite kind of material or micro porous material, so micro porous, meso porous material with definite structure. So, what are zeolites?

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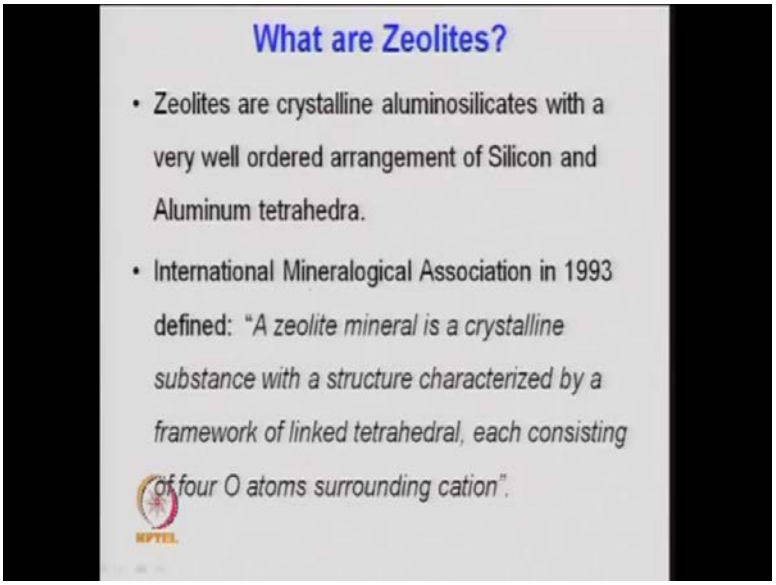

So, as I told that we look at a crystalline material in terms of catalytic activity. So, degree of crystanality becomes important and that will depend on the frame work and the structure the of that zeolite cage. So, it is not a definite pore opening, when you look at a

non-porous or material like your alumina or just silica or a clay material it has a cage type of structure. So, zeolites are basically crystalline alumina silicates with very well ordered arrangement of silicon and aluminum tetra hydra, so that is the important cage or structure building agent in the zeolite.

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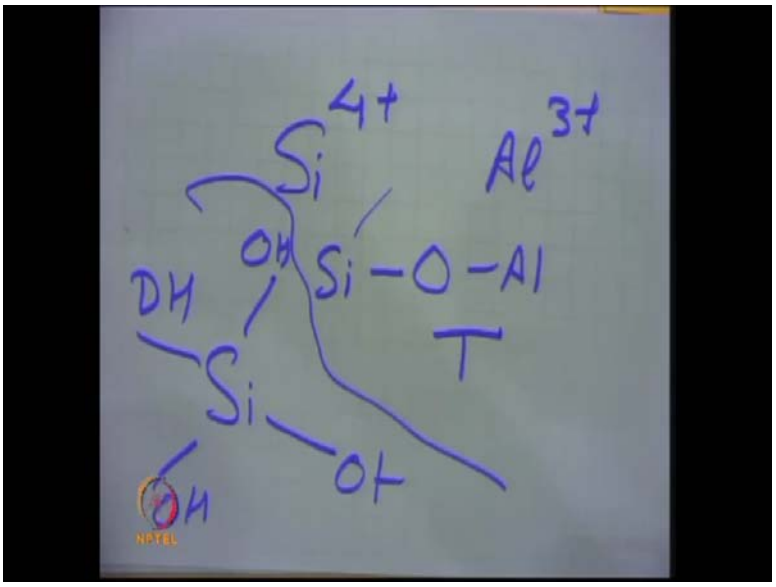

So, when I say zeolite it means the silica s i 4 plus and a l 3 plus now they so are connected and they are connected to the oxygen bridge. So, you will have a structure something like say s i o a l like this and then when I just look at s i it has like this O H O H O H so on O H. So, you have a structure like this a tetrahedron form because just like if you look at a methane molecule the hydrogen is attached to the carbon, which is at the center.

These are t atoms so silicon aluminum, we call t atoms and oxygen is bridged to that they are in the form of tetra hydra just like a prism structure. So, and the center you have a metal and the oxygen is attached with the branch h i. So, and that becomes a 1 cage of that structure building. Or primary building agent, which is based on this arrangement of the silicon aluminum atom in a frame work and depending upon the oxygen rings. You will have the openings poor opening or aperture.

The very definite structure, which is well ordered arrangement of silicon and aluminum tetrahedral, so when you look at like this, when silicon then oxygen then aluminum, then

again oxygen silicon aluminum and this builds. So, that frame work makes a frame work just a like a football bulky ball structure.

So, international mineralogical association because zeolite is very specific,so international zeolite association has certain guidelines, for defining the zeolite structured. So, you have to check crystanality, you have to look at the property and then you can claim the or you can say that this is a kind of zeolite. So, the numbers may be numerous numbers of zeolites, depending upon the preparation method depending upon the degree of crystanality, silicon to aluminum ratio. So, all these are important, and acidity of the zeolite bronsted type acidity, which is kind of stronger acidities Lewis type acidity? When you heat the bronsted ad acid catalysts and it release the water it converts to the Lewis type of acidity

So, these are important in the case of zeolite material. So, this definition, which says that a zeolite mineral is a crystalline substance with structure, characterized by a framework of linked tetrahedral. So, this is very important that how this tetrahedral is attached or linked. So, that is a structure building unit , each consisting of 4 oxygen atoms surrounding the cation a l or s i 4 plus 1 and so, when you are connecting aluminum it is providing a kind of negatively c electro negativity to our system. So, it has net negative charge, when aluminum is associated to the silicon atom. So, it means it can take a proton that is the definition brono acidity and this framework that is the framework, that is formed from silica aluminum and aluminum atoms based on these structures.

So, this contains open cavities in the form of channels and cages. So, how many aluminum atoms are attached to this silicon atoms depending upon that, you will have a pore structure in the zeolite or oxygen rings or that will be equal to the number of t atoms in the pore. So, and that will give you a pore opening. So, number of oxygen, which are 8 member ring 10 member ring 12 member rings. So, that will give you the diameter of pore opening of the zeolite large pore zeolite. It mesopores small pore zeolite, so that is the definition.

So, it will depend on the silicon to aluminum ratio, and also as I said that aluminum provides a kind of electro negativity. So, it means which it will, when you have more number of aluminums in the zeolite framework or silicon attached to the silicon then the acidity will be affected.

So, there may be 2 terms 1 is the acid concentration, another is the strength of the acid site. So, it means the increasing the number of aluminum, will affect your acidity concentration as well as the strength of the acid. You have to make a tuning So, the acid concentration as you increases the silicon, to aluminum ratio. So, it may decrease. So, that is the concentration of acid because, when your aluminum you attach because you're getting more and more electro negativity.

So, the concentration will decrease. So, you have to de-eliminate that if you want to increase the acid concentration, same thing on the other side the strength, which is acidity? So, it means you have to just look at the acidity, is because strength of the acid, which you are talking in terms of the ability to react with the base, which you just look at bronsted state type Lewis type acidity to strength is also important, which will depend on the presence of aluminum in the framework?

So, that time that is if you want to have higher acidity, if I just look at show you the graph the depending upon, this acidity of the zeolite as a function of silicon to aluminum ratio. This will go down like this to it means, if the more silicon then the acid concentration is lower.

So, if you and the strength of the acid is the reverse way, it means less silicon the more acidity acid strength. So, that is very important. So, 1 has to tune it and simultaneously depending upon this silicon and aluminum in the framework, the stability of the zeolite also changes. So, 1 has to tune in terms of the silicon to aluminum ratio acidity versus concentration of acid sites versus the stability of the zeolite. We will talk on these issues.

So, during the preparation 1 has to control these things, so these are usually occupied by the water molecules, so zeolites are hydrated. So, in the cage the zeolites are occupied by the water molecules in the form of O H O H. So, that it is a kind of what I said electro negativity. So, it has to take a proton, so H positive will be attached to that.

So, which is in the extra framework of the cation that is commonly exchangeable? So, this can be a kind act as a cation exchanger, and anion exchanger. So, that is why the zeolites are used, for water purification also, they have very good ability to exchange the cations or anions and these channels are large enough, to allow passage of the guest species

So, because they are now this is a structure, which has kind of pore opening? So, it can allow some molecules to pass through, that that is the zipping action molecule zip. So, zeolites are also a kind of molecular zip. So, that is in aromatic may not pass through that pore but, the methane molecule can pass through, that same thing the carbon picker son may not enter or sculpture poison, may not pass through the channel of a zeolite, if you have selected a definite pore size zeolite and depending on the kinetic diameter of the molecule, which is diffusion through that. So, it is a once a zeolite type catalyst, then diffusion maybe a dominating parameter because these are smaller pore zeolites. So, one has to take care in terms of the kinetic diameter of the molecules versus the pore opening.

