Heterogeneous Catalysis and Catalytic Processes
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Lecture - 18

Good morning, last time I was talking about introduction to zeolites. We discussed the composition of the zeolites, as I said that zeolites are water containing crystalline aluminosilicates depending upon the silica to aluminum or silicon to aluminum ratio different kind of acidity or concentration of acid sites that can be obtained in zeolites material.

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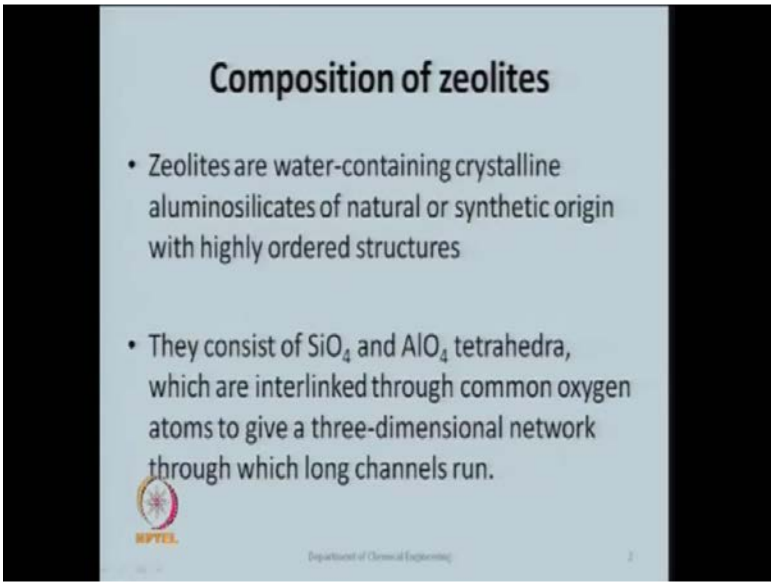

Composition of zeolites

- Zeolites are water-containing crystalline aluminosilicates of natural or synthetic origin with highly ordered structures
- They consist of SiO_4 and AlO_4 tetrahedra, which are interlinked through common oxygen atoms to give a three-dimensional network through which long channels run.

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So, this can be synthetic natural zeolites also clay materials or it can be made from some structured materials template using some templating agent organic materials. So, preparation I will talk later. The mille zeolites consist of silicon S i o 4 tetrahedra and aluminum A l o 4, these are interlinked through common oxygen atoms. So, as i said t o t a kind of structure what you get and the t can be the aluminum silicon or even it can be the iron material, some gallium, zerominium. So, different kind of other metals specific can also be introduced into the frame work of zeolite. So, it can give a 3 dimensional network through the long channel run. So, it is a k type structure, what you get or we get from the zeolite framework based on this t o t atom.

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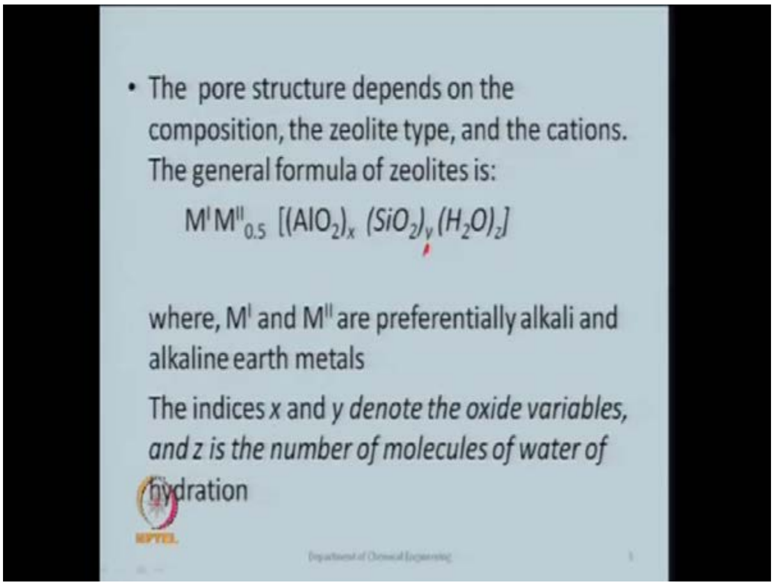

- The pore structure depends on the composition, the zeolite type, and the cations. The general formula of zeolites is:

$$M^{I}M^{II}_{0.5}\,[(AlO_2)_x\,(SiO_2)_y\,(H_2O)_z]$$

where, M^{I} and M^{II} are preferentially alkali and alkaline earth metals

The indices *x* and *y* *denote the oxide variables, and z is the number of molecules of water of* hydration

So, the important thing is the pore structure or channel size in a zeolite so that is basically depends on the type of zeolite. So, different kind of zeolites are available, different types of zeolites depending upon the patent ((Refer Time: 02:06)) name they have been named, depending upon the silicon to aluminum ratio, their pore opening and the type of oxygen in the members what you call six member, eight member and ten member. So, different oxygen in number of oxygen in the ring and that makes a definite kind of structure to that tetrahedral when, a secondary building block forms.

So, the composition wise if you see it has some cations or anions. So, M 1, M 2 and some 0.5 and the stoichiometry Al o 2, some x S i o 2, some y and this is water z. So, this x y z may vary depending upon the composition or initial raw materials taken amount of these raw materials taken for the preparation during hydro thermal synthesis. So, this can be M 1, M 2 these can be the alkali or alkaline earth materials in the zeolite.

So, x and y these denote the oxide variables and z is the number of molecules of water in the zeolite and basically, it provides the protons to the then, when you heat it then, water removes at around 550 degree centigrade and you convert that bronsted type acidity to Lewis acid sites.

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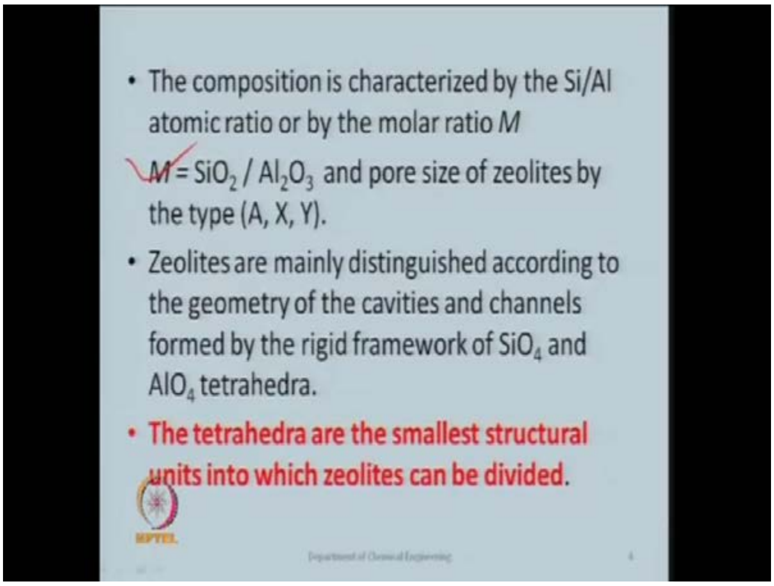

- The composition is characterized by the Si/Al atomic ratio or by the molar ratio *M* $M = SiO_2 / Al_2O_3$ and pore size of zeolites by the type (A, X, Y).
- Zeolites are mainly distinguished according to the geometry of the cavities and channels formed by the rigid framework of SiO_4 and AlO_4 tetrahedra.
- **The tetrahedra are the smallest structural units into which zeolites can be divided.**

So, composition of the zeolite as I said depends on the silica to aluminum ratio into the frame work and pore size of the zeolite and depending upon these two different names of the zeolite have been given or different types of zeolites have been produced like zeolite A, zeolite X, zeolite Y. So, which mainly depends on silica to alumina ratio or silicon to aluminum ratio in the frame work and depending upon the water content, the acidity will be developed and cage that is how these channels are interconnected. The primary building block and secondary building block. So, depending upon that condensation or whether it is the square from the square side or hexagonal side. So, you have a different kind of buckyball structure that is what, I was talking last time. So, cage openings will be different, depending upon the number of oxygen atoms in the ring. So, one thing is the distinction from the different categorize of zeolite A, X and Y, it based on the geometry of the cavities that is very important in terms of the pore opening or channel diameter, when you see the structure of a zeolites.

So, different kind of channels may form by the rigid frame work of Sio4 and Alo4 tetrahedra if it is a type of structure, which is a primary block basically and tetrahedra are the smallest structural unit into which zeolite can be divided, that is what I was talking primary building block so that will depend on the T atoms, which are connected to different oxygen.

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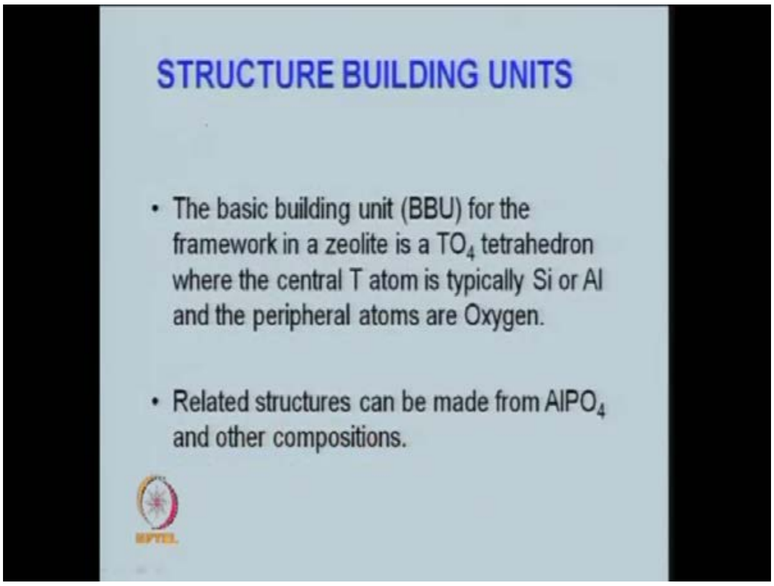

STRUCTURE BUILDING UNITS

- The basic building unit (BBU) for the framework in a zeolite is a TO_4 tetrahedron where the central T atom is typically Si or Al and the peripheral atoms are Oxygen.
- Related structures can be made from $AlPO_4$ and other compositions.

So, different silicon and aluminum and oxygen structure building unit. So, we were talking on that basic building block of a zeolite. So, basic building block unit which is even a primary unit basically, primary building unit, what I was talking last time, it depends on the frame work which is that, this TO4, that is Alo4 or Sio4. So, these say as I said that AloAl is not possible, because of the structural instability, the larger size of aluminum atom. So, AloS i is possible S I o Si is possible and any other metal like iron as I said, when idiom can be added to this frame work, that is T atom, we are saying here. So, T refers to silicon or aluminum or it can be iron also other metal and which are and depending upon the atoms, which are connected to the periphery of this oxygen, T atom oxygen atoms connected to these T atoms.

