Heterogeneous Catalysis and Catalytic Processes
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Module - 07
Lecture – 19

Good morning. So, last time we were talking about zeolite and the frame work of the zeolite structure, of the zeolite and effect of silica to alumina ratio on the composition on zeolite properties. Let us, look at some synthesis aspects of the zeolite also; today I will talk on zeolites synthesis but, before that.

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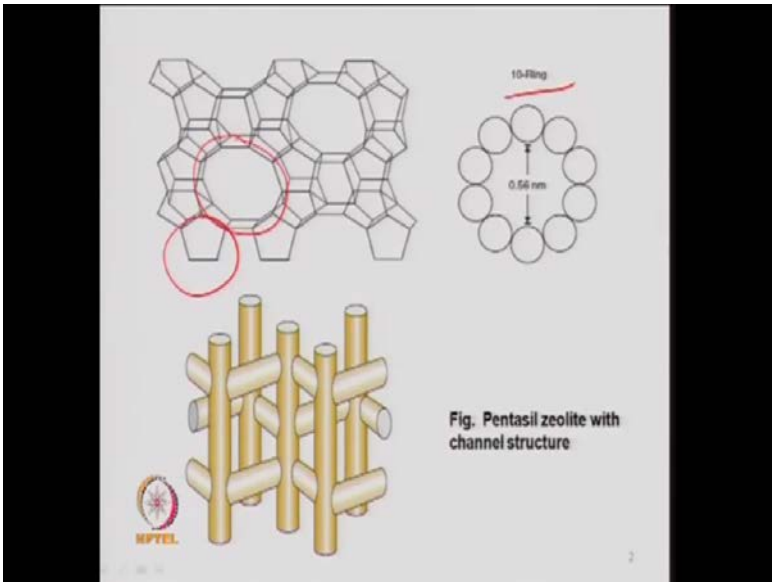

The some continuation of the last lecture where I was talking the formation of the pentasil zeolite, so these are 5 member ring and secondary build in log and then these are attached to the frame work so, different so 5 member rings which is your pentasil structure and which is connected so, basically when you look at this structure the cage opening that has 10 rings here in terms of 10 member options but, the orientation of that crystalline phase which I was talking yesterday it can be with the square opening it can be hexagonal opening and this is what a kind of pentasil zeolite.

So, which has a pore opening of roughly 0.56 nano meters so, these are different kind of zeolites and you can have accordingly this side diameter channel diameter and the horizontal channel diameter and that depends on the frame work of the zeolite crystal

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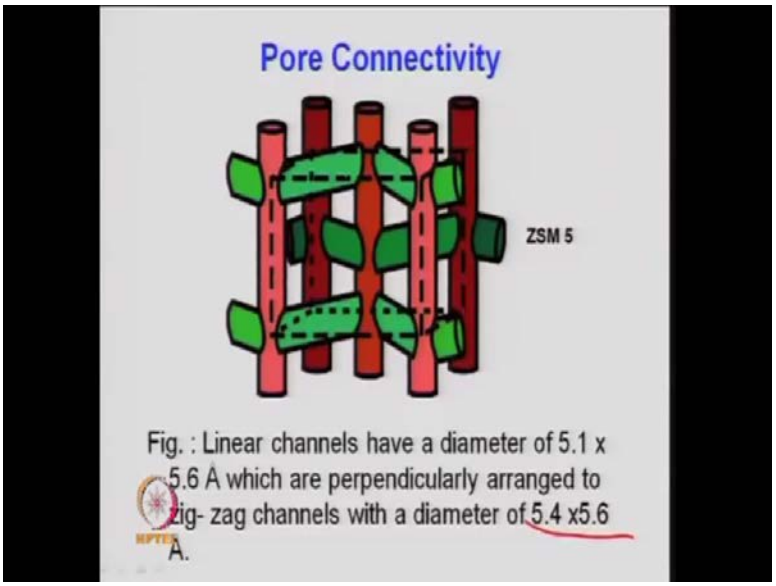

So, this is what the frame work has been shown here so, horizontal and the vertical so, the channels roughly if you look at here, the linear channels have diameter of 5.1 by 5.6.

So that, is the cage opening of the zeolite based on that the pentasil structure, the s b a secondary building unit and which has now condensed polymer and then the further condensation and you get a cage type structure so, here and if you look at vertical zigzag channels, which are arranged perpendicularly to this and they have roughly the cage opening of 5.4 by 5.6 angstrom. So, it means depending upon these are interconnected channels now, interconnected pores in the zeolite and that gives the very complex geometry of the pore and that is helpful in certain kind of chemical reactions.

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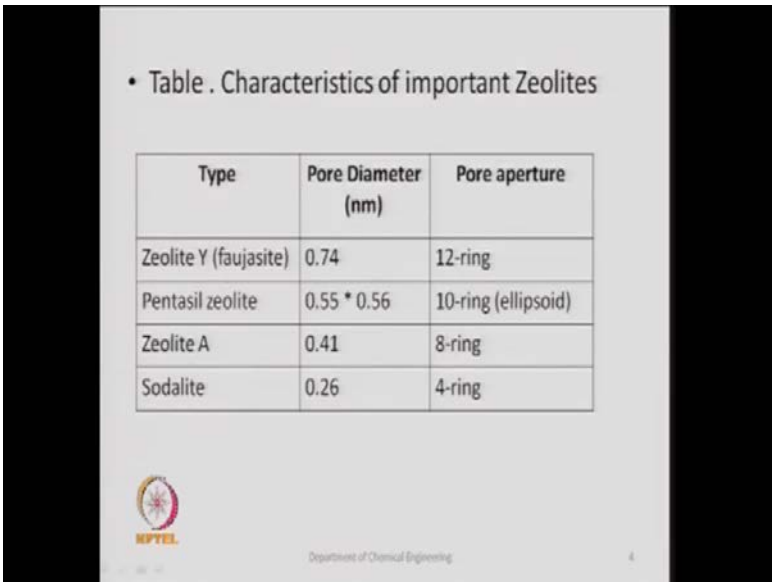

So, depending upon these the frame work or primary building units, secondary building units or silicon to alumina in the framework you have different kind of zeolites and different types of the pore structure and opening so, zeolite why which is a faujasite type so, large pore zeolite basically larger pore size 0.74 nano meter and 12 ring so, number of more the number of rings, the cage opening will be more T-O-T atoms which I am talking pentasil zeolite, that is in ZSM 5 category opening roughly between 0.55 into 0.56 so, for horizontal and vertical structure of that and 10 ring ellipsoid type zeolite a has a pore diameter of 0.41 nano meter 0.41 angstrom 8 rings in the structure cage, structure sodalite cage, it has pore diameter 0.26 so, comes in the category of micro porous or meso porous material and 4 rings.

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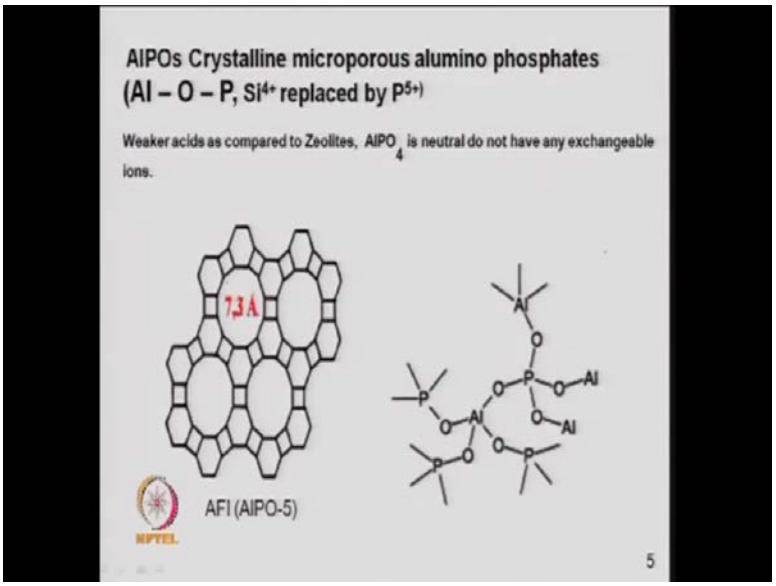

So, as I said that basically silicon Aluminum and oxygen is in the range so S i- O- A l structure builds like this something here, again oxygen's are connected to the frame work.