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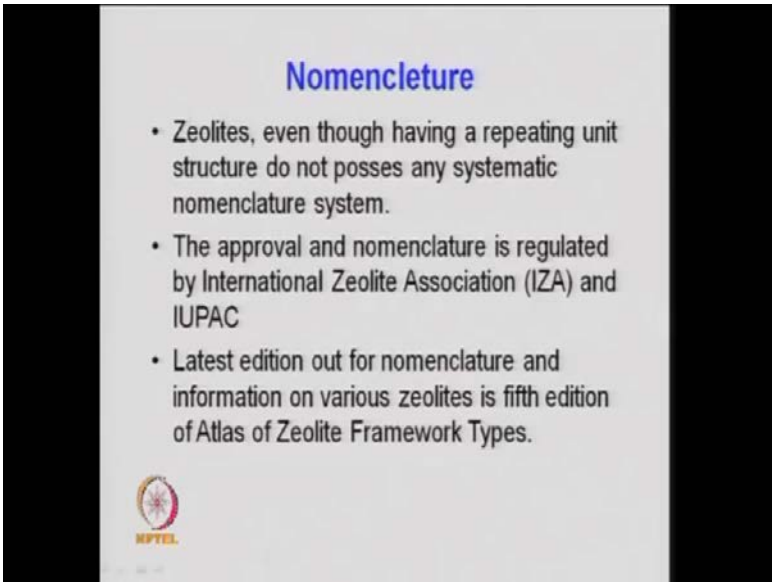

So, nomenclature if you look at that no definite nomenclature for zeolite and this is just a number which has been specified based on the preparation and the property of the catalyst, and it is the property proprietary. So, it has repeated units as I said silicon aluminum, and so on so on the structure is repeating but, it do not posses any systematic nomenclature system .

You have the silicon aluminum ratio maybe just 2 it maybe 500. So, you have zeolites with varying silicon to aluminum ratio in the framework but, even that the names are not well defined , you case you say that general some 5 but, with different silicon to aluminum ratio and that is zeoly mobile it is a mobile patent.

And same thing for the other also so that definite names are on nomenclature for zeolites are not available the approval and nomenclature is regulated by international zeolite association I Z A and also I U P A C. So, these 2 are the association, which define the structure or a depending upon the property or a structure they just give a certain kind of the nomenclature.

So, latest edition about and latest edition out for nomenclature and information on various zeolites, and what is the fifth edition of Altas of zeolite framework types. So, this gives you the information about different kinds of available zeolites for the different reaction because mainly in the petrochemical industries or refineries zeolites are widely used because they have a strong acid acidity which can be used for the cracking reaction hydro cracking reaction or wherever required.

So, and also they have a definite pore structure. So, you can have different framework of zeolite depending upon the t atoms, which is available and oxygen in the ring? So, 1 can select a definite kind of zeolite. So, it can be used for purification of the gases it can be used as a catalyst for the reaction it can be used as an adsorbent can be used for dehydration because they have the water absorbing capacity. So, they can absorb water.

So, they even the zeolite materials are used for the storage of hydrogen also so different kind of zeolite materials can be used for these purpose. So, the names as I said it are just activated to the name of the institution. So there is no definite nomenclature for the zeolite. So, zeolite socony mobile, which is they have named it z s m 5 these are penta structures. So, named as zeolite socony mobile m f 5 sometimes you call m o 5 framework, which is related to modernity fram, which is inverted that is the definition of m o 5 but, that is not a as I said this is not a very this does not give you any idea, about the structure it does not give you any idea about the silicon to aluminum ratio acidity. So, 1 has to look at those atlas or contact, that atlas in order to find the detailed property, which is patented.

Same thing for V P I 5 is Virginia polytechnic institute, they have the different kind of zeolite materials and they have just coded as V P I material m c m 41 is again Mobil Carbon Material. So, there can be different kind of these silicon materials or silica materials or some types of silica alumina also.

So, with different property, so when you have the different kinds of numbers on sum 22 so the different metal but, they can be the mainly reason as silicon material

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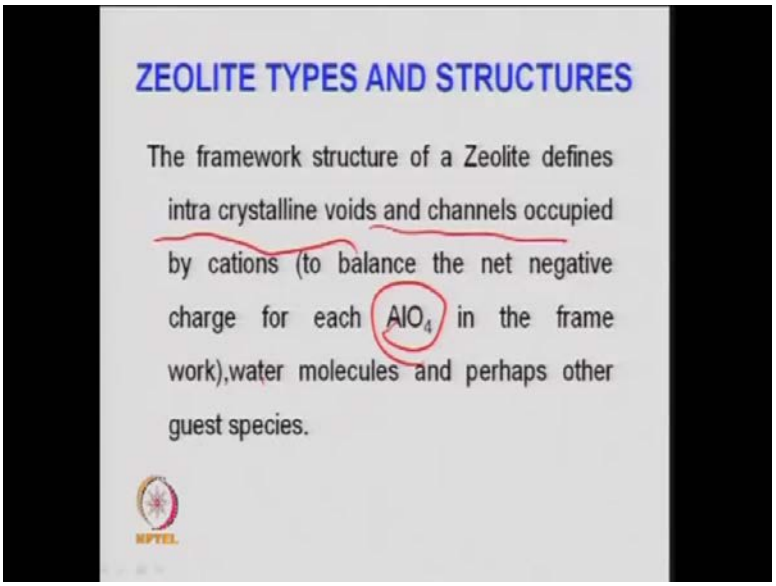

structure is very important, in the case of zeolite and accordingly, we talked the types of zeolites. So, the framework is structured that is the first thing of a zeolite, this is defined based on intra crystalline voids, so the based on the primary building unit, which is a cage type structure as I said?

So, what 1 primary this which may depending upon the number of oxygen or t atoms in that ring, you get a definite shape or a structure, so this crystalline voids and channels, which are occupied by the cations, so because as I said there's a net negative charge. When the aluminum is added to the framework same thing, when more silicon then also you get a kind of negativity electron negativity. So, that increases the concentration of the acid sites in the zeolite framework strength of the acid basically the strength of the acid.

So, this becomes important A l o 4 alumina in the framework and water molecules is also associated. So, that gives you kind of bronsted acidity because O H is a connected to that which has the ability to accept the proton negativity.

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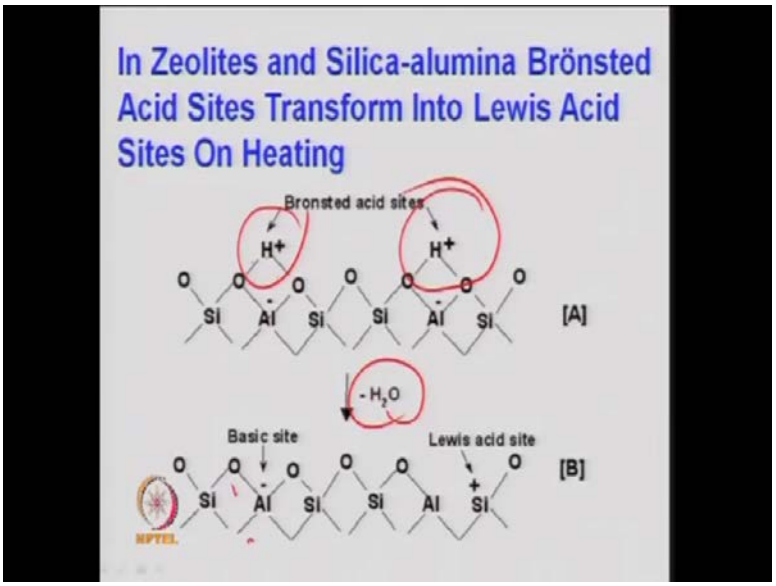

So, if you look at here in the zeolites the silica and alumina or aluminum in 1 way. The bronsted acid sites can be transformed into the Lewis or Lewis can be converted into the bronsted. So, that is 1 of the important aspect but, when you heat the bronsted acid catalyst to around 450 or 500 degree centigrade then the protonated because this is the what because of this proton they have the strong acidity. So, there can be a substitute for the alkaline reaction. Where h 2 s o 4 is used as a catalyst or any other reaction, where strong acidity is desired?

This is the 1 and when you hear them because these are associated with the so water gets h 2 it reacts with the oxygen molecule and the water goes, it lose water and then it converts to a kind of a Lewis acidic sites, which has just now they say it has released the water molecules now this is just a framework, which has the negative again aluminum here negative and it is just replaced by oxygen in the cage. So, these which are connected to the oxygen atoms because of the aluminum framework, which has net negative charge at they are released the water in the cage and attached water hydroxyl radical molecules o h growth that has been removed. So, that converts into the Lewis acid if you just heat it in presence of water again active water. So, it will again transfer to the bronsted. So, interchange it possible.

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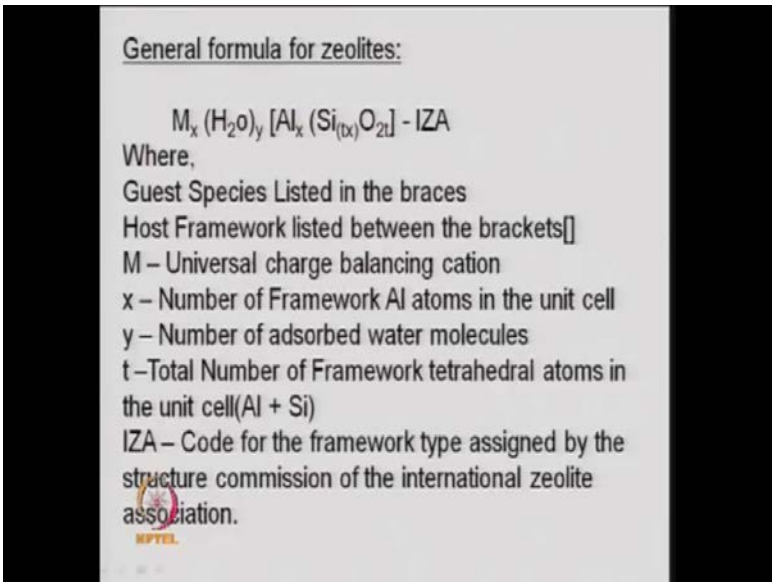

So, basically if you look at the zeolite formula. It depends on different compositions of aluminum and the silicon atom in the group. So, clay material also has something like this the calcium aluminite it's again a clay material calcium oxide and aluminum oxide site or Caroline, this porcelain material ceramic material. It can also have these kinds of the silicon and aluminum but, there is not a definite kind of structure.