So, structure building unit, the basic building blocks, primary building block and secondary building blocks, what I was discussing last time for the structure building of zeolites, that is the frame work of the zeolites, as I said it is a condensed primary blocks T o 4 or T o T atoms basically. So, first thing is that, the tetrahedra which I was talking here, this is the kind of structure, which is developed when you have a zeolite frame work. So, this zeolite frame work will depend on the number of silicon to aluminum atom in their frame work. So, here, the related structures can be in terms of aluminum phosphate also, when the silicon is a paste like phosphorous.

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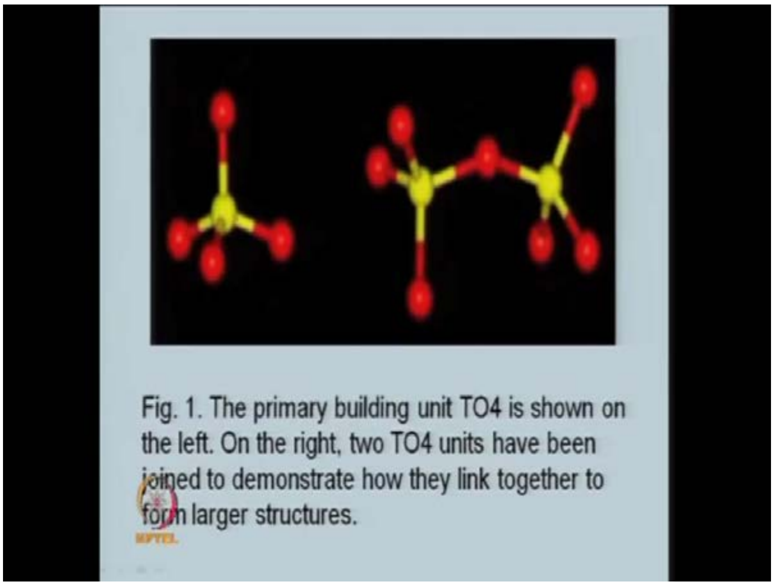

Fig. 1. The primary building unit TO4 is shown on the left. On the right, two TO4 units have been joined to demonstrate how they link together to form larger structures.

So, if you look at here, this is a kind of T atom, which is aluminum or silicon and oxygen is attached to that and now, when you have the primary block or primary building then, this is a 1 atom of that TO4 and then, this is another one and these two are interconnected now. So, TOT what I was talking. So, this is the structure which is related to the primary or p b u unit of a zeolite. So, and now the other will be attachments like this. So, another t will attached here and so on. The structure we built. So, you can have different kind of structure of the primary building units also.

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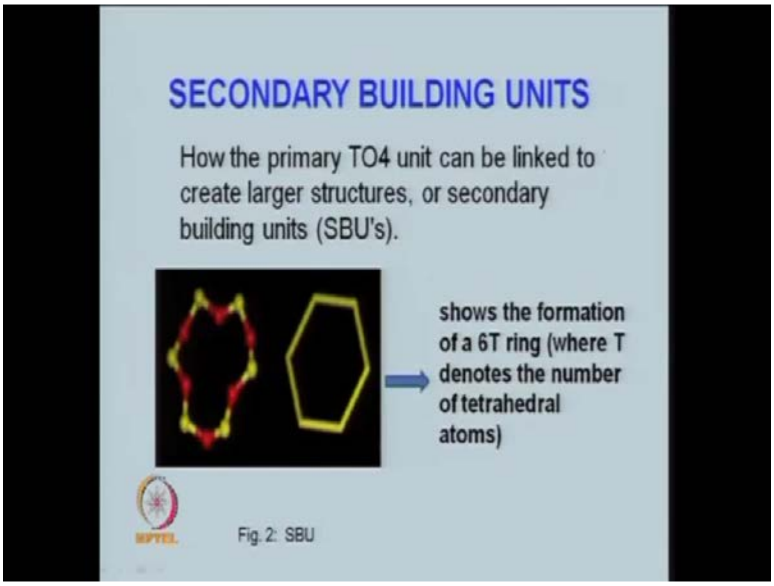

SECONDARY BUILDING UNITS

How the primary TO4 unit can be linked to create larger structures, or secondary building units (SBU's).

shows the formation of a 6T ring (where T denotes the number of tetrahedral atoms)

Fig. 2: SBU

This is what shown here, that how a primary TO4 unit can be linked to create a larger structure or a secondary building unit. So, larger structure will form the condensation of this. So, you can see here. So, this is what your T atom, 1 atom. So, TOT then again TOT. So, this is what1, 2, 3, 4, 5 and 6. So, here 6 atoms are attached to this a p b unit. So, you get a structure like a hexagonal type here, which is and a tetrahedral is forming. So, this is from the tetrahedral atoms whatever AlO4 or SIO4 and you get a structure like this 6 member. So, whatever the oxygen numbers here in the ring and that is also the number of T atoms in the ring. So, this is what primary building, which connected to make secondary building units in the case of zeolite, which is now in the form of buckyball when, you look at the condensation of these.

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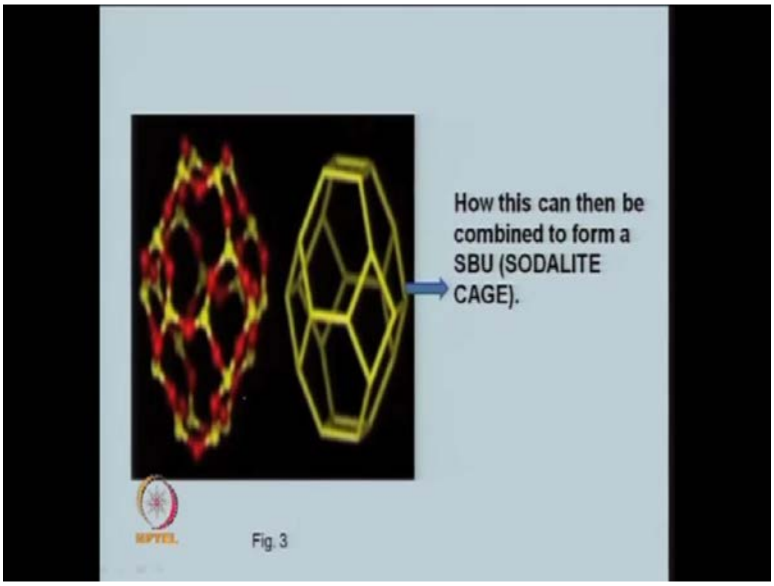

How this can then be combined to form a SBU (SODALITE CAGE).

Fig. 3

So, the structure this is 1 unit, which we have seen so far and now they, because it is an all T atoms are interconnected. Now, and you have a cage type structure from this primary. So, this is basically hexagonal frame work of the zeolite and you can see a kind of buckyball structure which forms. So, this is how what you call a sodalite cage in the case of z s m five zeolites. So, this is a secondary building of that from the primary building TOT units. So, and this now, this is just one and there can be different ways of arranging these and you can have different kind of these, this primary block primary building structure or secondary building unit of a zeolite frame work.

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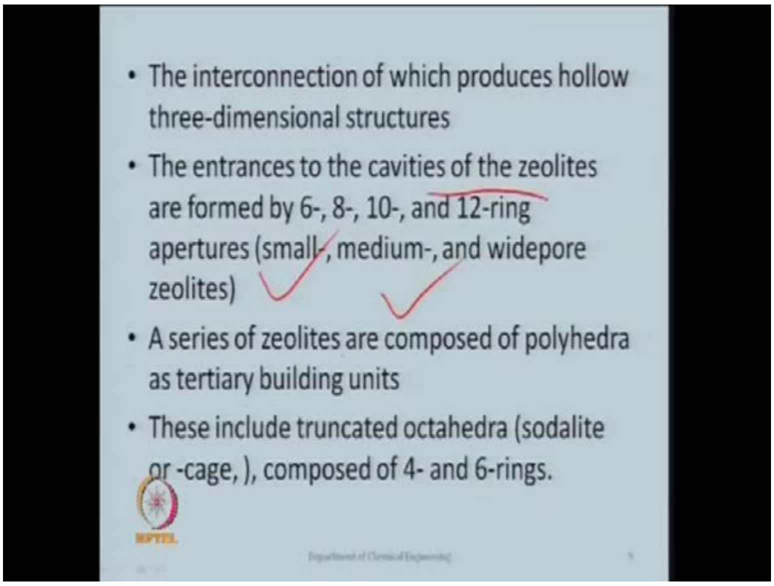

- The interconnection of which produces hollow three-dimensional structures
- The entrances to the cavities of the zeolites are formed by 6-, 8-, 10-, and 12-ring apertures (small-, medium-, and widepore zeolites)
- A series of zeolites are composed of polyhedra as tertiary building units
- These include truncated octahedra (sodalite or -cage,), composed of 4- and 6-rings.

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So, this is important, that is the interconnection of which produces hollow 3 dimensional structures. So, you get a 3 d structure in the case of zeolite material 1 d, 2 d, 3 d. So, different kind of structures can be obtained and the entrances to the cavities of the zeolite are formed by 6 8 10 and 12 ring aperture which may be now depending upon the number of oxygen's. So, these are the T atoms or number oxygen in the ring 1. Which, I was talking, so 6 membered ring, 8 membered ring, 10 member and 12. So, this gives you the opening of that cage. So, small pore medium pore or large pore zeolites. So, this gives you the diameter of that cage what you have seen here in one structure of that zeolite.

So, different frame works of the zeolite can be obtained by these interconnecting channels of the zeolite and a series of zeolites are composed of polyhedral as tertiary building units. So, now primary is secondary and tertiary and you have a definite frame work of a zeolite and that gives you, because now when you are looking the structure of that it has T atoms silicon to aluminum. So, silica to alumina ratio will be decided the pore opening that another depending upon the silicon to aluminum, because I said that aluminum introduction provides the electro negativity in the zeolite frame work. So, and a silicon is there that is also has some kind of electro negativity. So, the aluminum when you introduce it provides more and more electro negativity. So, your concentration of the acid sites will increase but when you have silicon higher than the strength will be higher for the zeolite frame work. So, depending upon these T atoms, the silicon or aluminum in the frame work you have the acidity or the concentration of the acid sites in the zeolite, which is the important property of the zeolite besides the pore size or shape selectivity of a zeolite what you call a molecular shape type zeolites also. So, if you look at that c of the zeolites.

So, they are truncated octahedral, sodality or cage type structure 24 membered rings, which can be there composed of 4 and 6 rings like that in it square opening hexagonal opening 5 membered ring. So, different kind of structures can be obtained from these primary building units. So, sodality cage if you look at it has 24 tetrahedra a buckyball structure, what I was talking. So, it has 24 tetrahedra and we call it polyhedral also and generally depicted by just I will show you the figure of this and which is here basically.