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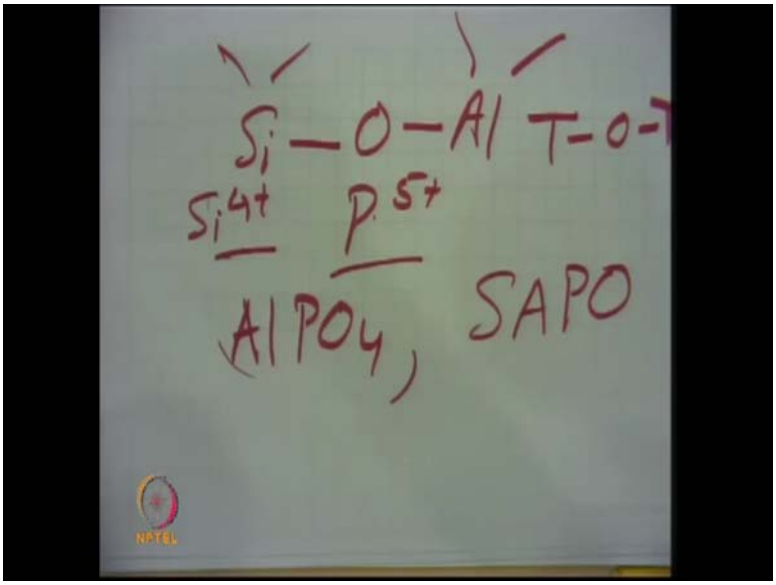

And this structure builds, sometimes this silicon can be this S i 4 plus can be replaced by phosphorous 5 plus. Which does not give the acidity to the zeolite rather a it can be a kind of neutral zeolite or mild acidic zeolite, it depends on the amount of this phosphorous. So, we can have different categories so what I said earlier also T-O-T

where T is either silicon aluminum or phosphorous also so, then it can be an either alumino phosphate zeolite ALPO4 sometime like this or also we called SAPO silico alumino phosphate.

So, there can be silicon there can be aluminum and phosphorous or all the silicon can be replaced from the framework by phosphorous 5 and that will again you will have a kind of alumino phosphate type of zeolite so, these zeolites have mild acidity to 4 reactions something like methane conversion to aliphane hydrocarbon so, SAPO can be used so, because, stronger acid sites may give more co, on the catalyst.

So, here the ALOP so, alumino phosphate type zeolite or in some cases the you just replace again the phosphorous by silicon you can have a SAPO type zeolites also, the weaker acids compared to the zeolites and ALPO4 type molecular acids they are generally neutral and do not have any exchangeable AL5 plus. So, the pore structure so, again you can see here the phosphorous oxygen aluminum then again oxygen phosphorous and aluminum so, on so this structure builds up so, which can be something like this roughly 7.3 angstrom of pore opening so, different kind of frameworks or this alumino phosphate zeolites can also be made by this.

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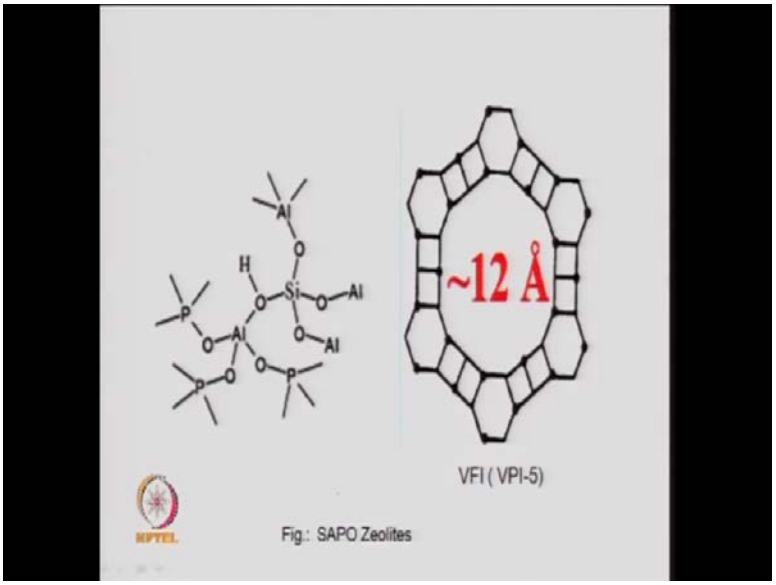

So, this is again a type of SAPO zeolite, where the origin of petroleum institute and this is a 12 angstrom and that is the pore opening of the zeolite and number of rings can be calculated 1 2 3 4 5 6 something like that so, different kind of silico alumino phosphate

zeolites can be formed depending upon the silicon to aluminum ratio and the phosphorous introduced into the framework of the zeolite.

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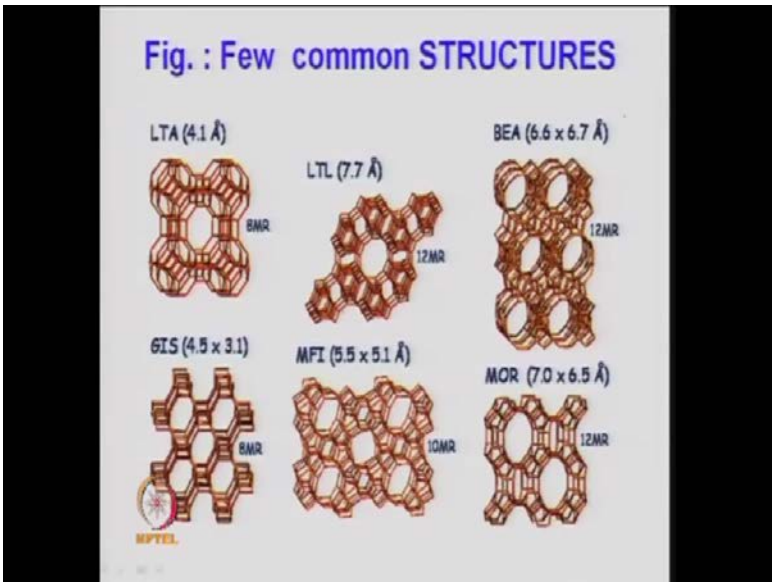

So, as I discussed last time there can be different kind of structures of the zeolite so, you have LTA 4.1 angstrom that is one kind of zeolite, then that is LTL type 7.7 angstrom pore opening another type of 12membered ring, this is 8 member ring, 12 so, diameter cage opening is increasing this is a 2 d structure type so, 6.6 by 6.7 so,12 membered ring again this is GIS 4.5 by 3.1 so, 2 d 3 d cage structures can be formed so,1d channel or 3 d channel so, there can be a 3 d structure in the form of zeolite material. So, different depending upon the option content the different option member ring can be associated to the zeolite depending upon the silica to alumina ratio in the zeolite and the structure of the primary building unit.

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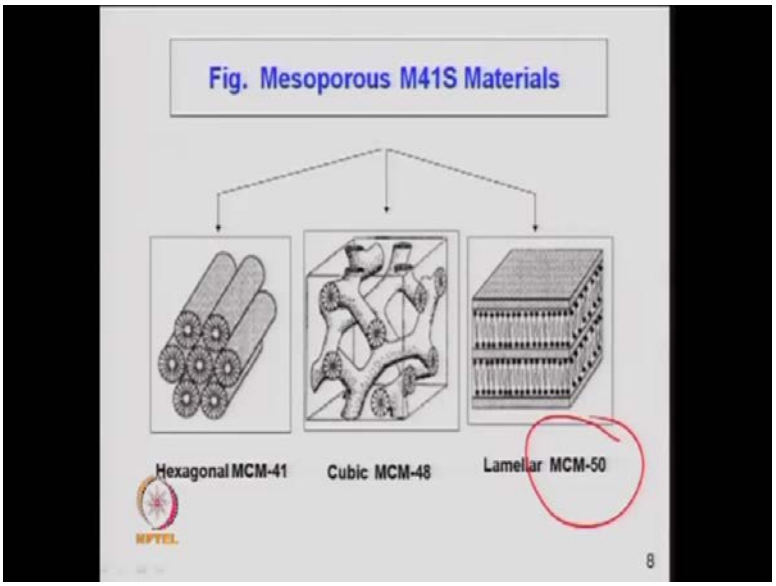

This is again another category of Meso porous material MCM Micro porous line or Meso porous materials and there again you have the different kind of say 3 d structure this is just a kind of 1 d structure and laminar structure, sleek type structure like k material so, different kind of these micro crystalline materials can be made by selecting the silicon aluminum and the preparation condition. So, they have very specific property in terms of the catalytic activity. So, generally there can be only a silica also with large amount of silica also as acidic in nature so, the different type of MCM materials can be prepared so, MCM 22 MCM 41 so, with high silica to aluminum ratio.