So, basically red mud or if, you say or different kind of clay material. That can have a kind of zeolite property but, not a very definite therefore, there are not crystalline in nature. So, you are when you prepare it to hydrothermal synthesis that plays a very important role. That at what temperature at what pressure the nucleation has taken place this gives you a definite kind of crystal.

So, crystal formation will depend on p h, it will depend on temperature; it will depend on the time or rate of heating and pressure of the hydrothermal synthesis. That is what it different method of preparation of zeolite materials compared to the traditional method like impregnation co-precipitation. But what was discussed earlier?

So, basically you see here that this is an any universal charge balancing, which maybe a cation. So, and contains water so molecules of water x, which is the number of aluminum atom in the unit cell, why is the number of adsorbed water molecule, which is written here on the zeolite t is the total number of framework, tetrahedral atoms in the unit cell. That is aluminum plus silica and IZ A is the code, as I said international zeolite

association, which defines the structure or defines the property named name them based on the property? Generally this aluminum x should be greater than 2. Because, S I O A, like that it will connect to minimum number of aluminum atoms are required, in the framework to give a kind of electro negativity.

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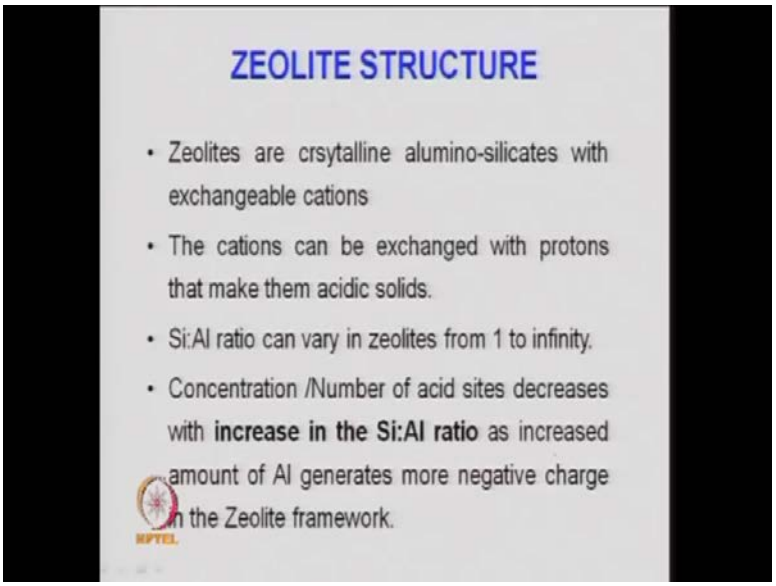

So, as I said zeolites are crystalline alumina silicate with exchangeable cations, the cations can be exchanged with protons, that make the acidic sites solids. So, this is what the property of the zeolite that it has the ability to exchange, the captions. So, caption exchanger and anion exchanger resins. So, they can in the zeolites exchanger they have the both type of ability to do exchange the cations in the zeolite from the zeolite framework. So, calcium sodium these can be added or protonated zeolite adjacent 5 like that, so you can have different types of zeolites gallium adsorption 5.This can be exchanged from the proton ammonia Z 7 5.

So, different kind of these exchange it's possible in case of zeolite material silicon to aluminum ratio can vary from 1 to infinity. That another important, which will decide your acid concentration and the strength of the acid catalyst acidity that is. So, concentration and number of acid sites that decrease with increase in the silicon to aluminum ratio that is what discussed here, so the concentration of the acid sites either it is a concentration or number of acid sites. That generally decreases, when the silicon to aluminum ratio is high.

And the reason is that because the presence of aluminum, it generates more negative charge in the zeolite framework, because aluminum is providing a kind of electro-negativity, whereas, silicon has 4 plus aluminum is 3 plus. So, when this is attached to this framework then there will be net imbalance, in the charge. So, you need it can take some protons, so that gives you the kind of acidity. So more aluminum in the framework .So, the concentration of the acid will be higher and that what this graph is shown here, so concentration of the acid sites will decrease as silicon to aluminum ratio is high. On the other side as I said the strength is also important.

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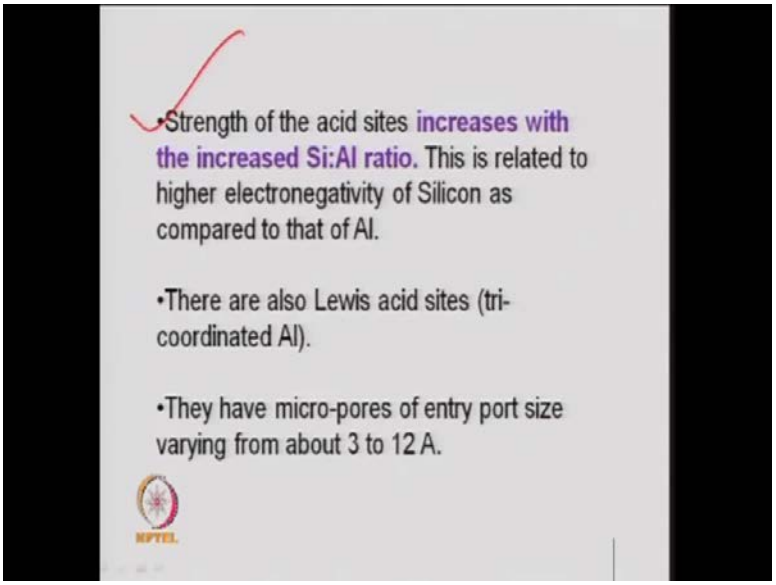

So, strength of acid site increases with the increased silicon to aluminum ratio. So, when your silicon to aluminum ratio is high then strength is high but, you cannot make a zeolite say as I said to very high concentration just on A L O A L will not be possible because, of the imbalance structural imbalance that is not possible .You just A L O L S i O S I is possible S I O A L is possible but, A l o. So, A l is not possible. So, because it has the aluminum has larger atomic moisture, so larger molecular.

So, that is gives you kind of imbalance in the framework. So, this is important here that you have to have certain kind of concentration of silicon to aluminum in order to match with your desired reaction activity. That is number of acid sites are very important no doubt but, strength of acid, whether it is bronsted or Lewis or, stronger acidity or weaker

acidity that is also important, which you can find out from the traditional method of characterization.

So, you can do 1 a t p d or i r s spectroscopy infrared spectroscopy can also just be paradigm. So, molecule absorbs and can be measured, and you can get the idea about the bronsted type and Lewis type of acidity. So, the same thing silicon term ratio in the zeolite can be characterized by mass n m r.

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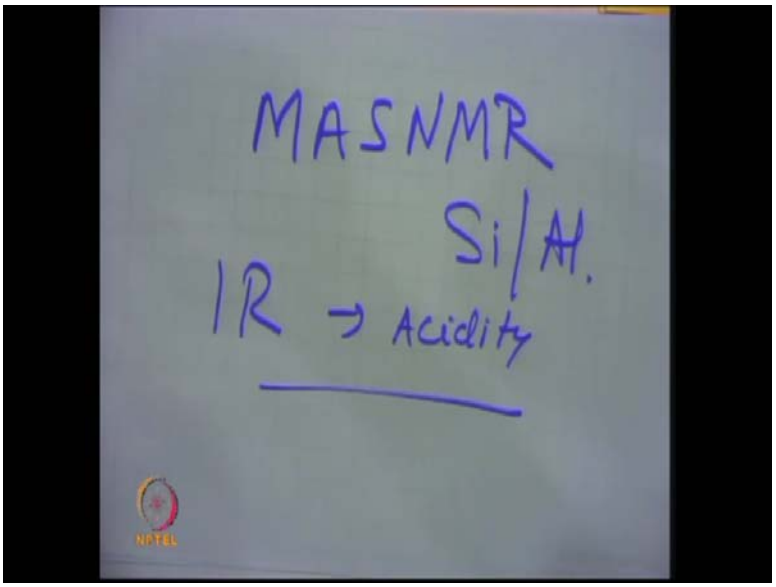

So, this is these are the methods, which generally used to find out the characterization of the zeolite to find out the silicon to aluminum ratio? So, 1 can find out silicon to aluminum ratio by using this technique mass n m r and i r can be used to find out the acidity or concentration of the acid. A combination of these 2 can give you the information about the complete acidity strength of the acid and type of the sites bronsted and Lewis type, so period in the you can have adsorption, and then you can study that.

So, also there are Lewis acid sites, which are just tri quadrate an l 3 plus, aluminum they have micro-ports of entry port size varying from 3 to 12 arms strong. So, zeolites properties are something like this. So, that they can have wide range wide pore size distribution pore size distribution narrow but, different kind of pore geometry maybe available depending upon the oxygen or t atoms present in the framework of the zeolite.