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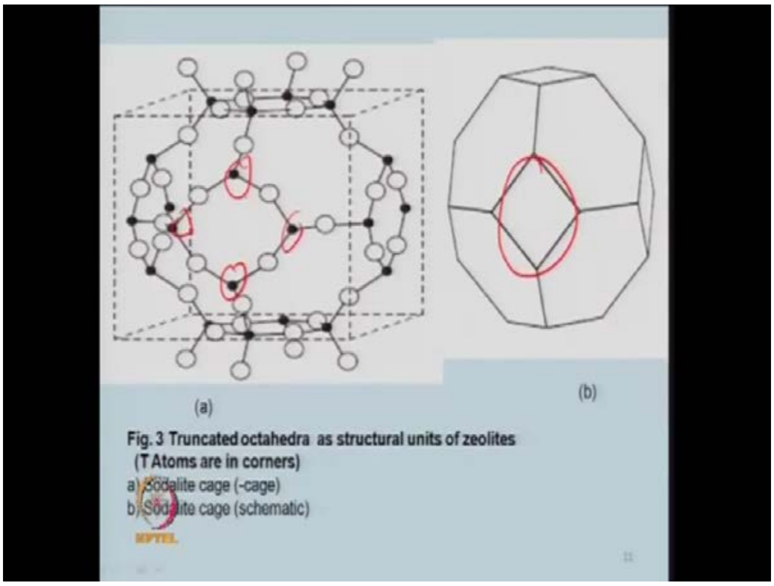

Fig. 3 Truncated octahedra as structural units of zeolites
(T Atoms are in corners)
a) Sodalite cage (-cage)
b) Sodalite cage (schematic)

So, this is what, the frame work of a zeolite here, the connected T atoms like this one black one are your T atoms and the white circles are your oxygen. So, they are connected to the corners and this structure frame work forms a 3 d structure what you look at here and this is what, I was talking connection to that bridge. So, square here this here. So, you have a 4 member here oxygen in this. So, whatever T atom 1, 2, 3, 4 and 1 or 4 oxygen in that and then, these are condensed the connection just like an. if you look a football a buckyball. So, these cages are connected together and making it just like a sphere so that is what, this different cages if you look at that and this is and these are formed, because of these connection of these different structures or the primary building units of that zeolite cage.

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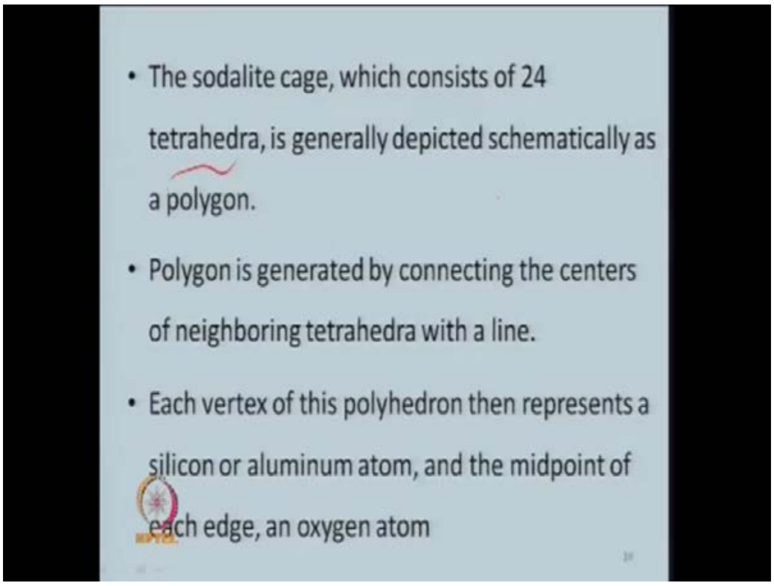

- The sodalite cage, which consists of 24 tetrahedra, is generally depicted schematically as a polygon.
- Polygon is generated by connecting the centers of neighboring tetrahedra with a line.
- Each vertex of this polyhedron then represents a silicon or aluminum atom, and the midpoint of each edge, an oxygen atom

So, this is what, the polygon which is generated by connecting the centers of the neighboring tetrahedra with a line so that is now depending upon this connection, you have a different kind of structures or frame work of the zeolite. So, each vertex of this polyhedron then, represents silicon or aluminum atom that is the corner is representing. Now, the T atom silicon or aluminum and oxygen are at the center of that. So, silicon or aluminum atom and midpoint of each edge is an oxygen atom now, s when you look at one square opening. So, corner is your T atom, because from those T atom and oxygen is connected and it is like a TOT what I was talking. So, all the time your structure will go like this TOT.

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So, silicon O, silicon O, aluminum likes that and then, another oxygen will be there and then TOT and then, this is the primary and then you have a cage structure by connecting those frame works. So, this is what is shown here. So, these are your T atoms, circled 1 and the center one is your oxygen atom. So, you can have different kind of cage. So, this is one kind of sodality cage, which is actually and schematic is shown something like this.

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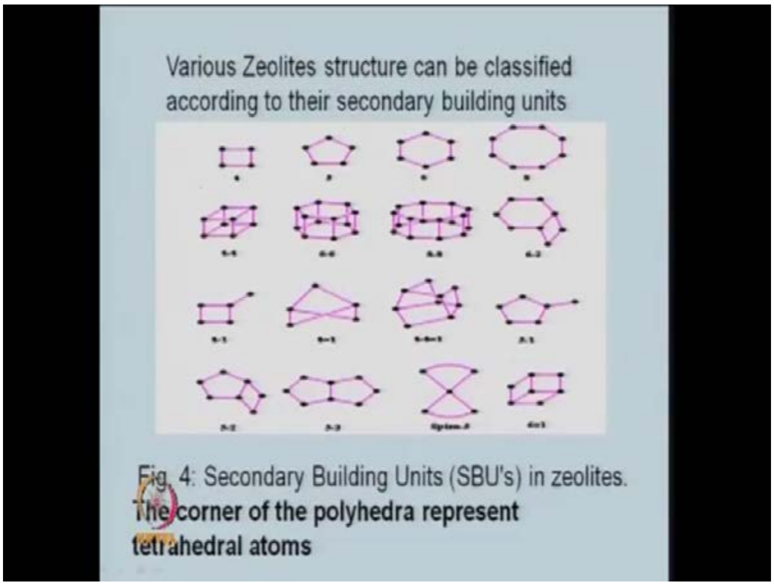
Various Zeolites structure can be classified according to their secondary building units

Fig. 4: Secondary Building Units (SBU's) in zeolites.

The corner of the polyhedra represent tetrahedral atoms

So, various zeolite structures now, because this is just 1, where you have seen this member ring 4 oxygen in the ring and then, they are connected in the sodality cage. So, it is depending upon this secondary building unit. So, these are different kind of secondary. So, 4 T atoms here, it is 1, 2, 3, 4, 5 T atoms, 6 T atoms, 8 T atoms. So, this can be a 1 d channel then, 2 d channels are like this is also 44668862 different kind of. So, this is what you can see, the square opening at the 62. So, 2-1 on one side and 6-1 on other side. So, you can have different combinations of the zeolite or zeolite frame work, which will depend on your preparation condition template, because template is the 1, which makes this frame work of the zeolite organic templates, so that you can have the different kind of sodalite cage structures or zeolite frame work and the corner of the polyhedral represents the tetrahedral atoms.

So, all these corners are tetrahedral atoms. So, these are T atoms basically and oxygen is in between. So, once these structures are formed then, secondary as I said that sodality cage. So, you get a different kind of sodality cage structure and they have been named like that, what I was talking for site linked type zeolite a sodality cage. So, there is different kind of structures of the zeolite and so on. So, zeolite A, zeolite X, zeolite Y, what we are talking and these are what the depending upon that, this silicon aluminum different oxygen and or basically in terms of the raw material which has been taken the concentration of the silica specie concentration of the alumina specie then, p h and then decision factor amount of water which is sowing the value of y in the zeolite.

Then, temperature which will give you a kind of nucleation crystallite formation time where the hydro thermal synthesis, because it is a autogenously passive synthesis at the high pressure under autogenously. So, it generates the autogenously pressure, because of the presence of water. So, you have and that time. So, reaction time or ageing time and you have the different kind of phase or crystal crystallization that you check during the time course of the formation or synthesis.

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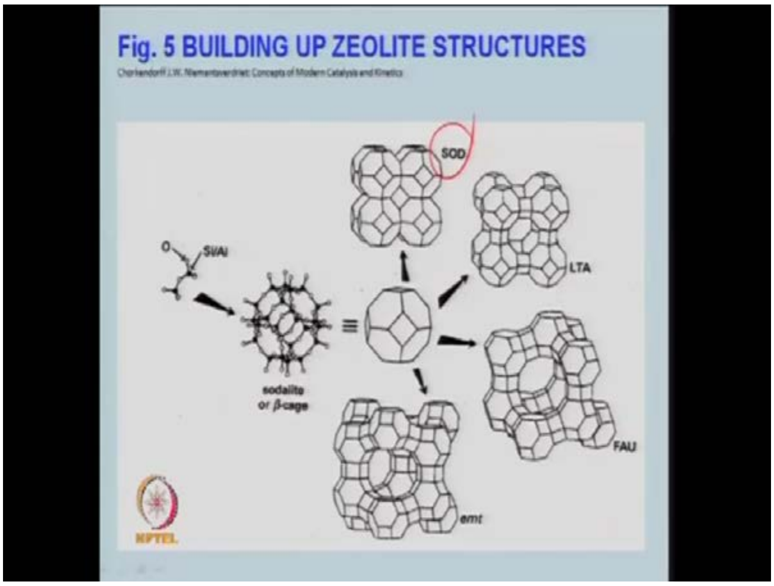

Fig. 5 BUILDING UP ZEOLITE STRUCTURES

Chorkendorff I.W. Niemantsverdriet: Concepts of Modern Catalysis and Kinetics

So, this is just a one kind of sodality cage which, we have already discussed. Now, how does it form from the primary building then, secondary building unit and then, the tertiary or which is nothing but a secondary building which forms the condensation of the primary building. So, this is one sodality cage structure, which helps seen in details with the square opening and 4 T atoms in the group. So, one cage and then, there can be the condensation of this tertiary building block.

So, 1, 2, 3 and 4 like that and so on. A buckyball structure and these are interconnected like this. So, 1, 2, and you can see that, several footballs placed in one cubic structure inside an inside the box. So, that will be cage structure of that what the sodality cage or a zeolite structure. So, there, that is what the 3 d type of structure what you get or a frame work which forms, because of the opening or because of the gaps between them. So, this is what the 1 sodality an there is again when, they are connected in a different fashion here, it is in this fashion but here this is something different if you look at here, the openings of that. So, connection is different in a polyhedral form the attachment of these are the structures which are connected.