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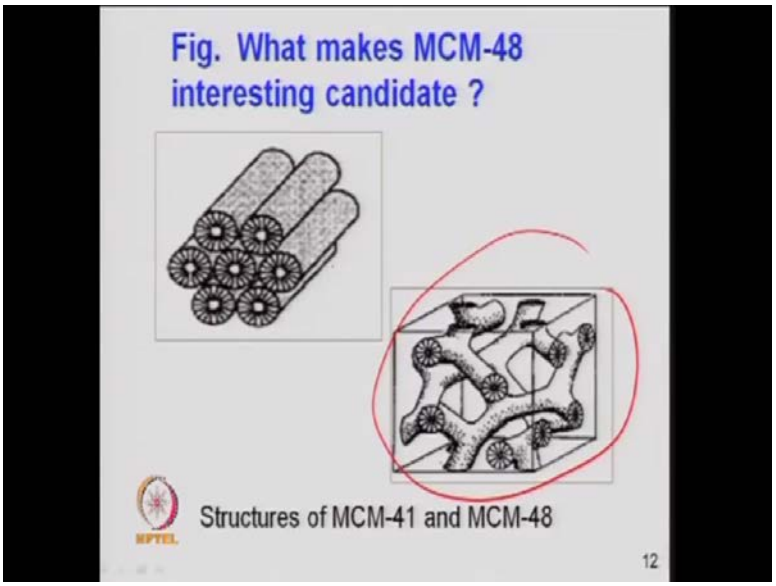

So, they have certain importance like this MCM 48 you see it is a 3 d type of structure and this is just an MCM 41 which has just a laminar or 2 d or laminar structure,1 d different kind of channels can be here.

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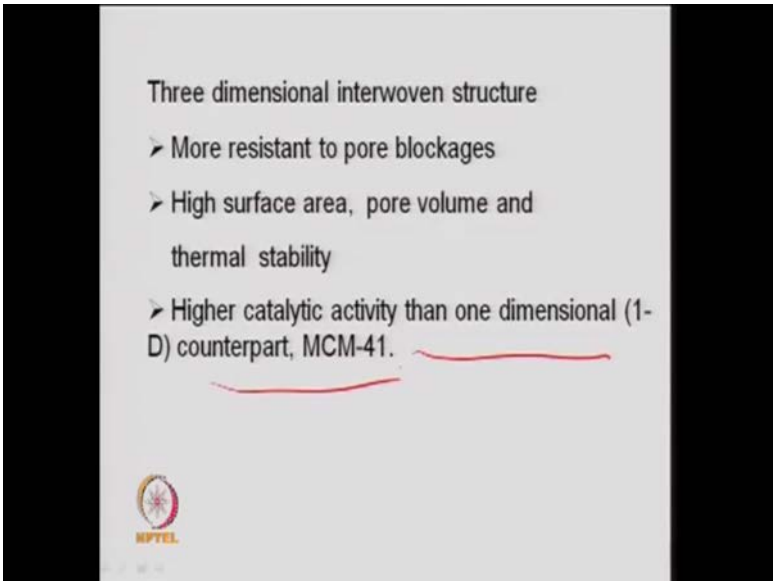

So, the important thing is that the MCM 48 is more resistant to pore blocking depending upon the cage openings and the acidity of that catalyst they have high surface area high pore volume and they have good thermal stability because, stability of zeolite is one of the important issue at high temperature, they do not sustain the structure collapse when you have high temperature because, the framework that collapse at higher temperature and higher catalytic activity than 1 d which is your MCM 41. So, MCM 48 which is a 3 d type structure has certain property in terms of the catalytic reaction so, they are better.

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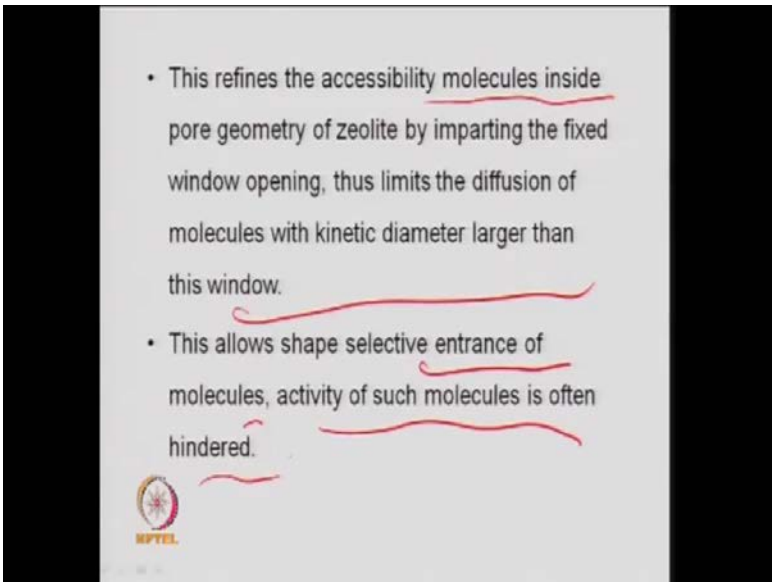

So, because of this 3 d it refines the accessibility of molecules, what I was talking the safe selectivity so, they are safe selective so, accessibility of the molecules inside the pore geometry of the zeolite by imparting the fixed window opening so, they have very definite window size and thus limits the diffusion of molecule within kinetic diameter larger than this window.

So, a larger molecule whose kinetic diameter is larger than the pore diameter or pore opening it cannot go into the pore of the Zeolite so, it becomes a safe selective so, all the time when we talk a zeolite material the pore opening becomes important because, the controlling parameter is the diameter or size of the pore because, these are Micro porous Meso porous material and that is to be compared with the kinetic diameter of the reactant species or also the protected species then you can have the idea about the product selectivity.

So, one can take a definite kind of pore openings or prepare a definite kind of zeolite material or molecular material depending upon the kinetic diameter of the reactant so, especially when you look like methane conversion to higher hydrocarbons or hydro ionizations reactions like the of these larger molecular weight paraffin's and you need to ionizes them for the diesel range of carbon or gasoline range of hydrocarbons and when you have physiotope reaction, then you get a series of product so, these products needs

up gradation so, hydro ionization required and when you do that, you need to find a definite kind of pore structure pore geometry along with the acidity.

So, diffusion and the kinetic is very important in these kind of definite pores so, it may not allow the larger molecule so, reaction is not possible if the pore size is too small so, that is also important so, you have to just look at this allows the safe selective entrance of the molecule, activity of such molecule is often hindered so, the molecules are larger or kinetic diameter of the reactant species is larger it may not diffuse into the pores of the zeolite and because, of that your total rate of reaction will be low because the molecules may not go into the pore so, there is no chance of the chemical reaction or very less limited chance of chemical reaction. So, one has to look at the kinetic diameter versus pore opening in the case of molecules reaction which is true in all catalytic reaction.

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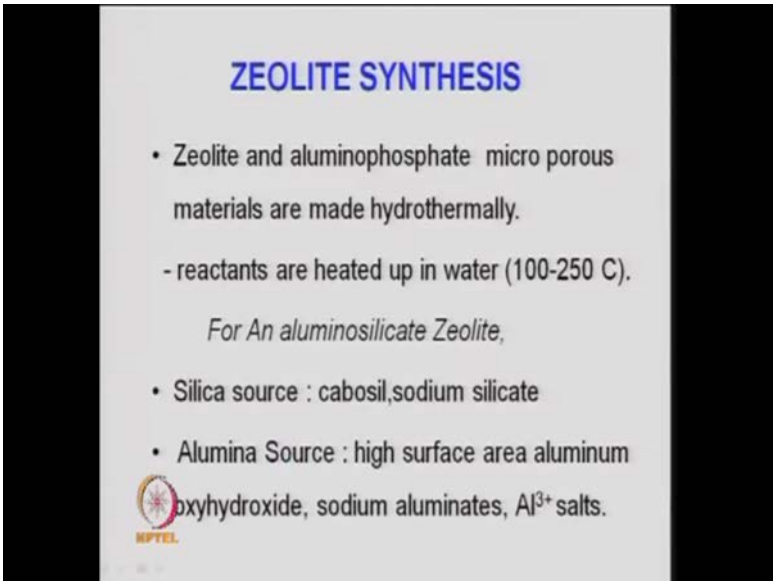

So, with this background let us, come to the synthesis because, once you look at this kind of definite structure definite pore opening a definite silicon to alumino ratio so, the preparation becomes very crucial part in the zeolite synthesis, unlike you are the non zeolite materials or other catalytic material like silica alumina or seria zirconia so, these type the weather preparations are well known or well defined in terms of either watt impregnations co precipitations solder methods.