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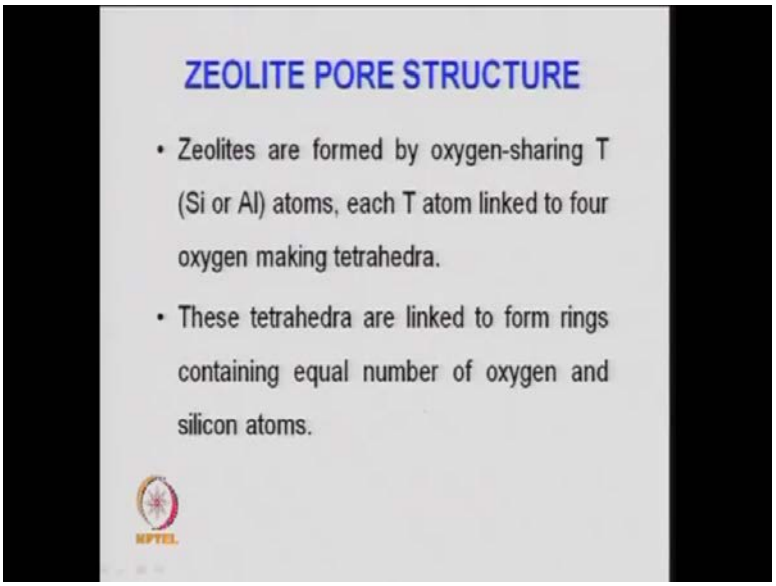

So, zeolite structure is formed it is shared by oxygen-sharing t atoms. So, t means silicon or aluminum each t atom is linked to 4 oxygen, and that makes a tetrahedral. So, it is a tetrahedral of alumina silicate. So, this is what as I said that aluminum or silicon is and then oxygen is connected, from the tetrahedral just like a prism structure. So, silicon is at the center and option is corrected at the corners of that, tetrahedral. So, these tetrahedral are linked to form rings containing equal number of oxygen and silicon atoms.

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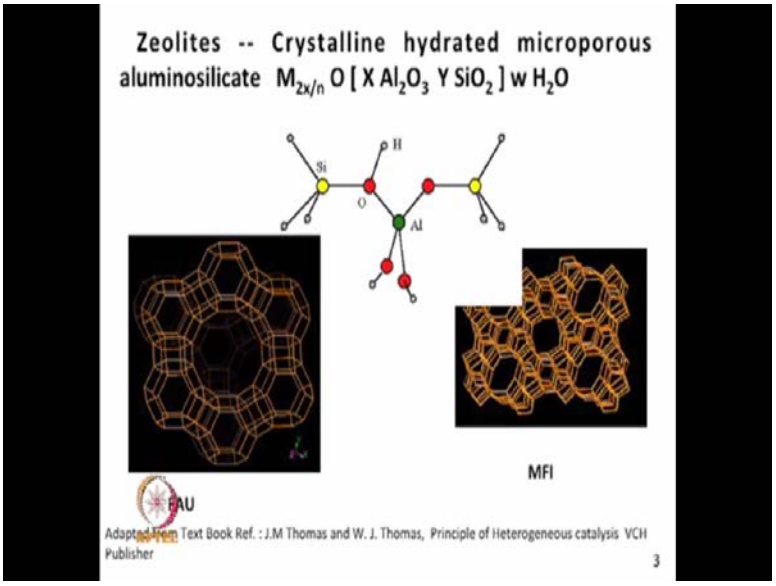

Now these are connected, which you see here the crystalline hydrated microspores alumina silicate is a kind of materials. So, silicon this is silica yellow is your silica silicon and these are the oxygen and here, it is aluminum and this is what the structure builds now. So, this is the continuation of the structure. So, you will get a kind of cage structure depending upon the number of rings here like this, so this is 1 unit of that and these units are interconnected and because, now you have a kind of this opening here, which may not be same? So, it is not a definite diameter basically; you have to define some a into b that is the side. What is the dimension on x side, and what is on the y side?

And how many these groups are present. So, this can be so this is just a peso side type structure, and this is m o 5, which you call z s m 5. So, what I mean to say that depending upon the cage aluminum silica. You will have different kind of this framework structure. How these are connected? That is how this metal structures are connected to that framework.

So, these will this is just 1 picture of the zeolite framework and you will just look at the further details of this, so the crystalline hydrated micro porous aluminosilicate. Which has a structure something like this? So, this is we have to look at the primary and the secondary building units this is. How what is the primary building unit that is 1 structure is forming .Which can be here you can see here 1, 2, 3, 4, 5, 6, rings but, there may be 4 also there maybe 8,10 like that

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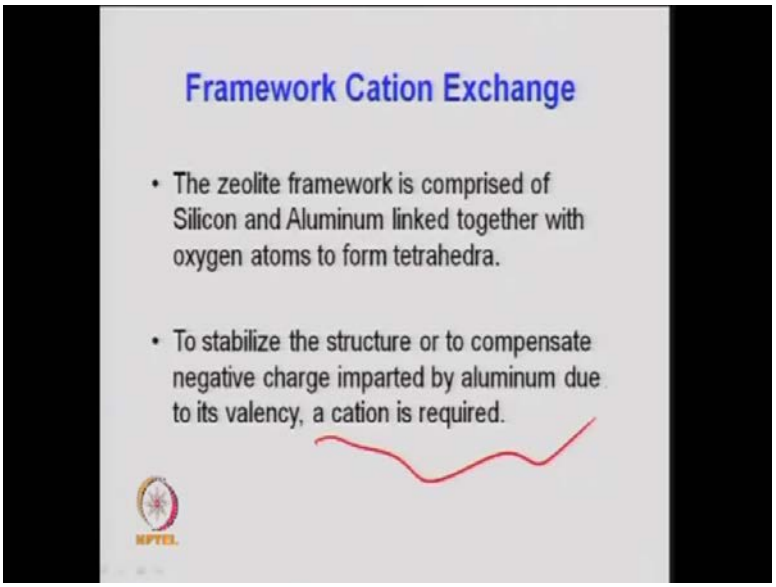

So it makes a framework so, zeolite framework is comprised of silicon and aluminum link together with oxygen atoms to form a tetrahedral. So, that is the first primary building, so silicon and aluminum are attached and in a tetrahedral form and makes 1 building primary building block, and to stabilize the structure or to compensate negative charge imparted by the aluminum due to its valency a caption is required. You need a Sodium or calcium or ammonium so some caption is required, which to the because there is a net negative charge to imbalance, that you need a cation. So cation exchange properties of zeolite are function of its intrinsic properties.

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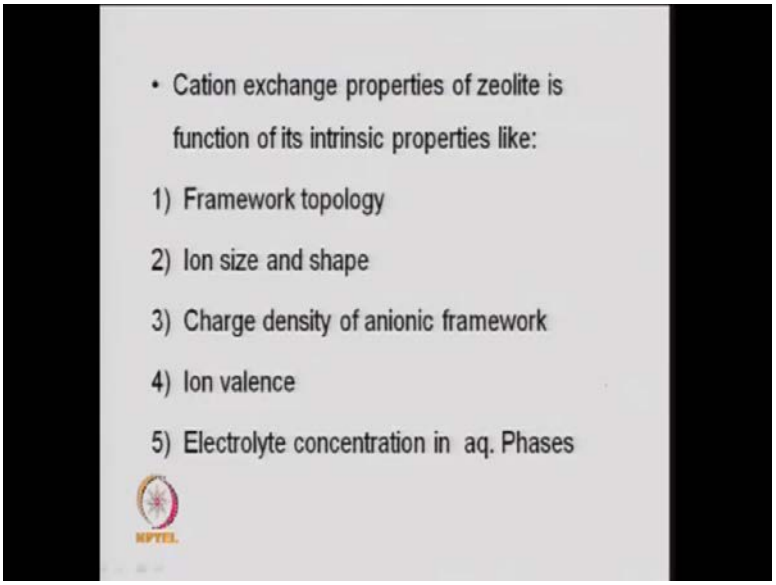

Or now depending upon the exchange capacity, you will have a framework topology. So, framework structure of the zeolite will form, then ion size and shape of the zeolite will be decided based on that charge density and anionic framework, so that is also equally important. So, this framework will be decided based on your silicon aluminum the ratio and the preparation condition ion valence, which is again depending on the captions number of protons? Which are required, electrometric electrolyte concentration in aqueous phase.

So, when you prepare the zeolite and this will be important a concentration of that. So, these are the properties. Which will decide the properties of the zeolite; these are the methods on framework that is the raw materials, which you select to have the concentration of these chemicals. Which have been taken to prepare this and then finally,

the concentration and the physical parameters like temperature time? So, that will also be important. So, preparation part I will take later.

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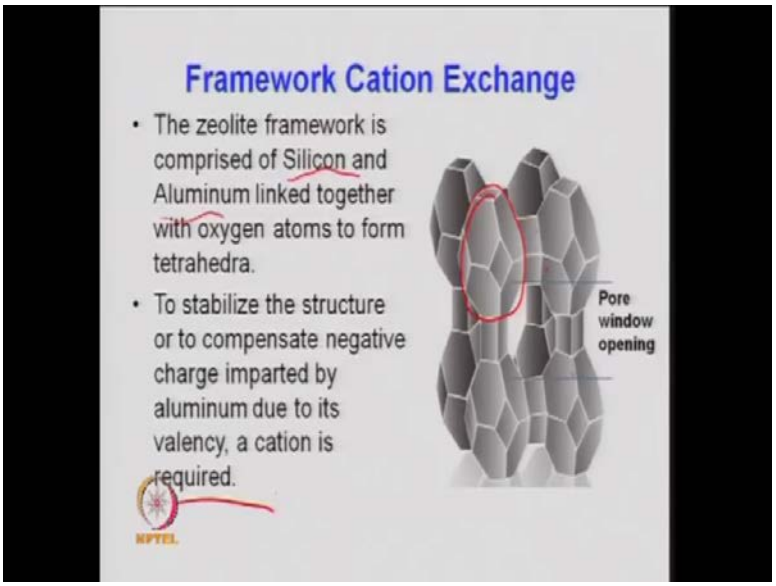

Then a framework of cation exchange does the same thing .What I talked is that it is comprised of a silicon, and aluminum link together with oxygen atoms. Which forms a tetrahedral, which is shown before also?