So, hexagonal or 5 member pentagonal like that. So, here also same thing, a different pore size you will have a different opening with thus, the silicon to aluminum ratio maybe same but the opening will be different, because it depends on how they are nor how they are connected that how the structure is connected and a different one their large numbers are cage number of cages are connected together and number of those silicon to aluminum or T atoms in the frame work.

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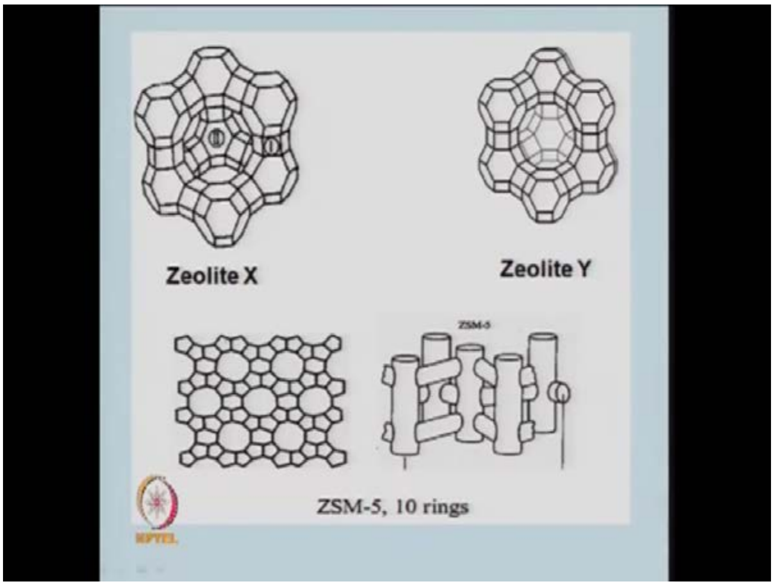

Zeolite X

Zeolite Y

ZSM-5, 10 rings

So, we categorize them or we just name them accordingly. So, the one structure, which is one type and second type here and the zeolite X, these are your zeolite Y with different opening if you look at here. So, it has different ring structure here compared to this one. So, size is different. So, and this is another one, though you can see the building block. So, this is different just a 1, 2 like that and they are interconnected. So, ZSM-5 pentasil structure here and this is the actual ZSM-5 channels pore channels in a 3 d arise so that is a ten ring 3 d ZSM5.

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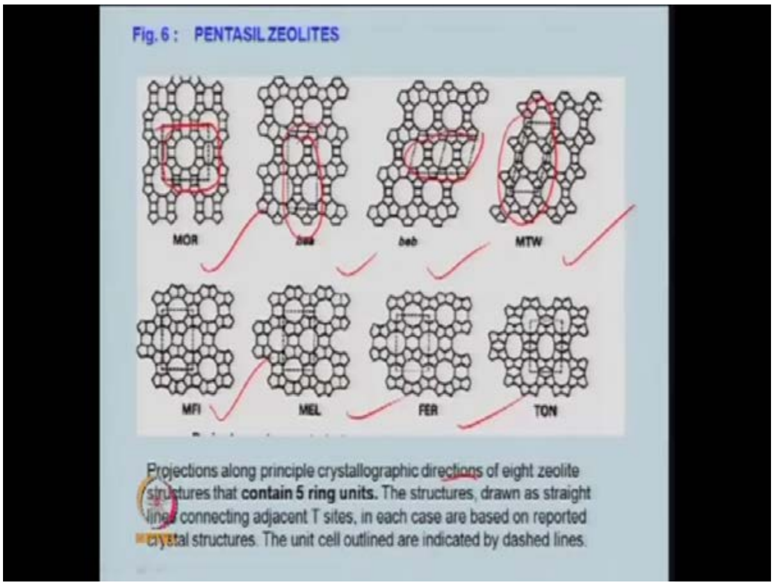

Fig. 6 : PENTASIL ZEOLITES

Projections along principle crystallographic directions of eight zeolite structures that **contain 5 ring units.** The structures, drawn as straight lines connecting adjacent T sites, in each case are based on reported crystal structures. The unit cell outlined are indicated by dashed lines.

So, the as I said that, the it depends on the projections of this primary building block or frame work along crystal crystallographic direction of 8 zeolite structures, which have been shown here. So, basically these all depends on the primary building blocks, which I have shown you in the earlier slides, like this and then, their orientation. That is the structure which is how does it project on that one primary block and how does it project that is the secondary block and then, the multiple have formed the tertiary block.

So, depending upon the projections of these crystal crystallographic directions you can have 8 zeolite structures, which contain just 5 rings unit. So, 1ZSM-5 I am talking which as a pentasil structure suppose but there also you can have different type. So, this is modernize if you look at here, if you read here, those directions of 8 zeolite structure that contain 5 ring units, the structure drawn as a straight lines connected adjacent T atoms and in each case these are based on reported crystal structure. The unit cells obtained is indicated by the task line.

So, this is one unit cell of a zeolite the here, it is the unit cell of a zeolite like this, in this case it is a something different like this. So, it means depending upon the arrangement or orientation of that crystallographic plane, the plane orientation just. So, different type of zeolite openings maybe arrived. So, a different structure of the zeolite may be seen in terms of the pore size. So, same silicon to aluminum ratio, same number of T atoms but the pore openings will be different. So, we categorize them depending upon small pore zeolite, medium pore zeolite and large pore zeolite with the same silicon terminal ratio, because as I said that zeolites are mesoporous material or the micro pores material and then, the pore structure of the zeolite, because they have the importance in terms of the shape selectivity. They are very useful for the reactions where, the selectivity may be an issue especially in the most for the hydro carbon industry or petro chemical industry where, selectivity has an issue one desired product is required in large amount compared to the rest.

So, suppose the coke is forming in large amounts. So, you take it at least in such way, that the coke which may be a poly condensed aromatization reaction the aromatics are there and they condensed and form an aromatic bridge and which is a poly condensed aromatic hydro carbon. So, the pore openings or the kinetic diameter of the pore this poison precursor or sulphur or whatever the coke precursor aromatics if the kinetic diameter of these molecule is a smaller than the pore diameter then, they will not go inside, they will not form the coke type of hydro carbon or the sulphur molecules if they are there.

So, you can have a kind of shape selectivity from the zeolite and especially when you look at a green catalysis nowadays then, you are looking in terms of atom efficiency or e efficiency. So, you are the product when, the multiple product may form from one of the raw material then, this becomes a very important just like methane convergent if you look at or fish trope reaction where, the product may be methane or wax also and the interest is towards the gasoline or diesel range of hydro carbon or methanol that is selective narrower range of hydro carbon then, there these kind of catalyst where you have a narrower pore size or a selective pore size distribution then, this may be a better option as a support or as a catalytic material.

So, depending upon these structures, we have different kind of zeolites here. So, and these are named as per the international zeolite association. So, the structure of the zeolite has nothing to say about moldenide if I say or beta zeolite, beta b zeolite or n o 5 zeolite, m l 5, this ferrite type zeolite, TON type zeolite. So, these are just the i z a named for a given kind of zeolite but here but I want to say that depending upon the crystal crystallographic direction, you can have the, how this crystal crystallographic direction orientation of one primary building and the secondary to form a multiple or a polyhedron, that depends on the type of the that is the orientation depends to give a given kind of pore opening in a zeolite and accordingly these have been numbered.

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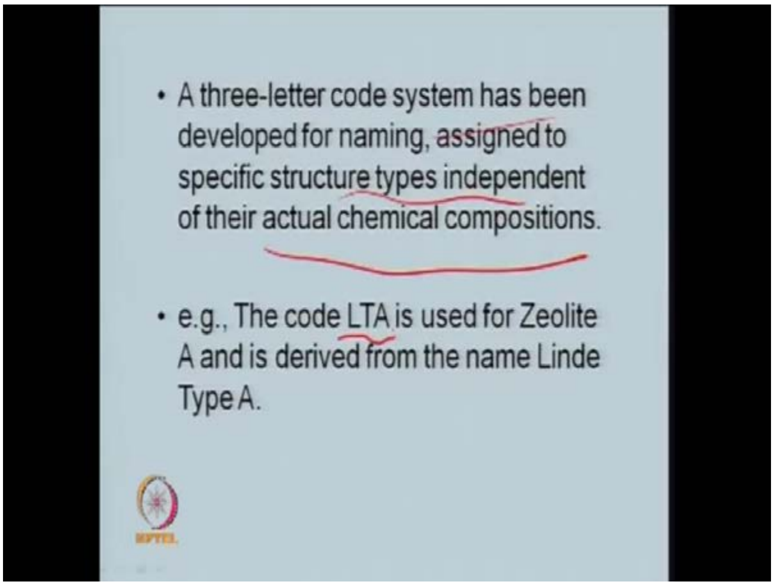

- A three-letter code system has been developed for naming, assigned to specific structure types independent of their actual chemical compositions.
- e.g., The code LTA is used for Zeolite A and is derived from the name Linde Type A.

So, the name, that is nomenclature for a zeolite as I discussed last time also that is very important. So, a three letter code system has been developed for the zeolite. So, to identify a zeolite or a type of zeolite a three letter code system has been identified that is what as I said that, i z is one which just designates a zeolite in terms of their pore size distribution silicon to aluminum ratio or the opening what are the cage opening what I said earlier. So, generally they have given a three letter code and which is related to a specific structure types and independent of their actual chemical composition.

So, whatever is the m or m 1 and m 2, which I talked in terms of the structure s i o 2 x or water y a l o 2 z something like that. So, these structures have nothing to do with that composition or name of the zeolite composition has nothing to do these are some patented names and the only thing that, once these numbers have been identified and one can compare the property of the prepared zeolite with those standards. So, these are kind of bench marks which have been tested for the certain reactions and their pore size, pore structure opening silicon to aluminum ratio these are well defined.

So, this is one important nomenclature for the zeolite material. So, just LTA suppose if you say. So, LTA is used for zeolite A and is derived from the name Linde type A. So, Linde again is company based on that the just like I was talking Virginia 1 or zeolites suconi mobil z s m. So, these are name numbers to identify the zeolite.