So, these are well defined but, in the case of zeolite synthesis the method of preparation is very important or very crucial and the it is a kind of reaction a kinetic controlled

reaction which is very slow reaction or ion exchange process, it takes a large time and a definite temperature because, the crystals or definite shape of the framework is forming on which the further condensation takes place so, you need a definite kind of structure will look at these kind of a definite zeolite preparation of a definite zeolite and these most of these information are in the form of patents.

So, all of you know now that they are either calcium silicate acuminate material so, alumino silicates or phosphorous can be imparted to control the acidity in one way so, basically either you see zeolite alumino phosphate or the Meso porous, what I said or moleculasy material they have one kind of process which is known as hydrothermally synthesis.

So that, is in the process of water and under autogenously condition you are just allowing the raw materials to come in contact and form a kind of gel, the formation of gel is very crucial because, the structure building agent which you are added and the type of gel that will decide the framework of the zeolite the crystallization which takes place during this process and then nucleation crystallization so, all these gives you the size of the crystals so that, is also equally important.

So, water a large amount of water may not be good hydrothermal does not mean that you need a large amount of water this may slow the process, it may hinder the process so, generally the temperature required for the reaction is 100 and 250 degree centigrade but, again it depends on the type of zeolite whether low temperature high temperature it depends on the type of silicon to aluminum ratio, which is desired in the final zeolite so, by having some numeral calculations you have to decide what silica to silicon to alumina ratio is desired in the framework, whether caution exchanger is required whether protonation is required or whether phosphorous is required and what to what extent so, you have to take a definite amount of these raw materials and then look at the amount of water.

So, effect of water may be one process. Parameter temperature may be another process parameter time of this hydrothermal reaction or synthesis reaction is a very crucial factor again because, the gel and the nucleation from that gel is depending on the temperature versus time correlation. So, just if I look at here alumino silicate type zeolite so, you

need a kind of silica source one can take any type of silica source so, cabosil sodium silicate which is just a glass material so, these can be taken or any other silica.

So, because the only definite amount of this silica is required and that is for the gel formation which is the initial reaction and then you need an alumina source so, again a basically high surface area alumina, aluminum or bomite powder or aluminum oxides or some kind of solution of that can be taken some which can form the gel or which can form some complex because, it is a reaction between the silicate material and Aluminate material so, it should these both these two should be in the solution form so, a definite solution or solvent is required to dissolve them so, any type of these materials can be used for this purpose.

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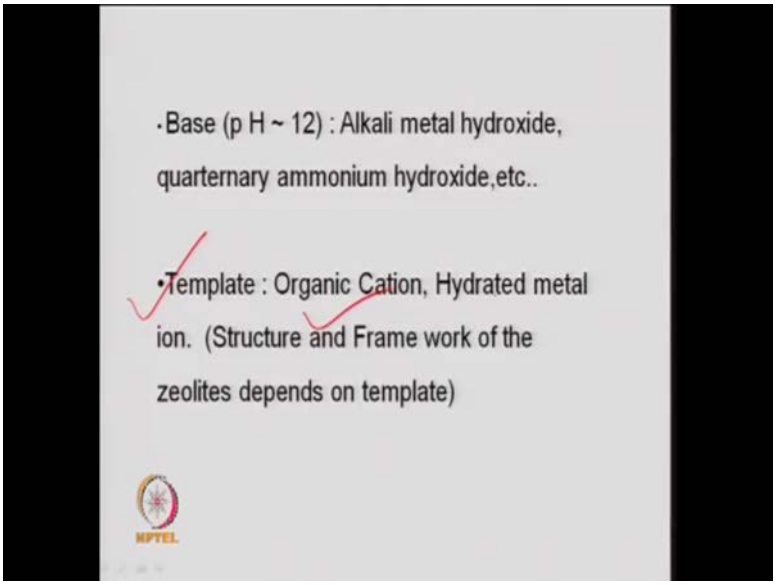

Then p H is very important generally the basic medium is desired 10 to 12 and that again depends because, it provides the hydroxide, during the reaction that has some important when you look at the complex which forms during the reaction and the structure, which builds that is a function of p H also. Then template agent is very crucial because, it decides the framework and structure of the zeolite the caution type arnometallic complexes which forms that template is a kind of masking on which these structure forms basically, your chemical structure or gel forms inside that and when that this template removes then you get that kind of framework of the zeolite.

So, organic cations, hydrated metal ions these can be used as a templating agent structure and framework of zeolite depends on the template so, selection of the template is also important so, you can use glycerol's you can use alcohols, iso propenol so, these can also act but, there are several other type of templating agent in the form of organic cations so, which can be the structure building agent for the synthesis of the zeolite. So, the process because as I said it is a kind of ion exchange process if it is you are adding some kind of cations to the system or protons to the system and basically it is a kinetic control slow reaction, very slow reaction you have to give enough time here.

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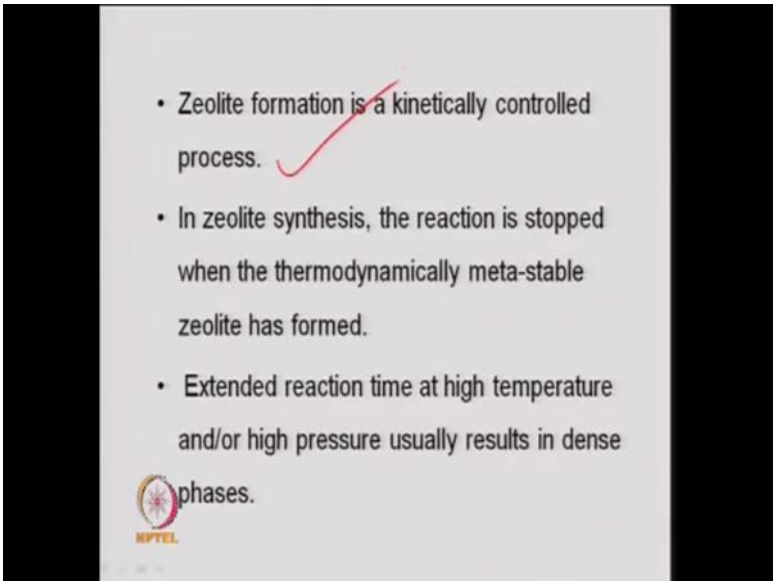

When slow reaction zeolite synthesis, the reaction is stopped, when thermodynamically Meta stable zeolite has formed. So that, is just from the thermodynamics so, you have to give enough time the reaction is kinetically controlled and based on that you have to just identify whether 24 hour or 7 days, sometime 20 days so, because the reaction or the kind of silicate to Aluminate framework which is forming depending upon the raw material.

So, if you look at that effect you have to check the time to time you have to take out your sample from that and take the XRD and then compare whether are you getting what you need actually item because, these should be a highly crystalline material and if you do not control that if you do not have the proper time and temperature relation or then you may not get a definite kind of zeolite framework. So, it may be a type zeolite you need

an ASM 5 or different x y these can form during that. So, it is a kind of growth of the crystal formation of the framework and the definite kind of framework as I said 4 membered ring 6 membered rings, 12 membered so that, is also equally important.

So, it may be an initial case may be, it may be a heat and trial also you have to just try in different conditions. So, extended reaction time at high temperature or at high pressure usually results in dense phase so, pressure purpose is to dandify the system and generally its autogenous pressure you have kept water or sufficient amount of water and given the temperature left it for say in a bath and the water gets in the system vaporized. So that, creates the pressure inside the system and that is why it is hydrothermal, what the word has been used.

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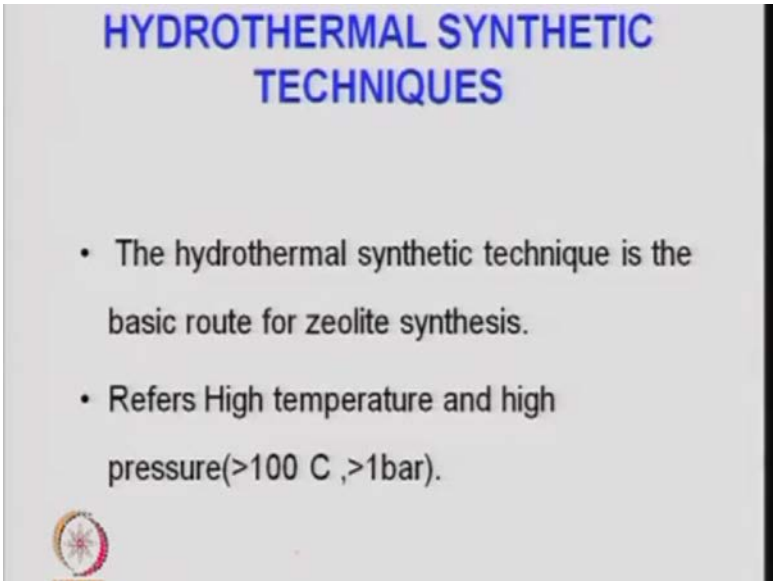

So, hydrothermal synthesis techniques which just briefly I will talk some procedural steps of the zeolite formation and the hydrothermal synthetic technique is basically a simple rule for the formation of zeolites and well known it is a the steps are well known but, only thing that how do you control the steps and to get a definite shape and that reproducibility is a crucial step and the high temperature and high pressure. So, generally more than 100 degree centigrade and pressure more than 1 atmosphere so, which is roughly 20 atmosphere 12 atmosphere so, at definite atmosphere the reaction can be carried out.