So, this is what 1 bulky ball structures. If, you look at just like a football structure. So, 3 d structure, it has a 3 d structure here and these are 1 frame work. Which are connected to that? So, this but, but ring here, you see here 1, 2, 3, 4, 5, 6, 6, member ring. So, this is that silicon and aluminum, these are linked together with oxygen atoms to form a tetrahedral, and to stabilize a structure or to compensate the negative charge. Which is imparted by aluminum a cation is required, that is what I discussed earlier. So, this is what the framework which forms in the case of zeolite. So, definite structure, so this is what is called pore opening window of the zeolite. So, that detail, we will talk later.

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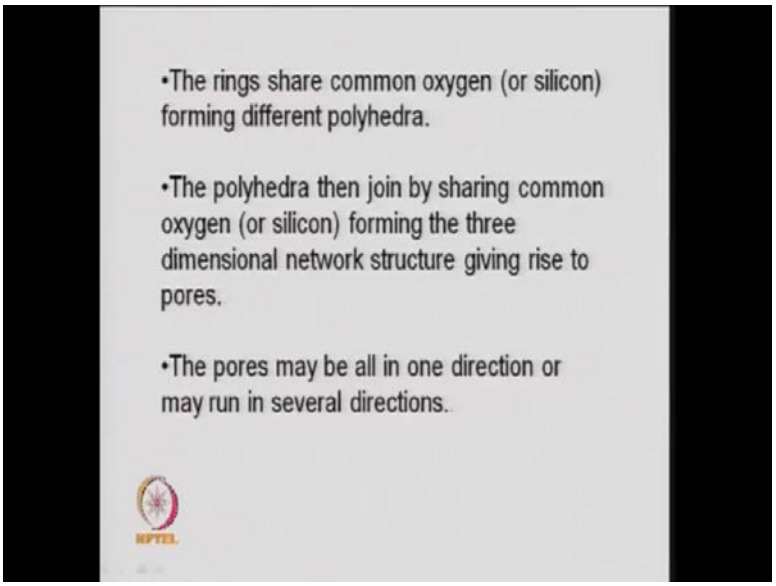

So, rings share common oxygen or silicon forming different polyhedral, now the depending upon the oxygen connected to the ring. As I said it may be 4 member it maybe 6 member 5 member, 8, 10, 12, different oxygen member rings zeolites are available larger the number of rings, the opening will be wider it will be wider. So, modernite, like that hozashied different kind of zeolites is available depending upon these rings.

So, polyhedral then join by sharing common oxygen or silicon forming the 3 dimensional networks a structure giving rise to the pores. So, that is the pore not like the pore in the amorphous solid or alumina materials. When you prepare the , this kind of materials the pores are just because of the hyper in the particle between the particle , or within a particle , then you define micro pores misopores micro pores there. So, here it is because of the arrangement of this silicon aluminum matter. And which makes some kind of cage, and then that is the opening of that pore, and the pores may be all in 1 direction or may run in several directions. So, they different kind of pores they maybe zigzag interconnected, so we will see that also the later.

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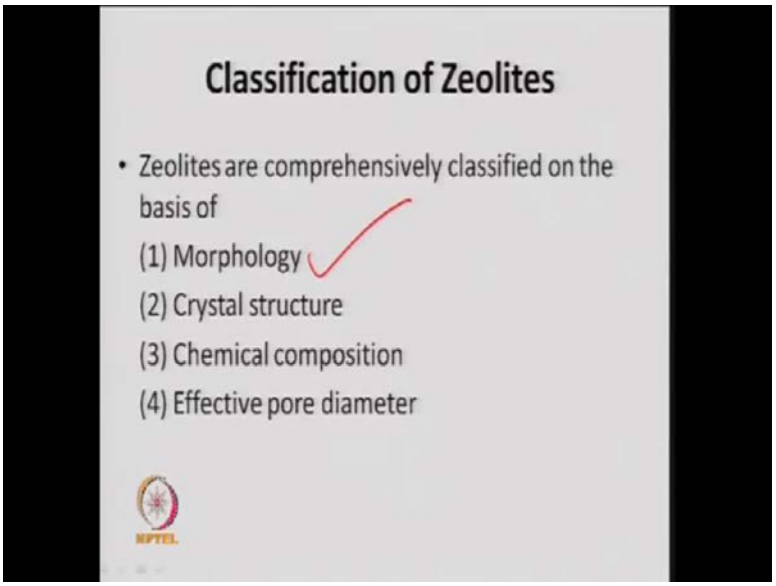

So, the classification if you look at for the zeolite. It will depend on morphology of the zeolite. That is what the cage structure silicon aluminum ratio, and because you depending upon that you will have a definite crystal structure, depending upon the raw material. You have taken silicon to aluminum ratio, you have taken, and you will get the chemical composition, and some captions, which have been added. So, you will have a chemical composition. Which I was talking some m is required? Some water is there, some silica is there some aluminum is there, so all these will depend on the composition, and the cage will be decided depending on the hydrothermal synthesis reaction.

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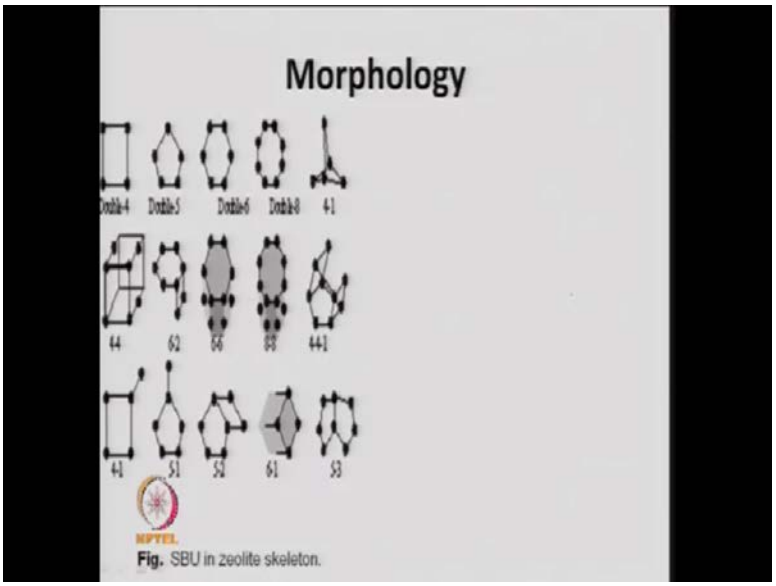

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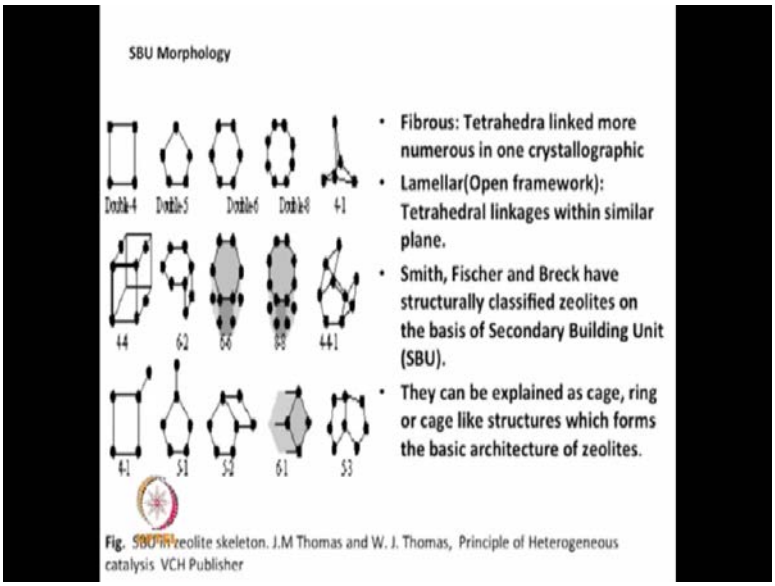

Fig. SBU in zeolite skeleton. J.M Thomas and W. J. Thomas, Principle of Heterogeneous catalysis VCH Publisher

A definite characterization is required. So, this is what you get in the case of a building block, secondary building block, from the primary building. So, these are nothing but, the structure building units in the zeolite. Sometimes we write s b u for the structured building unit in a zeolite. Which will be primary building unit and secondary building unit?

So, a structure of the zeolite will be because of the 2, 1, is the primary building unit another is the secondary building unit. So, secondary building unit is nothing but, the condensation of the primary building unit. So, it means just like if you visualize the pore formation though some benzene rings you should take so they come together, and then becomes larger, just like dehydronization water is removed, or sorry hydrogen is removed. And you have 1 where you have condensed molecule of 2 benzene rings, if you more benzene rings. So, it will go in a different form like anthracite. What you see like naphthalene?

So, you get different rings of condense polymer, by and that is your pore, which is less hydrogen and more carbon, just a de-hydrogen unit.