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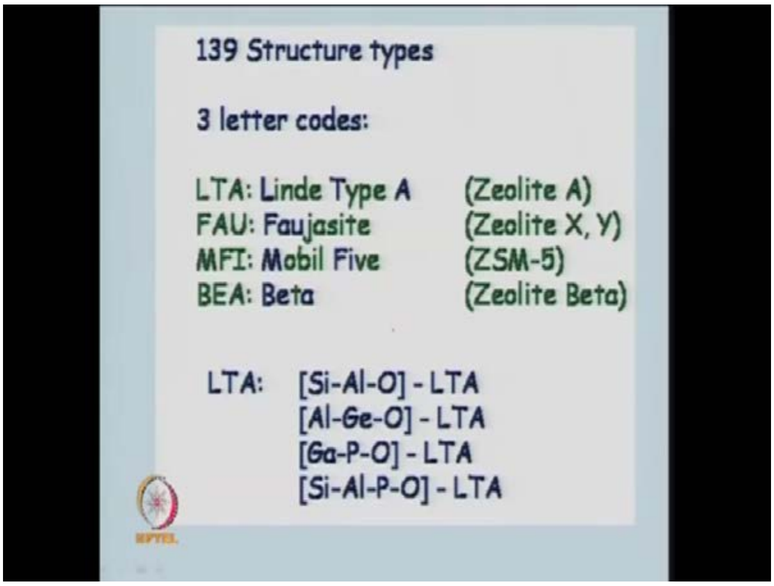

139 Structure types

3 letter codes:

LTA: Linde Type A	(Zeolite A)
FAU: Faujasite	(Zeolite X, Y)
MFI: Mobil Five	(ZSM-5)
BEA: Beta	(Zeolite Beta)

LTA: [Si-Al-O] - LTA
[Al-Ge-O] - LTA
[Ga-P-O] - LTA
[Si-Al-P-O] - LTA

So, here, this 139 structure types zeolites are available and even more then, that may be available. So, the three letter codes what I said LTA refers to the Linde type a Faujasite represented by FAU, MFI which is a kind of mobil five, BEA refers to beta zeolite. So, different kinds of zeolite are available in that say like LTA zeolite, a zeolite X and Y, they are for the type category ZSM-5 well known category of the zeolite. So, mobil sometime the mobil suconi so that is again, the name which has been given by the mobil group and beta zeolite, which is zeolite beta and that is the name.

So, like that you have, it can be silica aluminum oxygen, it can be a germanium in the frame work and it can be gallium, phosphate and oxygen again. So, different kind of zeolites are available in whether in LTA or ZSM-5 or MFI group or beta type or FAU type. So, silica alumina ratio may vary, pore opening may vary structure may vary.

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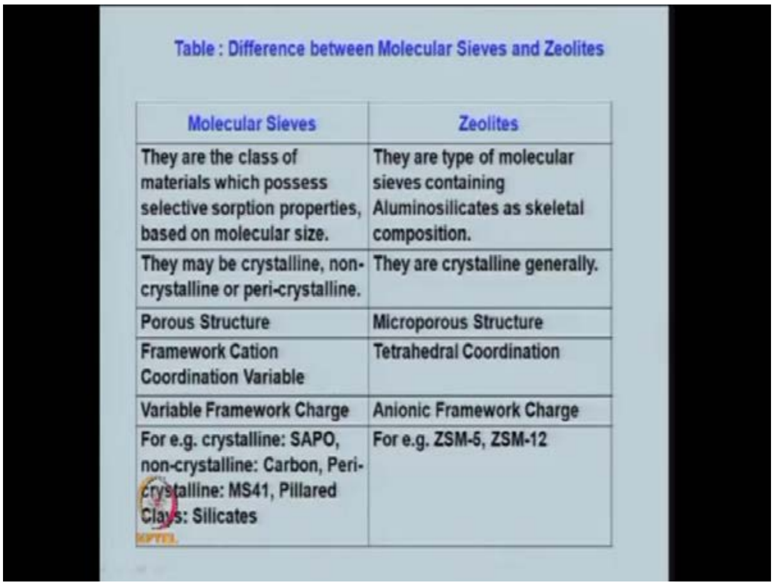

Table : Difference between Molecular Sieves and Zeolites

Molecular Sieves	Zeolites
They are the class of materials which possess selective sorption properties, based on molecular size.	They are type of molecular sieves containing Aluminosilicates as skeletal composition.
They may be crystalline, non-crystalline or peri-crystalline.	They are crystalline generally.
Porous Structure	Microporous Structure
Framework Cation Coordination Variable	Tetrahedral Coordination
Variable Framework Charge	Anionic Framework Charge
For e.g. crystalline: SAPO, non-crystalline: Carbon, Peri-crystalline: MS41, Pillared Clays: Silicates	For e.g. ZSM-5, ZSM-12

So, as I said that molecular sieve zeolites are also a kind of molecular sieve. So, the name says the molecular sieve, that just the molecules are being separated depending upon the size, the size of molecule and the pore size. So, one can separate the larger molecule from the smaller just like in a membrane. So, but there are certain differences or if you just look at the properties wise there is a difference between zeolite and the molecular sieve.

So, zeolites are class of material which posses selective adsorption properties. So, they have very good adsorption property, because as I said that, they are shape selective or sieving action is very important in terms of the pore diameter. So, diffusion may be a governing process here. So, selective adsorption property and that is based on the molecular size, where as if you look at in the zeolite in contrast to the molecular sieve, they are molecular sieves containing aluminum silicates as skeletal composition. So, they have the 3 d structures or they contain the aluminum silicon and in some cage type of structure.

So, the one thing in that here, it may not be a uniform in the crystalline may not be an important issue in the case of molecular sieve but in zeolite the crystalline is one of the important issue. So, the if definite type of zeolites, when we name that should have a definite crystallographic property and which you can differentiate from the x ray or x r d n analysis one can identify the phases formed they may be crystalline, they may be non crystalline or partially peri crystalline A, if you look at molecular sieve but zeolites are most of the time, they are crystalline in nature and that is their property. The definite and the phase is important property of the zeolite and they have a definite crystal structure.

So, both are porous in nature. So, molecular sieves are porous they can be but in the larger pore size also a wide pore size distribution may be available in the molecular sieve but in zeolite these are basically, micro porous or mesoporous material. So, most of the time we talk micro porous so that is important, when you look at a catalytic reaction activity then, framework cations and coordination may be this is a variable in the case of zeolite material, you know that it is a tetrahedron, that is a primary building unit in the case of zeolite but in the case of molecular sieves, it is not well defined.

So, it is just like a one d channel with some cations in the frame work then, variable frame work charge, because cations they may change. So, you can change the cations concentration type of cations. So, these are variable in the case of molecular sieve but in the case of zeolite, because it is anionic, because silicon aluminum they are connected in a definite area. So, a kind of electro negativity that is what you get in the frame work of the zeolite.

So, they are anionic frame work charge this for example, if you look at in the case of molecular sieve, the crystalline material are SAPO silica alumina phosphate type zeolites and non crystalline, these are carbon type of materials, carbon nano tube can be one type of that porous carbon materials, micro porous mesoporous carbon materials and Peri Crystalline materials, like MS41 again a code name pillared clays silicates clays are silicate types laminar structures. So, these can be a molecular sieve type of zeolites or molecular sieve size would say rather saying a zeolite there where as in the case of zeolite, because they are definite in frame work. So, ZSM-5, ZSM-12, most of these zeolites suconi mobil that is what, the type of zeolites are available or commercial use.

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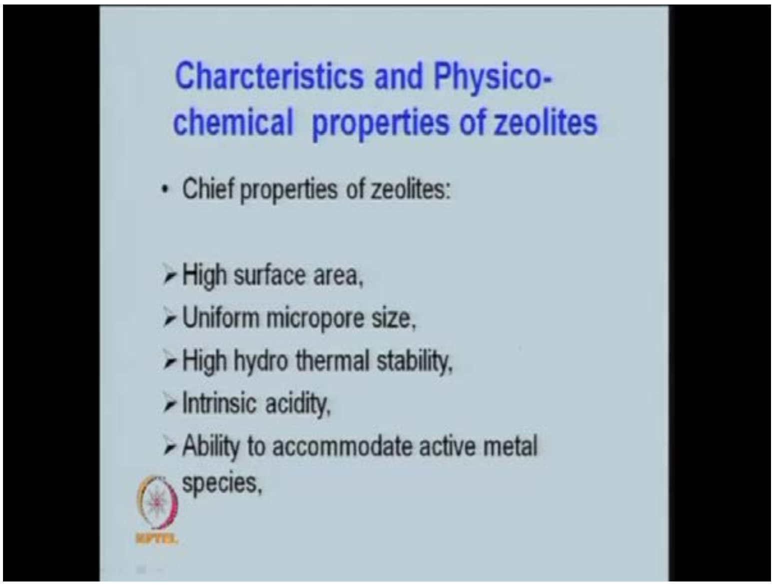

Charcteristics and Physico-chemical properties of zeolites

- Chief properties of zeolites:

- High surface area,
- Uniform micropore size,
- High hydro thermal stability,
- Intrinsic acidity,
- Ability to accommodate active metal species,

So, characteristic wise the zeolites are why zeolites important, because they have high surface area, because these are micro porous mesoporous material a smaller pores but large number of pores are available. So, their surface is high internal surface area and external surface area of the zeolite if you have a nano kind of zeolite material, nowadays again these kind of materials may be synthesized nano materials, nano zeolite, where external area may also be high so that is again an important issue and these kind of zeolites may be useful for some specific catalytic reaction also. So, they have very high surface area uniform micro pore size. So, unlike in your other commercial catalyst like alumina or silica, seriea and gerconia, they may have a wider pore size distribution.

So, depending upon you centering condition and calcinations, what you have done calcinations condition during calcinations centering may take place or at high temperature solid reaction. So, their pore size, it may vary in wide range but in the case of zeolite, the nucleates which forms and the crystals which develop during your hydro thermal synthesis, that is very important and the frame work depending upon the frame work of that zeolite their pore openings are in a narrower size range, because it is a kind of definite reaction or it when you talk a hydro thermal reaction basically, at high temperature and the sufficient pressure and you have the controlled P H some organic templating agents water and there, the nucleation take place. So, crystal forms and these crystal when, they grow, they have a definite kind of a structure.

So, perpetration of zeolite is entirely different compared to non zeolite materials. So, there are here, the phase and cage opening is very important. So, they have a uniform and micro pore size or micro meso pore type of size hydro thermal stability, because they are prepared under hydro thermal synthesis. So, they are thermally stable under certain conditions. So, only thing that, they are depending upon the type of zeolite and as I said nano size, nano synthesize zeolite material they may not be stable at very high temperature. So, roughly up to 550 degree centigrade or 600 degree centigrade, these kind of zeolites are thermally stable they sufficient acidity define the acidity. So, as I said, the acidity can be determined by air adsorption, i r spectroscopy. So, pyridine is used as a reference, because pyridine is a base. So, the molecules of or the pyridine adsorbed on the catalyst and then, it is measured adsorption is measured and then, you can have the idea about their Lewis acidity and bronsted acidity.

So, in a case of zeolite as I said that silicon to aluminum ratio is very controlled and important so that decides, the acidity also of the zeolite as positive ions which are there in the frame work and that provides the prognostic type of acidity. So, in the case of zeolite these are well defined. It is a well defined structure of a zeolite. So, the acidity is important and it is defined and they have ability to accommodate active metal especially. So, you can exchange that ammonia, exchange that is what gallium exchange at ZSM-5, which I was talking by replacing the protons and you can add sodium, calcium there ammonia there all kind of gallium. So, these kinds of metals can be added to the zeolite frame work by ion exchange method or by insufficient wetness method also. So, you can have modern mol ibid and m o at ZSM-5 mol ibid can be associated to the frame work or different copper gallium, which are good for some catalytic reaction.