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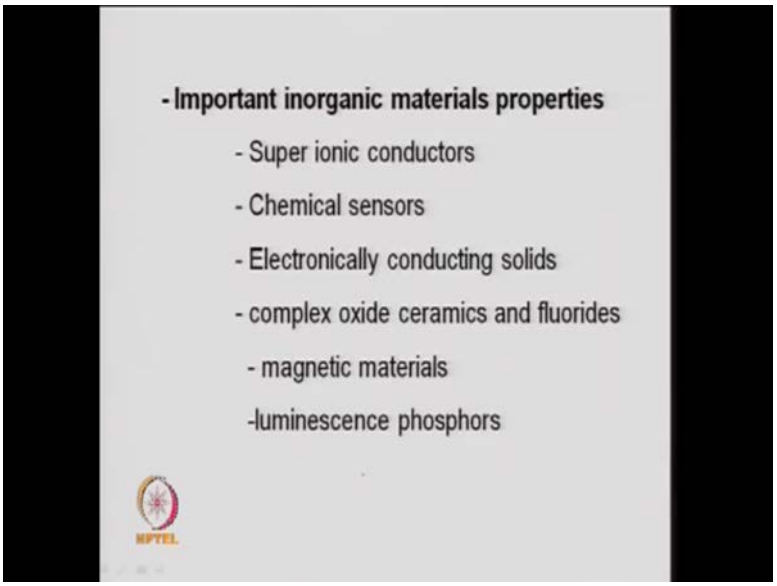

The organic inorganic materials which are used for this as a templating agent that is also equally important so, what kind of material should be selected say here inorganic materials, which are generally used they have the pseudo super ionic conducting property it is a kind so, they should have some ionic property chemically sensors electronically conducting solids complex oxide ceramics or fluoride magnetic and these kind of properties which are desired in the final material. The selection of the material raw material is important, when you have a different type of zeolites which I just talked here in this case. So, to have this kind of structure we need a different kind of raw material so that, is to be selected on a try again with definite properties.

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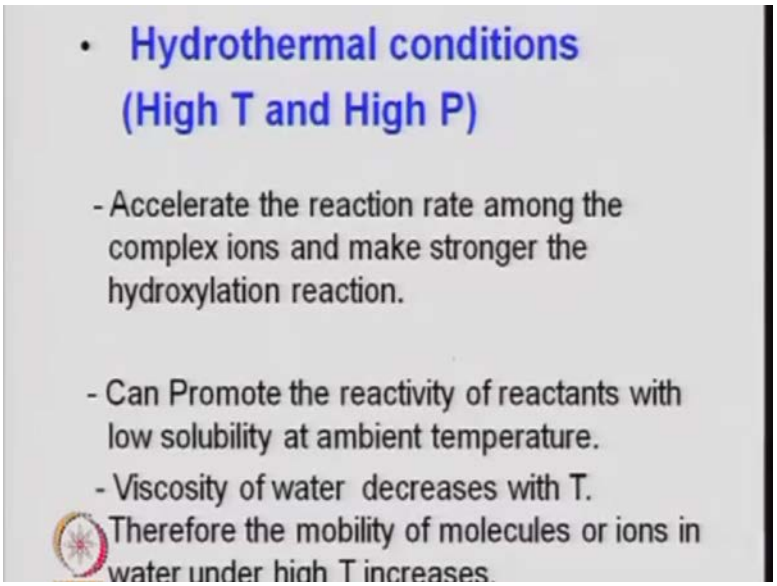

So, basically when you have the high temperature, high pressure so, as I discussed the basically the steps will be something like this.

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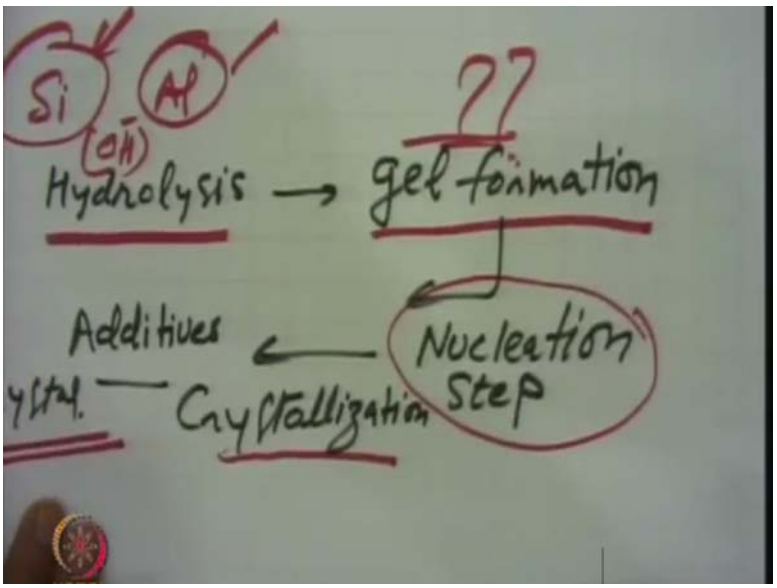

So, you have some kind of hydrolysis reaction so, hydrolysis reaction will be when you have a added silicates and aluminates in a solution form, solutions of these and control the p H so, hydroxyl lions are supplied and then this gives you gel formation so, it is a kind of gel technique but, you have oregano metallic complex and in the gel because, the metal particles are well dispersed same thing here.

Now, the templating agent is required so, gel form formed on some template mass and then this starts nucleation depend because, the temperature and time and pressure so, under this condition the small crystallites of that material silicate Aluminate material that starts forming and that grow crystal growth takes place that nuclides grow in size and you can add additives also at that point cation if you need sodium cations, calcium cation so, additives may be added and finally you get a crystal of that, further thing the calcinations drying ageing these will be the second step. So, basically the first step is this how you get this gel. So that, is very crucial and that depends on the type of organic materials and the synthesis condition

So, we are just talking on that issue at present so, need a high temperature and pressure so, why high temperature High pressure is required because, the first thing I said that it is kinetically controlled so, kinetic controlled reaction may need high temperature to activate the reaction so, the accelerate the action rate among the complex ions because, it is the raw material which you have taken its organic materials and hydroxyl ions you have taken so, there is a kind of the reaction between them the whatever the polymeric materials or cations you have taken that in the presence of hydroxyl group so, a definite p H as I said is desired so, p H is very crucial in that way.

So, the reaction rate will increase at this as you increase the temperature and make the stronger the hydroxylation reaction. So, it is a kind of hydroxylation reaction based on between the raw materials in the presence of O H radical this can promate the reactivity of reactants with low solubility at ambient temperature. So, when the temperature, the temperature is the solubility is poor when you have organic material and inherent organic so, the solubility will not be good so, one thing is that the p H is the diffusive factor again and the temperature may enhance the solubility of this so, you needs a good kind of solubility so, the temperature is desired.

Viscosity of water that is another issue so, the hydrothermal synthesis the polymeric material which you have taken and water added so it is a kind of some slurry type material and which may be in the form of emulsion form. So you need a temperature to reduce the viscosity of water so, again temperature is desired. So, the mobility if the viscosity is low the mobility of the molecules or ions in water at high temperature will be higher and that will the formation of the gel, increase at these condition so that, these are very important issues or crucial steps when the zeolite type of catalyst is prepared.