Same thing in the case of zeolites primary building block is formed. And now it is condensing on the over the other build similar structure. So, you will get a structure based on that, and that will depend again in your preparation condition hydrothermal ((Refer Time: 34:52)), because the time maybe 24 hours for that 48 hours 72 hours. So,

that is aging, and pressure is also important. So, very high pressure maybe required, temperature maybe required P H Z is the factor because there is a some kind of exchange, of the captions anions.

So, these are the secondary building units in a zeolite skeleton. So, 1 block has formed. Which are a tetrahedron structure, and then these rings are which is so 4 here it is so 4 member oxygen ring 5 member 6, 8, and like that 4:1 different form different tetrahedral form. And so these are different 6 sites like this 8, 8, 4, 4, 1, 3, d structure 4, 1, and 5, 1, 5, 2. So, there are different kind of structures can be formed, from this primary building unit, and that will be your secondary building unit, and then your structure that why you get wide range of the zeolite structures.

So, fibrous tetrahedral linked more numerous in 1 crystallography. That is 1 then second is lamellar structure just like a slip type structure, clay natural clay materials like your lunide, different type of ceramic materials. Which are the calceolate type materials? So, tetrahedral linkage within the similar plain. So, you will have a layered structure, lamellar structure. What you call and here it is a kind of different tetrahedral links. Which is more numerous in 1 crystallography, so you get a cage fibrous structure of that zeolite?

There are some other kinds also say smith Fischer and brick have structurally classified zeolites on the basis of the secondary building unit. So, this is another classification of the zeolite. Which is shown here, that what is the secondary building unit on the zeolite framework, and that maybe a classification for the zeolite? They can be explained as cage ring or cage like structure. Which forms the basic struck of the, architecture of the zeolite?

So, zeolite structure itself is very complex. If you look at, so as I said that it is a kind of 1 tetrahedron group, then as I said that they are depending upon the silicon to oxygen, or t atom or number of oxygen rings in the member oxygen in the rings. You get a definite, structure of that zeolite or framework of the zeolite and then there is a condensation of this primary building unit. And that gives you secondary building block, and then how these secondary building blocks are connected to each other, and you will have a different kind of a structure of the zeolite, so very complex method of preparation of the zeolite and getting the structure.

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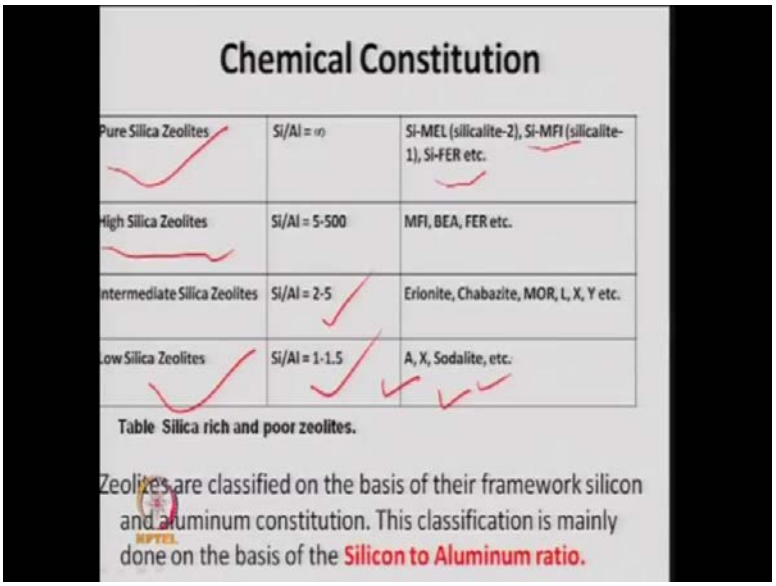

So, this is the chemical constitution of zeolite and as I said that the silica alumina ratio can be finite very high, and it can be very low. So, pure silica zeolite, where silicon to aluminum ratio is showing infinite, so roughly they are named as silicate literal silicalite s i m e l type, s i m f. I type, s i f e r ferrite type. So, there is different type of these zeolites, depending on the silicon to alumina. What basically? They are mainly silica materials, second 1. What they you have the traditional Pederson 5 type material?

So, you have silicon to aluminum ratio between 5 and 500. It can be 2 also, wide range basically and here, you have all your z m 5 s m i 5, beta zealots for etc. So, all these wide range of, so zeolites are available here, in these high silica zeolites materials.

So, depending upon the silica 12. I will show you need that depending upon; you need a kind of tuning in acidity tuning in strength, and tuning in the concentration of acid site. So, depending upon the reaction. You have to select a definite kind of zeolite and the pore size is different, so you have selected it accordingly, intermediate silica zeolites, where you are talking silica to aluminum ratio between 2 and 5, so your erionite chabazite chabazite modernite zeolite l x y. So, they have been named accordingly, and these have the inter silicon terminal ratio between 2 and 5. So, roughly you can say the lower side of silica to aluminum ratio, in this kind of zeolite. So, here the acidity will be high, that is the concentration of acidities will be high, here it is the strength is high acid strength is high, these are low silica zeolites.

So, where the silicon to aluminum ratio is between 1 to 1. 5, it is equal almost equal moles silicon and aluminum are numbers present are in almost similar, so as I said the aluminum is providing the kind of electro negativity in the framework.

So, that is the sometimes required. So, your zeolite a zeolite x zeolite sodality etc.So, they are generally in this range of zeolite. So, their pore structure will be different, so the silicon is lower side, so silicon to aluminum ratio is lower to the acidity that a concentration of acid site is higher, but, the strength of those acid sites may not be good.

So, you have to just tune depending upon the requirement. So, silica rich and poor zeolites. So, depending upon that, you have adapted property in a zeolite. So, basically now you can say that the zeolites are classified, on the basis of their framework silicon and aluminum constitution. So, this is 1 classification depending upon the silicon to aluminum ratio and framework of that zeolite. So, they have been named by I Z A according to these, like the if this is, this you can define in this range, if this is silicon to aluminum ratio 2 to 5. You can define in this type of zeolite and other things also need to be checked accordingly,

Pore size as I said opening pore openings framework. So, you have to do all the characterization required, first thing is that crystalanity, there you have to it has a drafted structure, so degree of crystallite, whether you get a crystalline structure, that is the first thing, surface area a definite surface area high surface area. So, these things are to be checked for naming them or giving them a particular kind of zeolite so it is classification is mainly done on the basis of the silicon to aluminum ratio, which is defined in this then this 1 is as I said depending upon the rings available.

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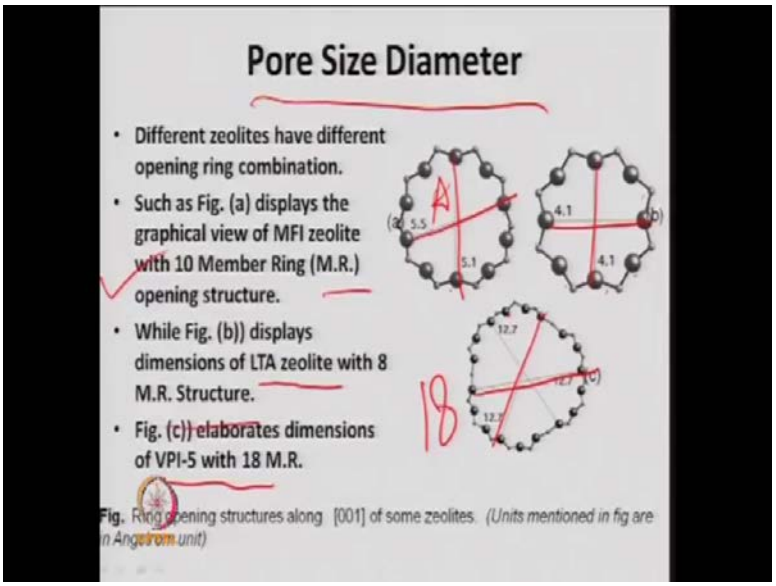

You have the different kind of frameworks, so opening of zeolites. So, generally when you define, you will sometimes you say average diameter pore diameter, but, all the time. When you talk zeolite catalyst? You define it to a into b, so it has 2 type of opening like you see here 5. 5 versus 5. 5, both this is same on both sides, which is the cage opening of that.

Here it is again 4.1 4. 1, here it is 12. 7, same but in some cases it maybe different also, 5. 5 this is like this 5. 5 5. 1, different, so all the time, when you define because it is a cage structure .So, depending upon the number of oxygen in the ring and the arrangement of these tetrahedral. That is the primary and secondary building unit, the opening varies, pore opening vary.

So, you have to define the zeolite depending upon the pore size or diameter of the pore that is again important, because you see the size of these pores here, so different zeolites have different opening ring combination. So, if you see the figure 1 it displays the graphical view of the m o 5 zeolite a 10 member in the ring. So, there are 10 oxygen rings in this, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10.

So, 10 opening ring if you look at here, this displays a dimensions of l LT A zeolite another type, this is defined by the linear group with 8 member ring. So, here it is 8 member rings 1, 2, 3, 4, 5, 6, 7, 8. So, diameter is reduced same thing for the third also,

so depending upon this oxygening arrangement, you can have different kind of pore size or diameter of the zeolite.

So, and again this is depending upon the structure, so ring opening structure along 0, 0, 1 of some zeolites and unit mentioned in the figure are in the angstrom unit. So, these are defined in the angstrom unit third 1, this is Virginia institute. So, they have defined this 18 member, here, so this has 18 oxygen in the ring and they pore size of roughly, if you look at opening 12. 7 angstrom.