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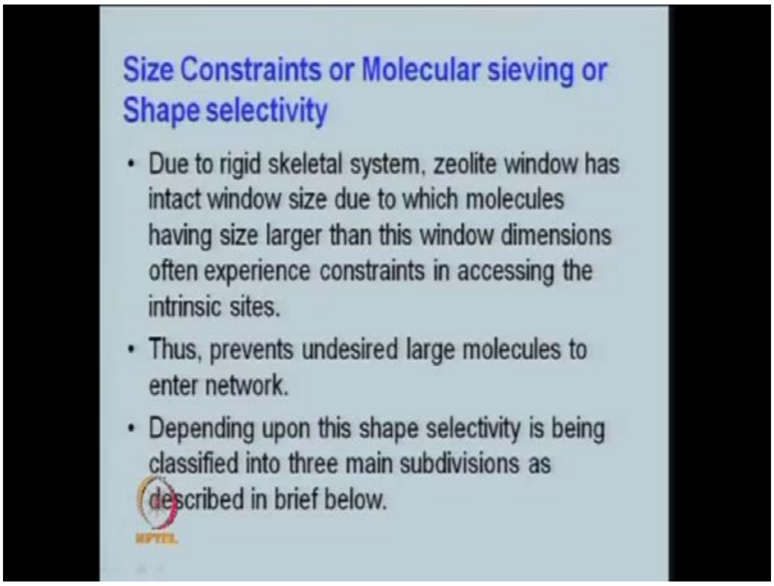

Size Constraints or Molecular sieving or Shape selectivity

- Due to rigid skeletal system, zeolite window has intact window size due to which molecules having size larger than this window dimensions often experience constraints in accessing the intrinsic sites.
- Thus, prevents undesired large molecules to enter network.
- Depending upon this shape selectivity is being classified into three main subdivisions as described in brief below.

So, size constraints if you look at or molecular sieving, because we are talking about the pore opening is also important in the case of zeolite the catalytic activity is not only because of this silicon to aluminum ratio which is providing the acidity but also the pore opening, because that controls the mass transfer or diffusion in a pore. So, your that when you have the certain the of course, the diffusion may be dominating if your molecular size are larger relatively larger or the conditions are not severe so that is one issue in the case of zeolite material the reaction may be a diffusion controlled also, if you are not properly designed your catalyst. So, when I used to check that also. So, as I said that it has rigid skeletal system all zeolites they have a definite frame work and very rigid skeletal system. So, because of that the zeolite window has intact window size. So, definite a pore opening, that I was saying, because of the buckyball structure where, you can have 6 membered ring, 4 membered 4, 4 or 6, 6 2 d channels.

So, they have a definite kind of opening and depending upon that some molecules having size larger than this window dimension they often experience constraints in accessing the intrinsic sites they cannot reach. So, it will depend on the kinetic diameter of the molecule versus the pore diameter or pores opening. So, should not say pore diameter in the case of zeolite because it has something like a into b the channel diameter it may have a different size. So, a into b five point seven times whatever into the five point four or whatever cage structure which may have different openings on x and y axis.

So that is one thing so that is a kind of sieving action. So, how many molecule can diffuse inside under a given condition temperature pressure where the diffusion coefficient is to be calculated for that given molecule in a mixture and then you can calculate that diffusion how many molecules are diffused and then accordingly we have to calculate so that is one sieving that is the restriction.

So, this prevents the undesired large molecule to enter the network so that is good in one way if you have the multiple reactant especially and some of the reactant some of the especially are there which are present in the reactant are impurities like sulphur molecule when you have hydro desulphurization reaction and the sulphur all larger molecule of red sulpher what I am talking a thiophene dibenzo thiophene which are large sulphur molecule. So, these can be separated or sulphur removal can be done by using a selected type of zeolite material just by adsorption it can act as sieving material.

So, in a definite kind of zeolite material I can have the feed stock from which the feed that is the naphtha or larger molecular weight compound can be retained they cannot pass through that zeolite material but smaller can pass through that. So, your cleaning or purification type unit and that can be one way that. So, because they are shape selective or I can have the other way also like just it is a polymer or some kind of poly condensation as I said aromatics are forming and aromatics are forming because of the say some or sorry coke is forming because of some aromatics which is present in the feed larger molecular weight aromatic hydro carbon. So, they may not go along with the hydro carbon feed mixture. So, they may be stopped.

So, zeolite will not allow them to pass or this can be a transition also that is during the reaction some kind of intermediate forms which may prone to go formation so that is what I said that the suppose you are taken methane molecule methane can diffuse inside a zeolite. So, it will transform into a larger molecule it will form some kind of say oliphene oliphene can react further they dehydrogenate or they oligomorize. So, they can form a larger larger molecule but when your pore openings are limited then it cannot form a very large molecule but it can form only selected range of hydro carbon suppose c 5 c 6 c 10 depending upon the kinetic diameter of those molecule and that can be that can easily come out in a given time diffusion length is also important in that way so that your further larger molecular weight compounds can be stopped because the pore length is small.

So, your diffusion resistance will be low in that case or simultaneously it will not allow to form a very large molecule because the diameter of the zeolite pore is smaller. So, that. So, these kind of sieving action can be molecular sieve is very important in the case of shape selective zeolites when you look at the reaction where you do not want to have the undesired reactions or undesired product in the reaction so that in that way, the zeolites are shape selective. So, product selectivity may be important or some time, it can sieve the reactant and which are undesired reactant raw material that can be selected as a shape selective. So, depending upon this shape selectivity and these are classified into 3 main sub division that is what, I already discussed that.

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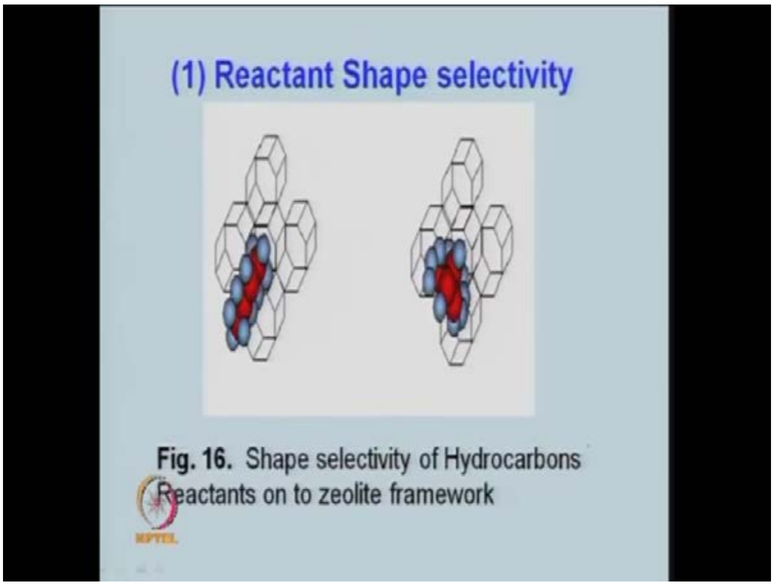

(1) Reactant Shape selectivity

Fig. 16. Shape selectivity of Hydrocarbons Reactants on to zeolite framework

So, I should just talk that first shape selectivity of the zeolite, which is related to this one reactant shape selectivity.So, reactant shape selectivity is something, where you have just look if you look at here, the molecules are oriented like this. So, they can pass through that but in reactant especially which is something like that, it has the difficulty to pass through the pore, because it is something like a isomer or it is a kind of ring compound so that may not pass but if it is along the compound, it is just like a stretch in paraffin hydro carbon this is something like your suppose butane or heptanes so that can pass through the zeolite frame work but this kind of molecule which may be aromatics or some isobutene that may not go, because the structure has branches. Now, so that has different kinetic diameter so that is a reactant safe selectivity.

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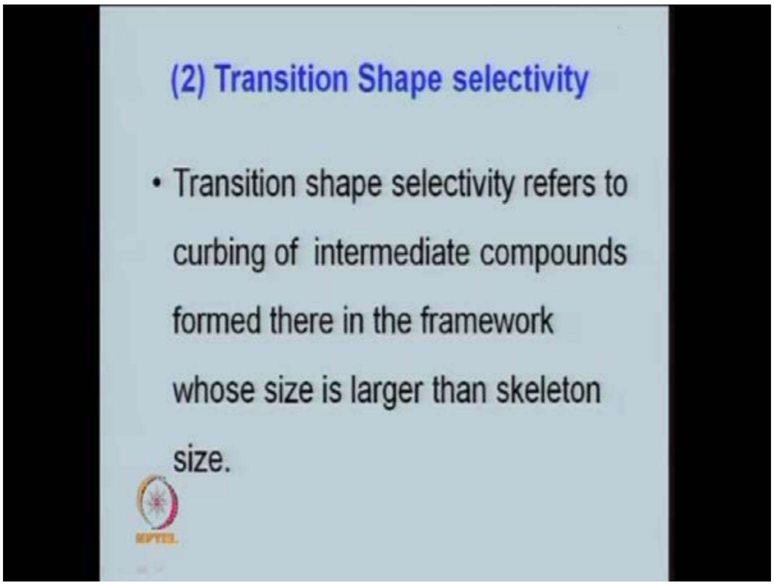

(2) Transition Shape selectivity

- Transition shape selectivity refers to curbing of intermediate compounds formed there in the framework whose size is larger than skeleton size.

Second step is the transition shape selectivity, which I was discussing so that is refer referring to curbing of intermediate compounds that formed in the framework of the zeolite whose size is larger than the skeleton size so that is what, I was saying poly condensed aromatic hydro carbon which is a coke precursor.

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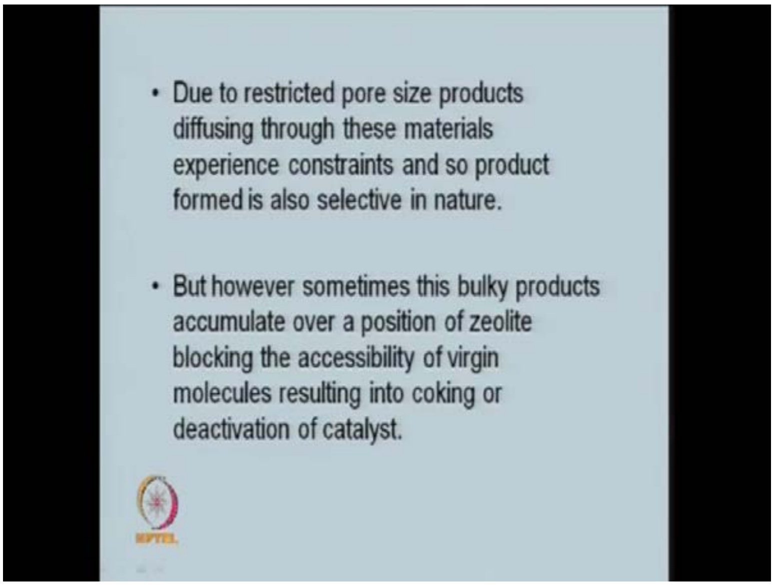

- Due to restricted pore size products diffusing through these materials experience constraints and so product formed is also selective in nature.
- But however sometimes this bulky products accumulate over a position of zeolite blocking the accessibility of virgin molecules resulting into coking or deactivation of catalyst.