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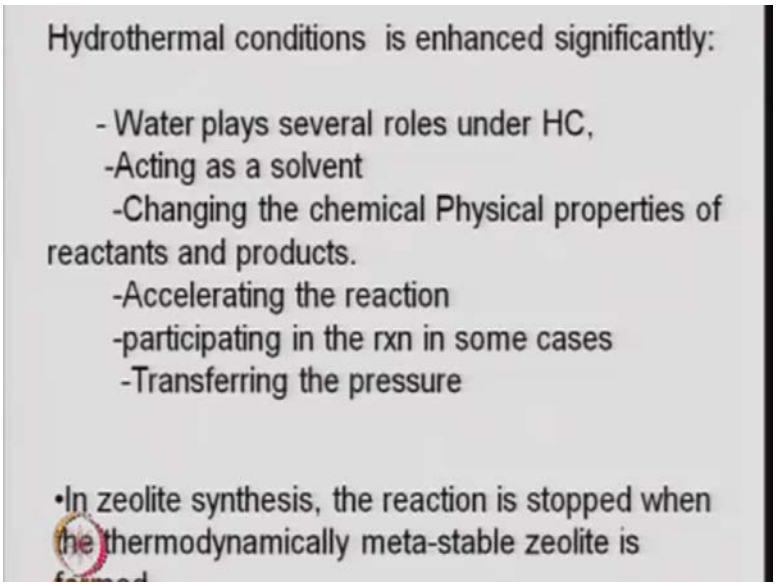

So, hydrothermal conditions that is very important that high temperature, high pressure condition so, water plays a very important role during hydrothermal conditions so, under hydrothermal conditions water is acting as a solvent. Viscosity is decreased because of temperature properties are enhanced one way changing the chemical and physical properties of the reactants and the products.

So, large amount of water is not desired but, a definite amount of water is required to create a kind of hydrothermal pressure. So, pressure inside the system; it is the pressure which is because, of the water vapor at that condition so that, is also important definite concentration of water is desired and under this condition because, now the pressure increase the molecule will be closer so, it is a kind of where the pressure may have a role from the thermodynamics also, it accelerated the reaction water also participates in the reaction, in some cases because, water goes into the framework of the zeolite access to which you see and it also provides the pressure, when you have the temperature inside the system.

So, during the zeolite synthesis the reaction is stopped when thermodynamically Meta stable zeolite is formed because, from the thermodynamics so, the crystallization which is taking place and when you have a high temperature and time the nomination will start so, one has to control that.

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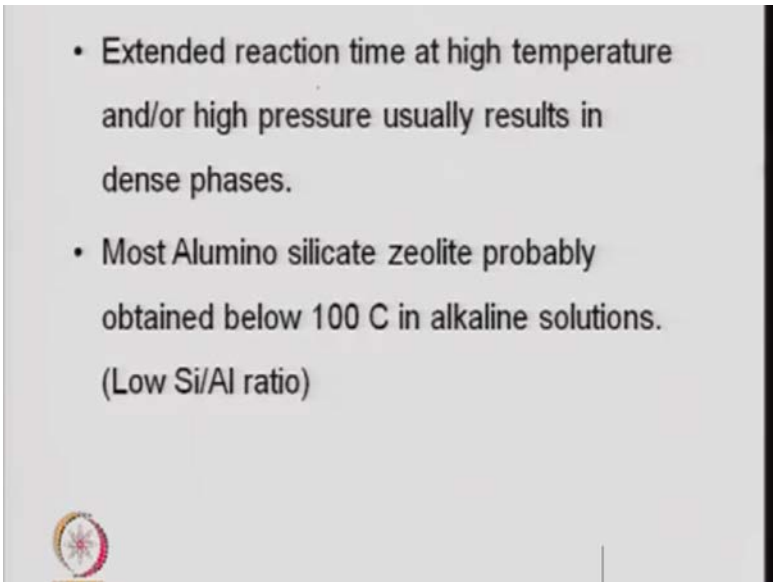

So, extended reaction time at high temperature and or high pressure usually results in a dense phase so that, may not be desired very high time that is 7 days 20 days is you have to control that you need a sufficient dense phase for the reaction to have a gel and then to form a definite structure of the zeolite but, again the time is crucial. So, because I said if you go keep on increasing the time, then crystals agglomerate, the crystal size will increase a definite crystal size is desired when you look at the surface area of the zeolite so that, is important.

So, most of the alumino silico zeolites they are generally produced below 100 degree or just at 100 degree centigrade because, the water has to be in the gas form or vapor form in the alkaline solutions so, for the low silica alumina ratio generally the temperature is around 100 degree centigrade but, when the silica to aluminum ratio is high in the zeolite framework the temperature should be kept high 100 70 200 degree centigrade.

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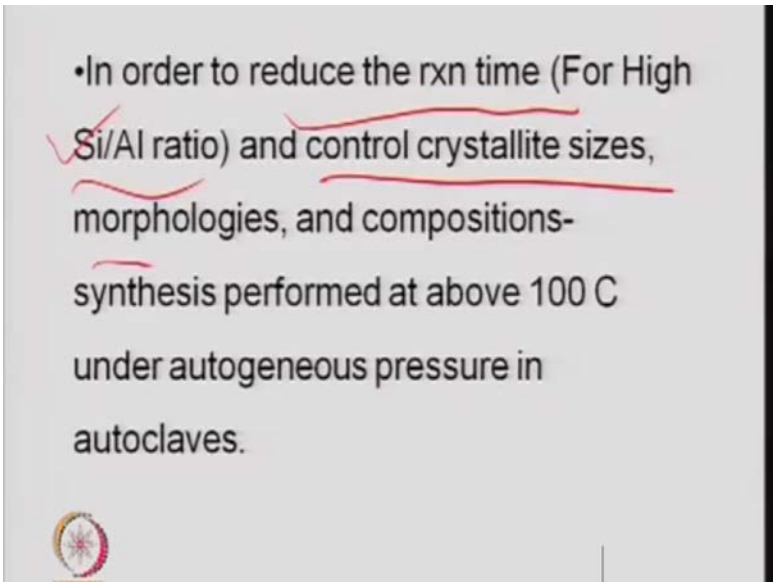

So, in order to reorder to reduce the reaction time especially when you have a high silicon to aluminum ratio, you need in the framework and control the crystal size that is again important as I said morphology composition synthesis performed that is generally done above 100 degree centigrade because, temperature high kinetics will be high so, one thing is clear that when a silica is high in the system then rate may be slow at 100 degree centigrade so, you need to have the temperature. So, higher temperature is required when the silicon to aluminum ratio is high otherwise your time may be higher. So, temperature versus time plays a very important role or crucial role in the hydrothermal synthesis. So, the pressure is autogenous as i said so, reaction is carried out in an autoclave.

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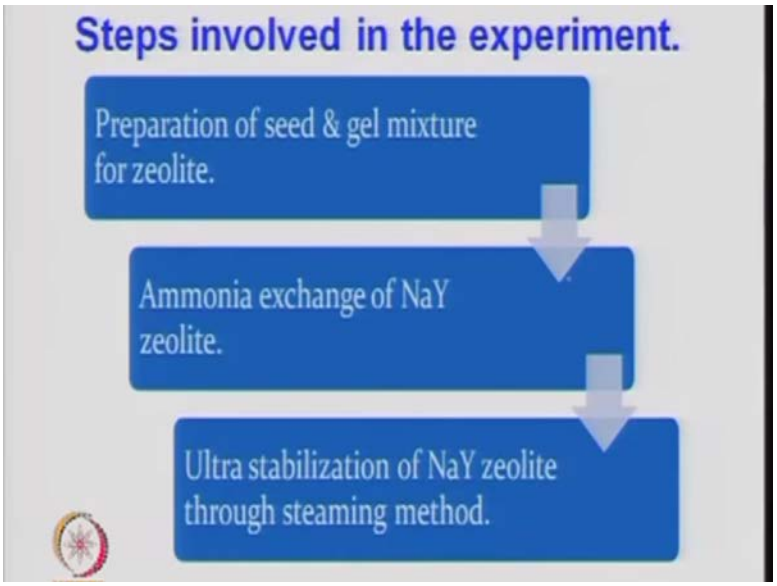

So, the major step involved during the zeolite synthesis or any molecular synthesis is that the preparation of seed and gel mixture for the zeolite so, gel formation is the one of the important seed is desired in some case certain cases whether it is a the sodium cation sodium potassium, these may be added to add these to the zeolite framework gallium. So, whatever the proton exchange zeolites if required so, ammonia exchange of sodium y zeolite so, if you need to replace these by ammonia cations exchange so, ammonia type of zeolite is required proton type of zeolite so that, is if required sodium y zeolite if this is the second step.

Then ultra stabilization of sodium y zeolite through steaming method, sometime steaming is done to have a that is the widening the pore sometime and sometime this also provides a kind of hydro that is a protons to the system when you have a sufficient kind of treatment with a stem sometime dealumination is required so, mild acid treatment is done to remove the aluminum from the framework of the zeolite so, dealumination is another part in the same step of the zeolite formation because, as I said that silicon to aluminum ratio if it is high. So, your concentration will be less but, strength of the acid site is more sometime you may have more loose type of acidity in the zeolite.