So, that means the number of oxygen. Which is in the ring, which should be equal to your t atoms also, so same number of t atoms they are silicon and alumina, whatever you said? So, t atoms will decide your pore size, or ring size and there is even a table for the classification of the zeolite.

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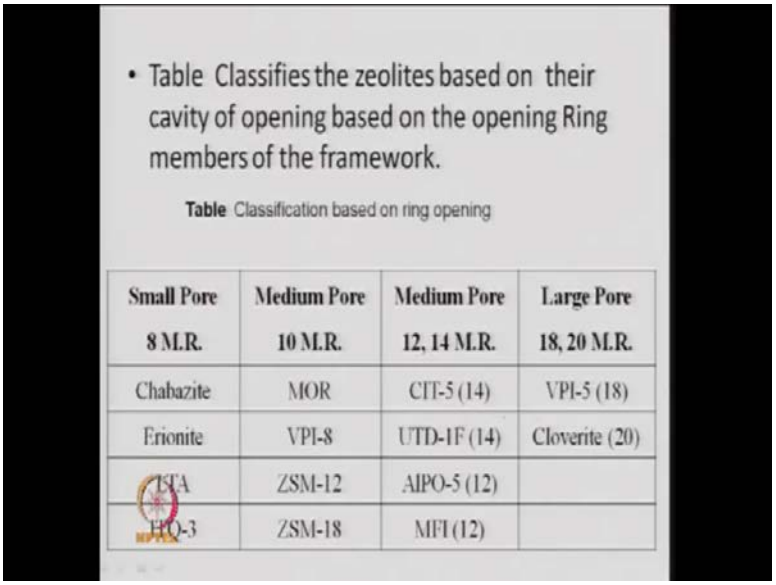

So, this is based on their cavity of the opening, based on opening ring members of the framework, as I said before that oxygen rings available in that and accordingly, you have a classification, so 8 member ring that is 8 action members in the ring. So, you have chabazite chabazite erionite l t which is linde and i t q 3, these are the fit tend names for the zeolite and depend. So, these depend on the number of rings that is the small pore type zeolite. Which I have shown here, we will go back and just these once.

So, as I said here it is 10 member 8 member and 18 members, something like this, you know so 8 member ring 10 member. So, depending upon that the structure has been classified or structures has been classified, as a small pore medium pore medium pore with 12 to 14 member ring and large pore with 18 to 20 oxygen in the ring.

So, this 8 member means these type erionite l t a i 2 a 3 chabazite. So, these are defined in these medium pore 10 member rings, so mordenite V P I, 8 Z S M, 12 Z S M 18. So, zeolite materials but is to Virginia and modernists again, they are 10 member ring, and categorized at medium pore zeolites. Again in the medium pore, which are slightly larger than this they are in C I T, 5 U T D- 1 F 14, A L P O-5. Which is phosphate type m o 5? So, there are again the medium pore zeolite with different type opening, and these are again the based on the patent site or name. Which the company, which have developed them, organizations large pore, like V P I 5 18 and chloride, which is 20 member ring? So, these are the another characteristics of the classification of the zeolite depending upon the pore opening,

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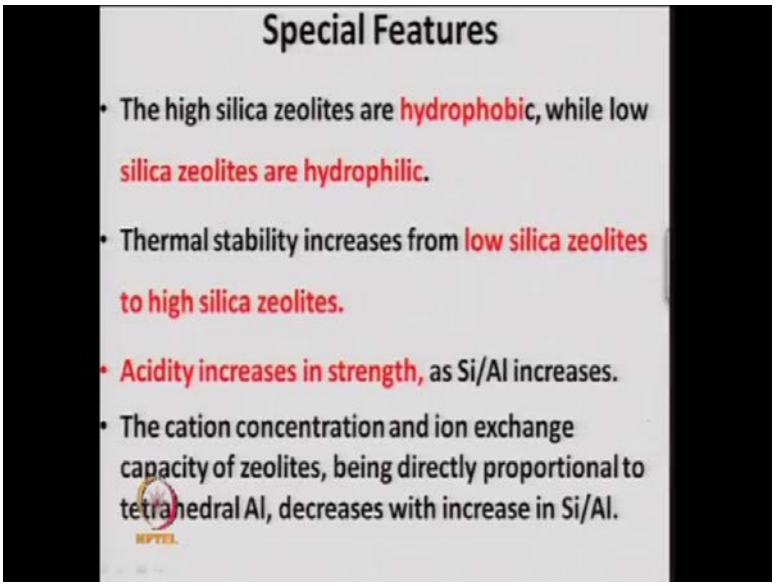

So, important property of the zeolite, as I was talking earlier also the high silica zeolites is hydrophobic. So, zeolite has a property, it has the ability to absorb water to take the water or to relief the water do not accept the water. So, hydrophobic or hydrophilic, so this type of growth, which have high silica zeolites, they do not accept water, they do not have the ability to absorb water, so known as hydrophobic zeolite.

Whereas when the silica is low in the framework, then they have a tendency to at high absorb water. So, it means, if you dry or if you want to get suppose 100 percent alcohol 90 from 97. 5 alcohol rectified split, and you want to convert it into pure alcohol, with generally used to blend in the gasoline petrol? So, you need a molecular same material that time low silica zeolite will be good, because they can absorb the water from the ethanol. So, you can make a complete water free alcohol. Which is from your distillation not possible, because of the equilibrium governed process?

So, that is the kind of materials can be used. So, hydrophobic means they have the high silica zeolite, they do not accept water and hydrophilic, they can absorb water, low silica zeolites. Then thermonsibility is again important, as I said that silicon to aluminum ratio or aluminum in the framework, that change the acidity but, the stability also varies. So, here the thermal stability increases from low silica zeolites to high silica zeolites. So, that is again important, that if the silica is high in the framework they will be stable.

So, stability will be high for high silica zeolites, so the acid concentration as I said strength of the acid and this stability. So, you have to tune it. When you look at a particular kind of zeolite .When the process is required, because z s n 5, it cannot sustain more than 550 degree centigrade. So, your cracking reactions, where the temperature is above 550 and you need to look at a slight additive in to increase the soluble or stability of the this kind of zeolite.

So, that is important acidity. I talked that before it increase with so acidity of the zeolite increases with the strength that is if I look at the acid strength. So, silica alumina ratio increases the acidity increase in strength. So, high silica to aluminum ratio acid strength will increase, so this is 1 thing that high silica to zeolite will have thermal stability, acid strength will increase but concentration of the acid will be poor. So, when you add the aluminum to the framework, then the concentration of the acid increase.

So, acidity because aluminum, if you look at S Z alumina it is emphatic, it does not have very good acidity. So, but silica has kind of acidity. So, when you look at the framework of the zeolite. You have the intension is to tune the acidity, and the strength of the acid. So, aluminum may have a Lewis acidity but, you have some kind of bronsted acidity is required. When you have to tune the alumina silicon to aluminum ratio in the framework? So, that is what the definite tuning is required in terms of silicon to

aluminum ratio, and the thermal stability versus the concentration of the acid site and the strength of acid site that is bronsted Lewis.

Cation concentration and ion exchange capacity of zeolite. That is again important because most of the times. They are used an ion exchange or cation exchange, for water purification. So, that is directly proportional to the tetrahedral aluminum, this decrease with the increase in silicon to aluminum ratio.

So, when silicon to aluminum ratio is increased, then the exchange capacity will decrease because the aluminum is providing a kind of electro negativity in the framework. So, that is again important, because the kind of imbalance thus silicon has 4 plus aluminum has 3 plus. So, when these 2 are connected into the framework that changes the kind of electro negativity. So, it changes the electro negativity, so that is again important, that ion exchange capacity of zeolite in the tetrahedron that decreases when the silicon to aluminum ratio is high. Building units, so I was talking the structural building unit, or S B U here ,it is same as structural building unit or greasing building unit. Which is made up of primary building unit and secondary building unit?

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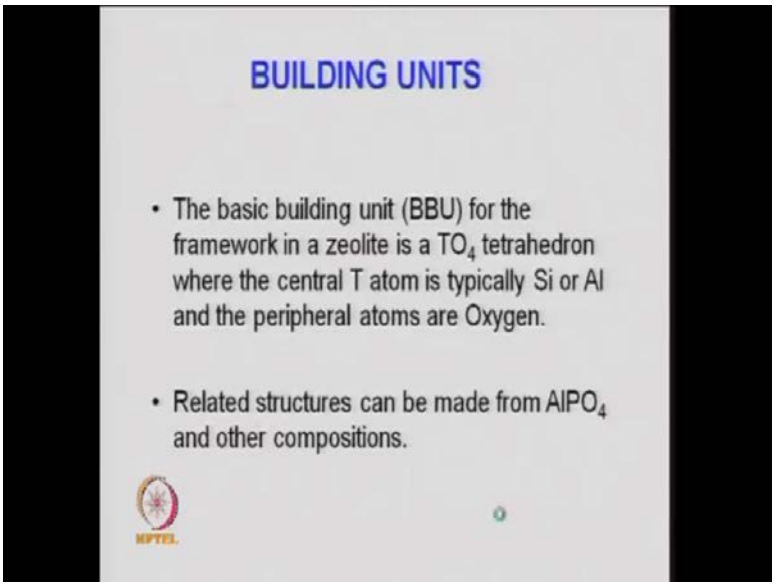

So, the basic building unit for the framework of zeolite, which we call T O 4 silicon a tetrahedron, where the central t atom maybe silicon. It can be aluminum and the peripheral atoms are oxygen. So that is what I discussed.