So, these may not go into the frame work of the zeolite or it may not form inside the zeolite, because of the pore size. So, due the restricted pore size the product diffusing through these materials, they experience a constraints and. So, product formed is also selective in nature, you do not get the undesired large molecular weight compound, because of this transition safe selectivity nature of the zeolite.

So, but sometimes when, the bulky products accumulate over a position of the zeolite, that blocks the accessibility of virgin molecule resulting into coking or deactivation of the catalyst. So, these are some limitations, that sometimes their zeolite pore as you seen in the case of catalytic cracking f c c fluid catalytic cracking the because of the hydro carbon, which gives you a large molecular weight hydro carbon, when it cracks it forms some kind of say gasoline range of hydro carbon c 5 to c 10 with some iso paraffin more iso paraffin, these are desired or some kind of diesel also you can get but sometimes beside these, there may be.

Because it is not just a single reaction, there are several multiple reactions, secondary reactions do take place during that time and when this happens, the coke may be also one of that and that blocks the deactivation of the coke catalyst. So, in fluid catalytic cracking you need a continuous regeneration of the catalyst and that is what the fundamentals of the design of the fluid catalytic reactor and you need a regenerator also side by side and there, the generally these zeolites or stable zeolite catalyst are used.

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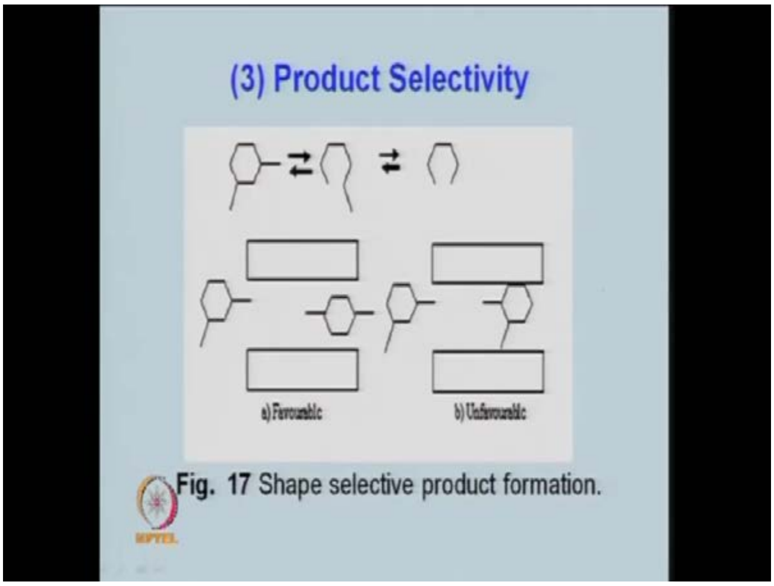

(3) Product Selectivity

Fig. 17 Shape selective product formation.

So, this is what, the product selectivity I was talking that, there can be a 1 ring compound, which opens like this and forms this. So, when you have a favorable reaction, you want a favorable reaction, this should form that is just like say if you look at the zilene separation if I just ortho meta para all kind of zilene may form, when you have the isomerization of zilene ortho meta para but a definite meta as I say undesired para zilene may be desired one. So, you can have the some kind of isomerization like this but this may be unfavorably Meta zilene. So, this is what, the safe selective product formation. So, if you have a proper tuning of the zeolite pore size.

So, it has nothing to do with the acidity of the zeolite, that is different, that may have to look at in a different aspect that, this cracking desired what kind of acidity is required but now we are talking just based on the molecular sieve, that is the type of molecular sieve in action with some acidity is there in the catalyst but now we are just talking based on the shape and size of the molecule. So, it means, this kind of reactions or adsorption, they are related to the kinetic diameter of the molecule versus the pore diameter or channel opening of the zeolite. So, 1 has to look at the channel size of different zeolites a, b, c and d like that, whatever there and the reactant especially their kinetic diameter under the given condition what molecules can diffuse or cannot diffuse and then, 1 can have the selection of a particular kind of molecular sieve zeolite for a given reaction.

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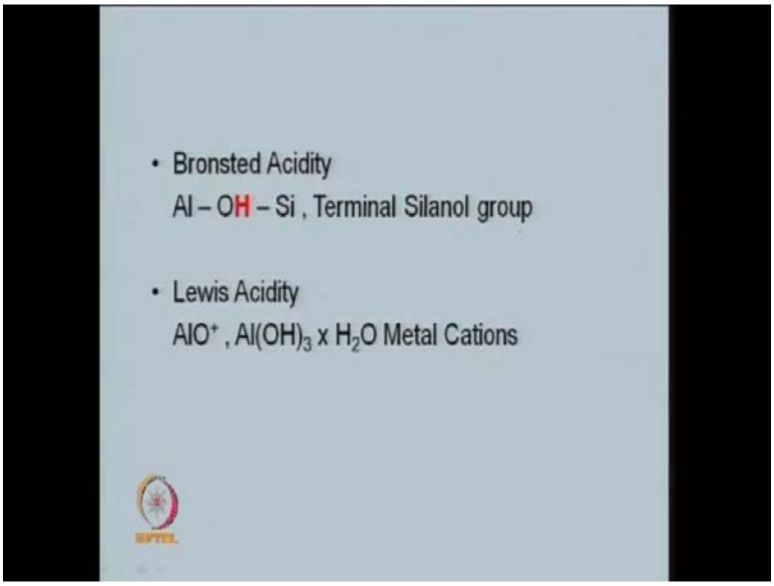

- Bronsted Acidity
  Al – OH – Si , Terminal Silanol group
- Lewis Acidity
  AlO^+ , $Al(OH)_3$ x H_2O Metal Cations

So, let me go back now again. So, we were talking now, the structures of the zeolite and before that, the acidity of the zeolite. So, we have already said about that, two type of acidity may be possible in zeolite 1 is known as bronsted acid sites, which is because of this proton as plus so, terminal silanol group and contains the H and when you heat it goes through the Lewis acid sites, which are basically because of these presence of these in the frame work of the zeolite stronger acid sites and weaker acid sites, protonated zeolites or these ability to exchange the proton or ability to donate an electron. So, depending upon that, the bronsted acids or Lewis acidity is defined correct. So, the bronsted site means, it can donate a proton.

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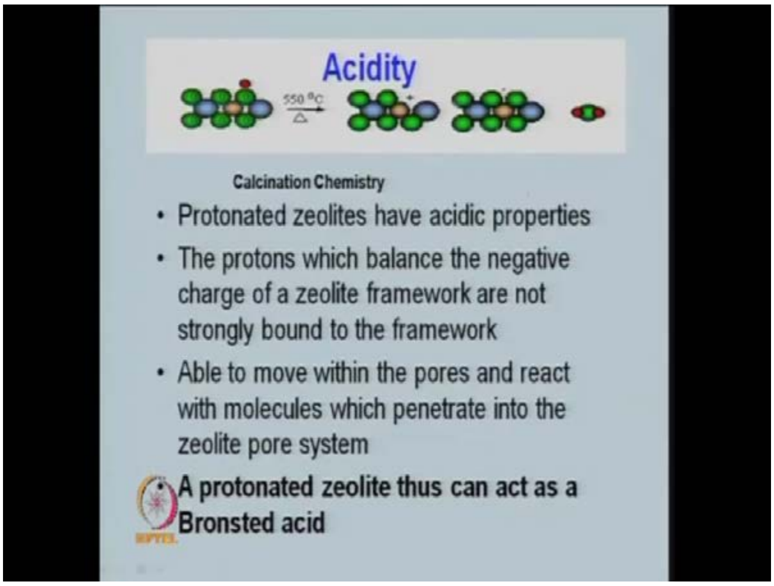

Acidity

Calcination Chemistry

- Protonated zeolites have acidic properties
- The protons which balance the negative charge of a zeolite framework are not strongly bound to the framework
- Able to move within the pores and react with molecules which penetrate into the zeolite pore system
- **A protonated zeolite thus can act as a Bronsted acid**

It has proton Lewis site means, it ability to accept an electron, this is what shown here. In the case of zeolite when you heat it to a 550 degree centigrade temperature then, this bronsted site which is shown here, H proton that converts to a Lewis acid sites like this and some kind of negativity. So, it can donate this electron here and the water gets separated. So, this is your water. So, this is what, the shown here in the transformation this to this.

So, protonated zeolites, they have the acidic properties as I discussed before also and the proton which balance the negative charge of the zeolite frame work are not strongly bound the frame work. So, they can mobile in one way. So, they are not strongly bound to the frame work. So, they are able to move within the pores and react with molecules, which penetrate into the zeolite pore system, because they are mobile in the frame work of the zeolite. So, when the reactant, especially just like a cracking reaction, you need a kind of proton protons there. So, it forms, because the cracking is basically based on the carbon mechanism.

So, methane carbon the cracking of say heptanes, the even pentane and earlier it was naphtha cracking, the paralysis naphtha basically for oliphene but cracking of naphtha is basically for the gasoline range of hydro carbon. So, f c c cracking which you see now for atmospheric gas oil or vacuum gas oil or residue v r, so that is based on that is zeolite based catalyst are used, because they have the strong H positive ions there. So, they this is based on cracking reaction is mainly based on the carbonium ion mechanism and then, the secondary reactions take place and you get the kind of gasoline range of hydro carbon which is known as f c c gasoline. So, this is important in the case of bronsted type of acidity.