So, then you need to treat with some cations as I said gallium may be one or the you need a prorogated zeolite so, you can treat with some kind of acid substantiate and to reduce the aluminum you can do certain kind of dealumination so, steaming is one but,

not very effective in that way for dealumination. So, mild treatment with some e d t s a ethyl diameter triacitic acid can be used or a very dilute concentration of sulphuric acid can be used to chill a distillate these aluminum from the zeolite framework but, that there may be a probability of collapsing the structure, when you have very strong acid taken for this dealumination so, proper care is to be taken while dealumination.

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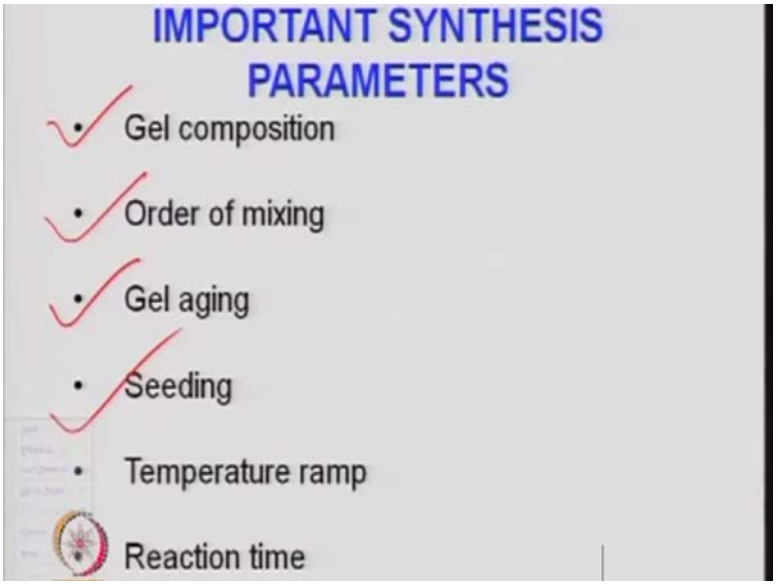

So, important synthesis parameter for a zeolite production is gel composition that the depends on the initial amount and type of the silicate and aluminates precursor so that, is one composition of the gel which will depend on the hydroxyl ion also added into the system during the further reaction order of mixing so, type of stirrer that is suitable kind of stirrer aging of the gel, that is time required to give the nuclear formation you are drying that gel, the gel has to be ruptured in the mask inside that mask so that, aging is important type of seeding material.

So, seeding not in all case but, in some cases seeding is required temperature ramp so, rate of change of temperature with time that is again important sudden heating or slow heating reaction time so, time of reaction is again important.

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Again the factors which affect the synthesis is chemical composition that in terms of that batch composition, the batch in order to get a definite silica to aluminum ratio for the given mass of the zeolite you have to make some preliminary calculations or primary calculation and based on that you have to select the amount definite amount of these raw materials silicate aluminates hydroxyl ions templating agents. So, all these need to be calculated before preparing the zeolite and finally, you have to cross check it through different a technique that is the analytical instrumental methods.

So, silicon or aluminum source so that, these are very important so, what silicon sources silica materials, alumina materials sources are important in terms of getting the final silicon to aluminum ratio in the zeolite framework. So that, is what you need to calculate alkalinity very important p H of the gel as I said 10 12 so, generally we are seeing which is to be kept so that, is very important because gel formation is related to the p H of that is hydroxyl ion helps in that water content that is again important because, it is a hydrothermal synthesis.

So, amount of water how much is the pressure that is required that is very crucial for the zeolite synthesis inorganic cations so, these may be required so, their amount their type concentration organic template structure building here so, this will form the structure so, the type of that ring or type of that chain, which we being used in this organic template

that is important so that, will give you the final shape of the crystal or framework of the zeolite.

Solvents type of solvents used to dissolve these silicon aluminum sources. So, these are important crystallization temperature and time I have already talked so that, is very important we will see the effect later and pressure which is autogenous pressure so, all these are important for the synthesis purpose.

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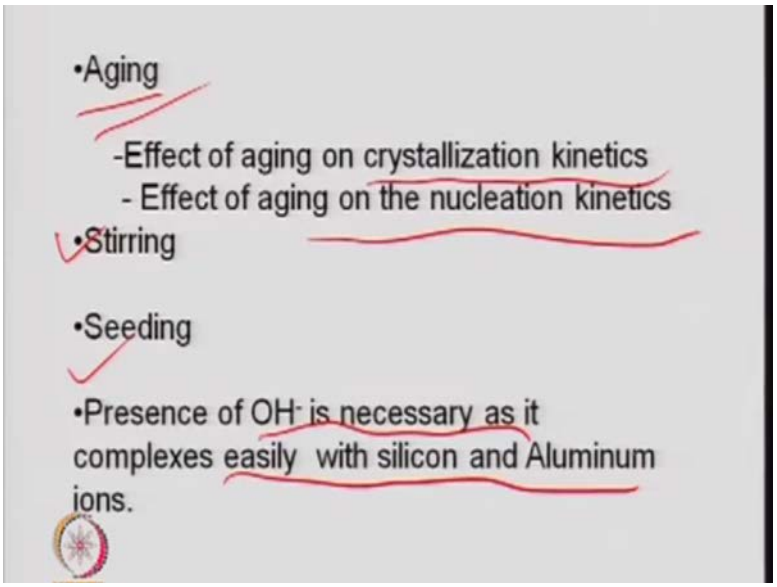

So, aging you know that aging effect of aging on crystallization kinetics it can be a separate chapter one can have the r and d in this, that what type of zeolites are desired and what happens to the structure of the zeolite after this, that is aging and the how the crystallization changes rate of crystallization on this aging time of aging temperature time and look at the growth of the crystal and effect of aging on nucleation kinetics. So, these are important because your final crystal size or type of the crystal these depends on this aging time aging temperature and time stirring is important seeding is important and hydroxyl ion is necessary as I said again that this complexes easily with silicon and aluminum ions so, the kind of complex which forms during the gel will depend on the p H and so that, is very important the polymers which have been taken and at what condition this transfers or reacts into the gel structure. So, this is a kind of what the sole gel type technique what you have learnt before.

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So, just briefly the steps are here so, precipitation of gel phase which I talked that when the preparation of catalyst is desired so, the gel phase is to be prepared so, precipitation of gel phase so that, will depend on the p H of the solution so, you have to just control the p H time is important and temperature is important RPM is important rotation speed starring speed then dissolution of the zeolite material, the nucleation of the zeolite material, which as I have just shown in the steps continued crystallization of the crystal growth of zeolite. So, this is again when the during the crystallization or nucleation formation this process will continue.

So that, is what the time you can keep for 20 days one can keep for 7 days 14 days because, the crystallization continues so, too much time may increase the size of the crystal growth of the crystal, that may not be good when you have a you need a nano synthesize zeolite. Sometimes these are desired very small particle size of zeolite which

may give you the larger external surface area also so that, is very important and sometimes if you look at your methane conversion to liquid fuel that time this nano synthesize zeolite material may be good. So, one has to look at that also but, the structure may collapse when you have a nano synthesize zeolite material.

Then dissolution of the meta stable phase so, here you may you may additives also you may add seed agents also to get a final zeolite phase and nucleation of more stable or meta stable phase or phases so that, process depends on your aging time and temperature

till we get a final crystal so, in between depending upon the time you have to take out the sample and check the XRD. So, you have to look at the crystallinity so, definite crystallinity degree of crystallinity and then you can stop or you can identify the time.

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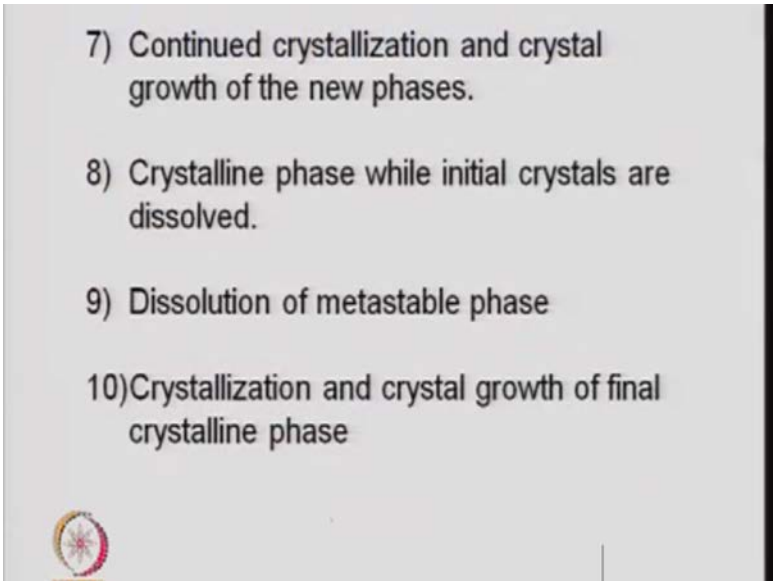

So, this will continue depending upon the continued crystallization and crystal growth of the new phase so, phase may transform if your time is high. So, as I said that you can have a zeolite a at one time t 1 but, the same zeolite you may convert to zeolite x or y depends because, your time is different. So, because the phase is changing so, when you look at a definite crystal phase that is important so, when I say that it is MCM 41 it means it has certain kind of definite phase also or a crystal also same thing for the MCM 41 so, this the difference when you have a different kind of zeolite materials.