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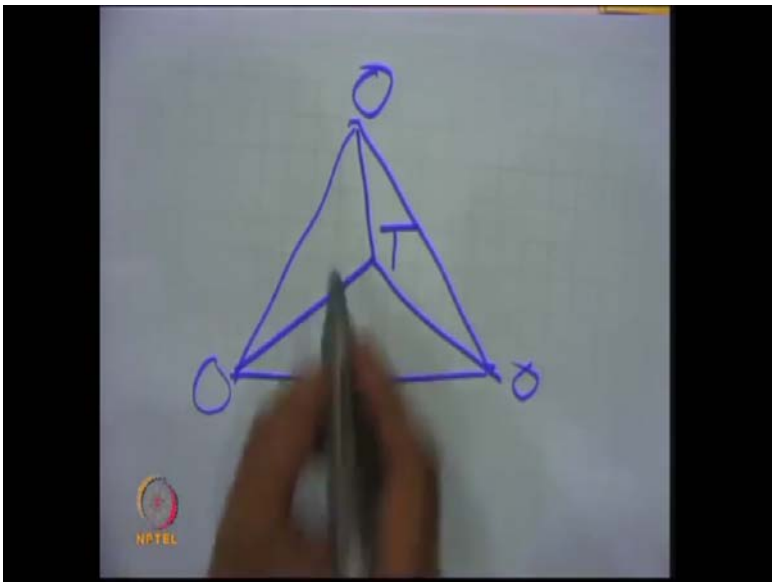

So, you have framework something like as I said structure like this, you have t atom here and oxygen is connected on this, so this is a kind of prismide basically like this, prism structure. So, here 1 more structure where oxygen is connected, so it is a kind of a prism, which may have a different bases as here yeah, primary building secondary building so member rings. So, 6 member 8 member 4 members like that.

So, T atom is at the center and the oxygen is connected to the corners of these, T or 4 the oxygen atoms are connected in the form of that prism. So, now because of this the structure can be made in the form of an L P O 4. That is alumina phosphate support type zeolites. So, instead of silicon, you can have phosphorous also in the ring. So, that is another type of zeolite known as silico alumina phosphate sapo, so that the part of this is by phosphorus p.

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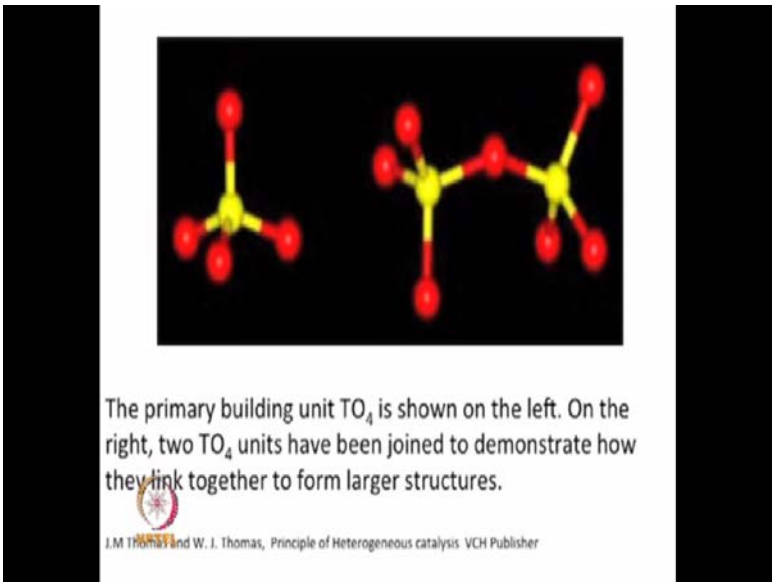

So, like that you can have different structures. So, here if you look at as I have shown here a rough structure. So, this 1 is actual, so this is T atom and oxygen is connected to this, so this is about different structure. You will get like this a tetrahedron, and when these 2 are connected. So, this is 1 group and this is another 1, so oxygen and these 2 atoms. So, T O T , and this can be aluminum also, so 1 is your silicon framework, and another is your aluminum framework or phosphor P O 4 groups , and this can be a connection. Now another group will connect here another group will connect on another and chain builds, and this will provide a kind of electro negativity or in the framework imbalance.

So, the primary building unit of T 4, which is shown here, this side and on the, 2 T or 4 atoms have been joined to demonstrate. How they link together to form a larger structures? So, this structure builds so depending on the t atoms. So 2 t atoms have been connected and so on and once that primary building is formed then secondary building unit , so this is what you have seen here this 1, so 1 primary building unit and now this is what they are connected and making a ring. So, these are connected and making a ring a 3 d structure basically, so how the primary t o 4 unit can be linked to create larger structure or a secondary building unit.

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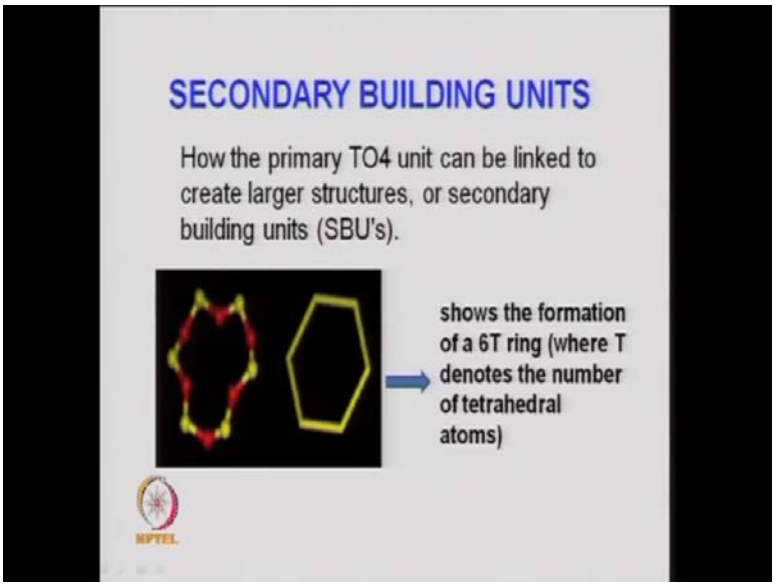

So, that is the primary building units are condensed together, and forming the secondary building unit as I said, so this is a formation of a secondary building unit. So, structure wise you look like this the rings are there 1, 2, 3, 4, 5, 6, member here, so 6 T ring. So, whatever the as I said number of o atoms in the framework ring, that equal to the number of T atoms are there, because that is what the so the formation of the 6 T ring. Where t denotes the number of tetrahedral atoms? So, these are the number of tetra, and makes a cage structure basically, a bulky ball structure.

And the simplest is the sodality cage, and this can be nothing but, the 6, 6, framework, which forms so they can be 24 building blocks like that because it is a nothing but, I said condensation of that primary building block, so depending upon the number of T atoms, which are connected to a ring. You will have different structure. So, this is what you can see here now a sodality cage is formed. So, this formed, this has formed from here , so this T atoms so these all are your T atoms here like this.

So, this is g1 to the condensation structure. So what you see here yellow, that is this yellow the 1, 2, 3, 4, 5, 6, they are connected like this, and forming a cage or its in the form of a tetrahedron. So, this makes a structure if you look at like this in the form of this cage, and this is known as a bulky ball structure.

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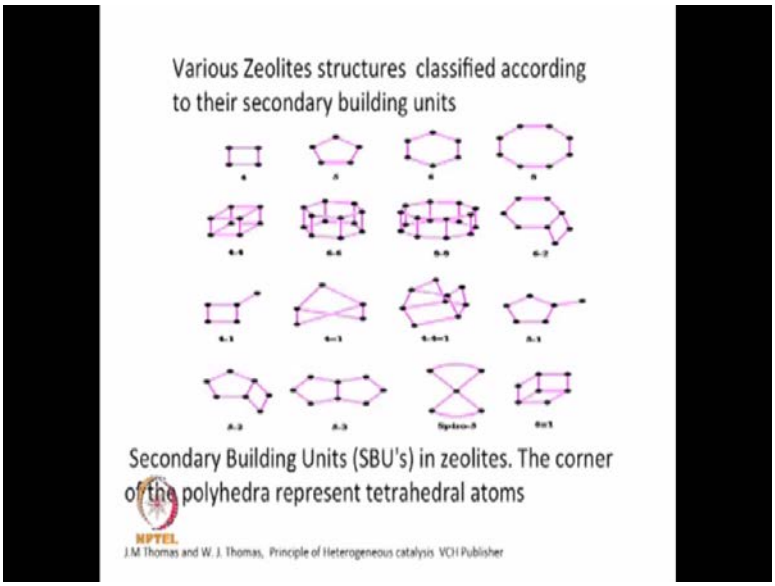

What I was talking in the beginning just like a football, this is the formation of 6 t rings, where t denotes the number of tetrahedron? And finally, you get a something like structure known as sodalite cage, a bulky ball structure. So, these are this is 1 primary building unit connected and made a 1 secondary building, and then condensed together and these structures, and it has formed just like a buky ball structure, and that is known as a framework of zeolite also, sodalite cage. So, I will continue it next time, which you can see here, so these we will discuss next time.

Thank you.