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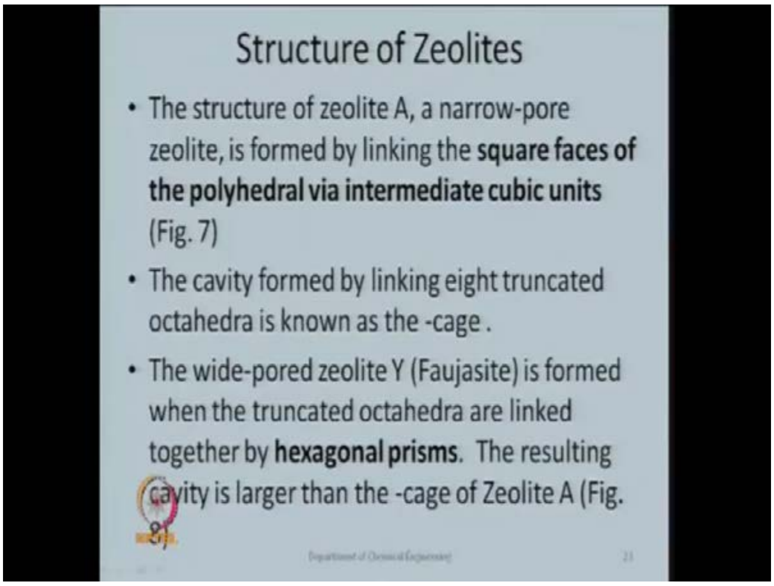

Structure of Zeolites

- The structure of zeolite A, a narrow-pore zeolite, is formed by linking the **square faces of the polyhedral via intermediate cubic units** (Fig. 7)
- The cavity formed by linking eight truncated octahedra is known as the -cage .
- The wide-pored zeolite Y (Faujasite) is formed when the truncated octahedra are linked together by **hexagonal prisms**. The resulting cavity is larger than the -cage of Zeolite A (Fig. 8)

So, a protonated zeolite, thus can act as a bronsted acid structure wise if you look at that we have talked so many times, structures of zeolite which is a type zeolite linde a. So, it is a narrow pore zeolite and which is formed by linking the square faces of the polyhedral via cubic units. So, this is the same thing, what I talked before that, the primary building then secondary building and then a tertiary.

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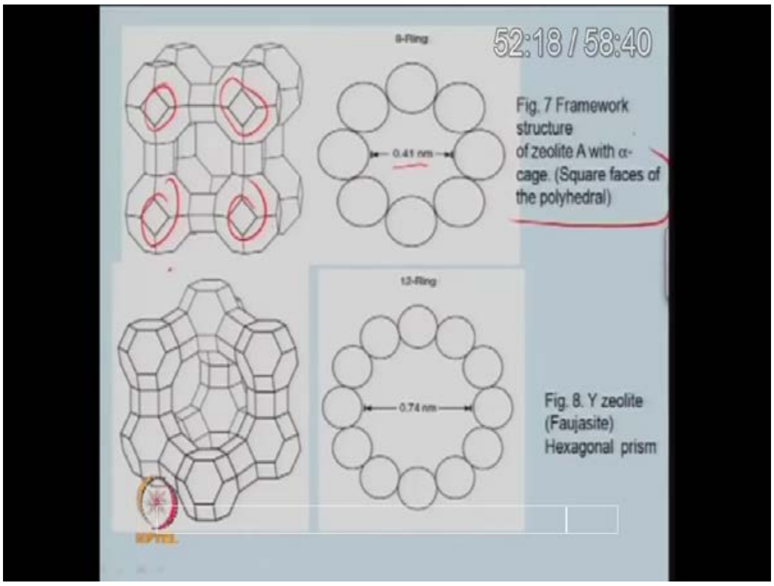

Fig. 7 Framework structure of zeolite A with α-cage. (Square faces of the polyhedral)

Fig. 8. Y zeolite (Faujasite) Hexagonal prism

So, in a type you have a square faces of the polyhedral which is connected by intermediate cubic units something like, what is shown here, this is 8 member ring here and zeolite a type structure. So, this is one if you look at these kinds of connections here and these are, this is the bridging between two buckyball structures. So, one sodalite cage, another sodalite cage and they are interconnected. So, you have the channels which are something like this, based on this connection of roughly 0.41 nanometer. So, same on both side.

So, 8 ring, 8 member ring but bridging is from the square side here. So, the frame work is structure of zeolite A with alpha cage. So, square faces of the polyhedral are interconnected, that is what I said that, several footballs are placed. So, which is face is now with frame work of that crystal is attached or oriented so that will give you a kind of opening of the pore. So, the cavity formed by linking 8 truncated octahedral, that is known as the cage alpha cage, beta cage what I was talking different kind of cage structure sodalite cage structure can be obtained from this.

So, in the case of wide pore zeolite say zeolite Y. So, narrow pore zeolite, it may because you know that narrow pore zeolite means, it will have 4 number of rings, 6 numbered rings like that and again in hexagonal to hexagonal or squares are edged faced what I said projection of that. So, in case of wide pore zeolite that is larger diameter zeolite which is just for example, a zeolite Y, faujasite type. So, faujasite is a large pore zeolite, linde A that is type a zeolite is a narrower pore size zeolite ZSM-5 is kind of mesopore zeolite. So, wide pore zeolite Y, which is faujasite so that is formed, when the truncated octahedra are linked together by a hexagonal prism. So, the small pore by square and these are connected by a linked together by a hexagonal prism and this resulting cavity is larger than the cage of zeolite a. So, you can see here.

So, this is now the 1 hexagonal, this one. So, these are connected, all these hexagonal after the frame work is connected in this way whereas, see both are similar buckyball structure. So, but the connection instead of here, it is now from this side, this is one which is shown now projection here and the same structure is here if you look at in here this side. So, it means the orientation of that frame work one cage sodalite and there are several sodalite cages are attached. So, they have some square some hexagonal frame. So, which is connected to that another cage and making a structure. So, you can see here that, this is 0.41, nanometer but here it is 0.74 nanometer and the number of oxygen. Now, in the ring are 12 rings. So, this is Y type zeolite which is based on the hexagonal prism.

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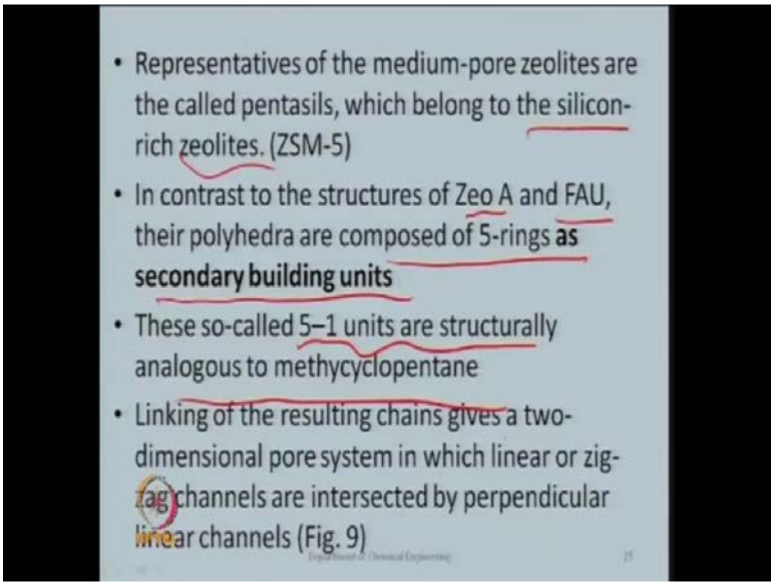

- Representatives of the medium-pore zeolites are the called pentasils, which belong to the silicon-rich zeolites. (ZSM-5)
- In contrast to the structures of Zeo A and FAU, their polyhedra are composed of 5-rings **as secondary building units**
- These so-called 5–1 units are structurally analogous to methycyclopentane
- Linking of the resulting chains gives a two-dimensional pore system in which linear or zig-zag channels are intersected by perpendicular linear channels (Fig. 9)

So, representative of the medium pore zeolites, these are known as pentasil. So, structure wise which I have shown before also. So, pentasil zeolite and belong to the silicon rich zeolites ZSM-5. So, in the case of ZSM-5 in the silica to alumina ratio goes from say, 10 to 500, high silica alumina to silicon to aluminum ratio. So, in contrast to the structure of zeolite A and faujasite, which we have seen earlier, their polyhedra are composed of 5 rings as a secondary unit. So, in A, it was 4 in the secondary building, the different building blocks which I have shown before. So, in the case of zeolite A, it was 4 in the case of faujasite. It was hexagonal prism, which you have seen in this case this, this is 4, this is 6 in the case of zeolite.

It is 5, so that is what they are known as pentasil zeolite. So, they have 5 rings as a secondary building unit as b u and that is why they are mesopore in nature. So, it means the 0.41, I told as a micro porous point seven one nanometer is a kind of a macro pores or larger pore not the macro pore but these are smaller that is in between these two what.

In the case of zeolite or faujasite, we do not have the macro pores basically, because they are already in a frame work of the zeolite not the pore space between the particle, so that is what the zeolites when you say ZSM-5, these are meso porous type of metal, which has the between say 20 angstrom to say 50 or 100 angstrom something like that. So, these are called 5, 1 units and are structurally analogous to methyl cyclopentane. So, just like if you look at methyl cyclopentane, the structure of the ZSM-5 is something like similar to that here.

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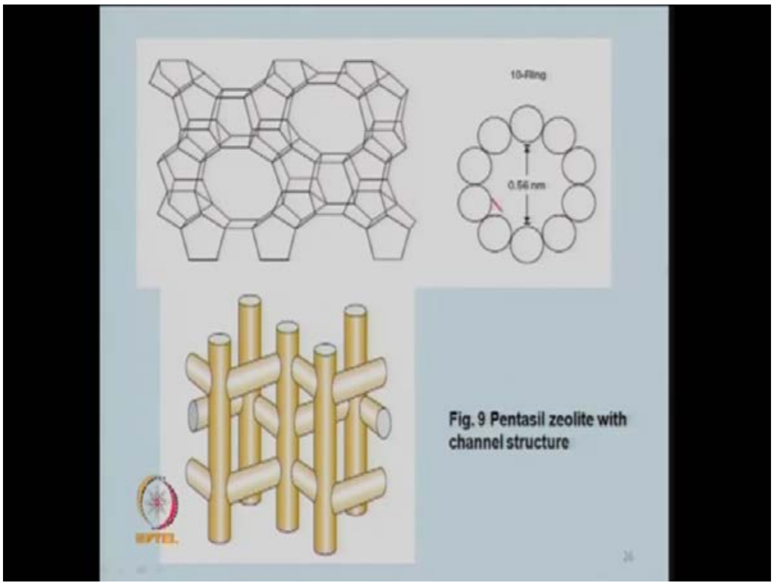

Fig. 9 Pentasil zeolite with channel structure

So, roughly 0.56 nanometer, this is the opening and these are 10 rings in this oxygen rings but the frame work is from the pentasil structure, which is shown here if you look at here, this is 1 like this. So, all these pentasils have made this 1 cage and this is what referring to this. So, this is your s b u basically secondary building unit where, all these centers will have T atoms here, all these corner will have these corners have T atoms centers has oxygen atom and then, these are connected with that pentasil and this is making 1, 10 membered ring, 1, 10 ring. So, it can be 10, 8 and 12 like that in the case of zeolite itself, different kinds of zeolites are available. So, this is what, the channels of that zeolite.

So, linking of the resulting chain that gives a 2 d pore structure in which, the linear or zigzag channels are intersected by perpendicular linear channels. So, there can be a different kind of structure of ZSM-5 which is here in the terms of pore opening. So, ZSM-5 is something like a pentasil zeolite with this kind of channel but silicon to aluminum ratio may be varying, it can be different. So, I will stop here and I will continue it next time.

Thank you.