So that, is very important so, crystalline phases while initial crystal so, while the initial crystal are dissolved so that, chains so, you have to identify dissolution of meta stable phase crystallization and crystal growth of the final crystalline phase so, these all are similar step what I talked earlier also but, the depends on the aging time temperature and the conditions of the reactant that is hydroxyl ions inside the system and we may like the cations also in between.

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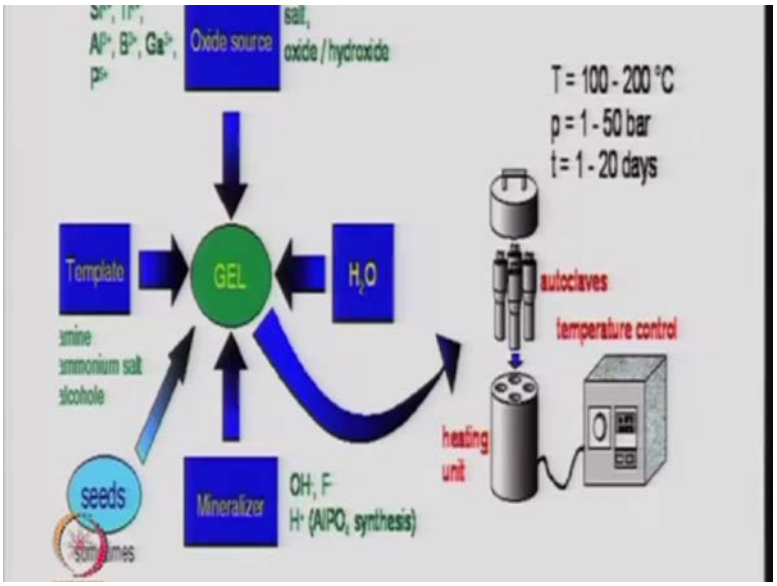

So, this is just a typical picture so, this is a kind of autoclave system a reactor system so, you put your samples here, all the material, all the raw material silicate source Aluminate source so, just like it is a container a box a vessel which can sustain a high pressure. So, because you need a high pressure which may be of the order of 50 atmosphere 50 bar and time may be 20 days 30 days or 1 week 2 week like that, temperature may go 100 to 200 degree centigrade which can be controlled by a temperature controller pressure controller.

So, you can have a pressure gauge in the system to control it with safety valve is desired if pressure exceeds beyond that it should safety valve should be released used workable so, all these kind of silicon source titanium can be used aluminum boron gallium phosphorous so, each depending upon whether you need what type of zeolite is desired

you can take these raw material or precursors of these so, silicate as I said silica source aluminum source, if you need some titanium into that titanium boron so that, can be used gallium can be used in the framework .

So, these oxide source salt oxide hydroxide any form of these can be used so, this will be dissolved in some solution is important the type of solvent which is taken so, depending upon the solubility you have to select them the solvent and then give sufficient time and it will make a gel you have to add the templating agent which will be amines, ammonium salt alcohols. So, these can be used as templating agent water is required so, water is

added so, all these things are added in this vessel and vessel is tightened close the vessel and put it in a heating bath bomb whether it is a kind of bomb knob.

So, you put it in that bath heating bath at the given temperature and control that so gel will form and then you may if required the seeding agent you add the seeding time to time you have to just look at that, you can add well before add closing this you add all these also mineralize if required. So, you add those mineral sources also, small concentration sometime acid it can be H 2 O 4 is added or some say sodium hydroxide can be added so, these can be added here so finally, you will have this kind of system and you will get the synthesis of the zeolite.

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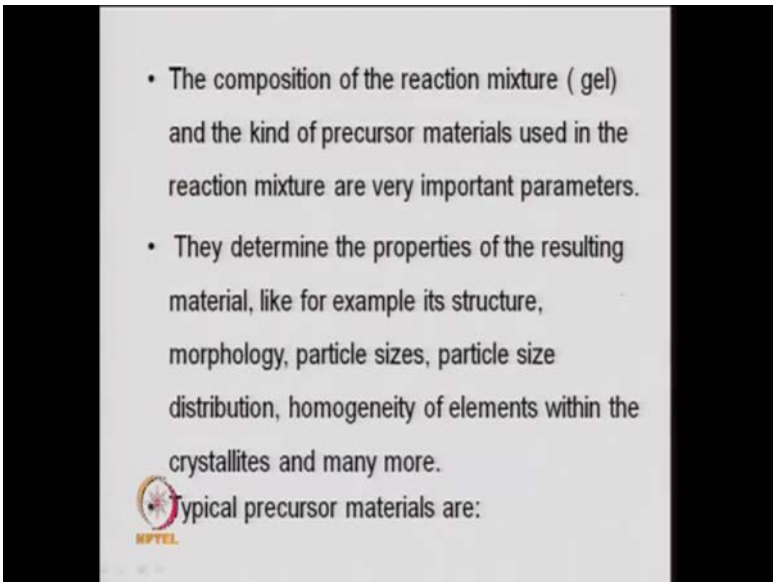

So, the composition of reaction mixture that is gel and the kind of precursor material used in the reaction mixture, they are very important as I said for the zeolite synthesis they determine the property of the material for simple morphology particle size distribution, homogeneity. So, all these will depend on the type of the raw material so, these are all I have discussed basically.

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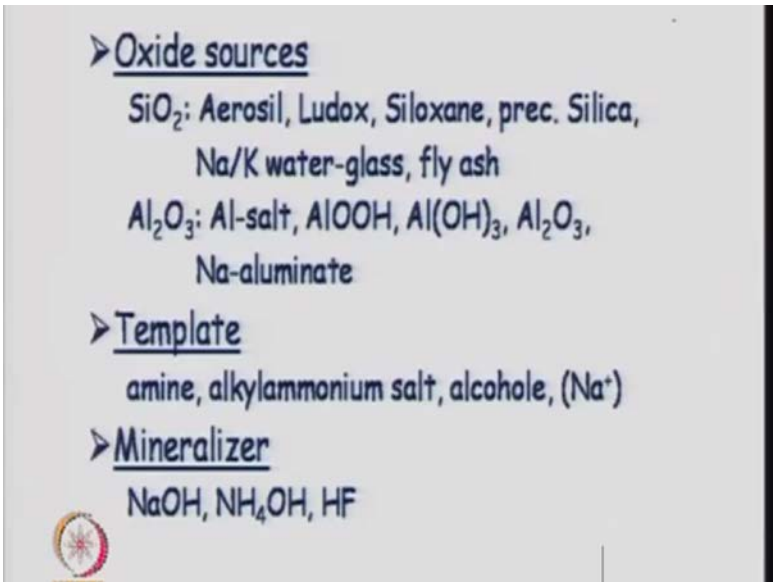

So, oxide source as I said it can be for silica material it can be Aerosol, Ludox so, it is a kind of chemical silicate chemical Siloxane it can be pieces silica material just any silica sodium potassium water glass. So, glass material it is also silica fly ash will also be a source of silica so, these kind of any silica material so, the depending upon it can be new r and d approach also supply astrome some say coal gasification plant can be taken or used zeolites say spend catalyst now a day plenty amount of spent catalyst comes so, after supplinary treatment that can be reused in the process also ZSM 5 take the raw used spent ZSM 5 just grind it and give the proper treatment, pre treatment and then reuse it in the process so that, can be another r and d option for this.

So, same thing for alumina salt also, any alumina salt so, alumina hydroxides alumina sodium Aluminate or as I said again the spent alumina materials so, with after proper treatment because, the crystal goes deactivation may be problem so, depending upon the type of the source or say refinery fertilizers so, they have the alumina as a catalyst so, distillate the material metal part first and whatever the used alumina lefts residue lefts that can be treated properly.

Then you need a templating agent because, it is a structure building agent so, any amine can be used alkyl ammonium salts can be used alcohols can be used so, these can be used as a templating agent sodium salts of this so, these are organic materials so, can be used

as a templating agents structure building agents, mineralize sodium hydroxide ammonium, hydroxide, hydrofluoric acid, these can be used as a mineralize.

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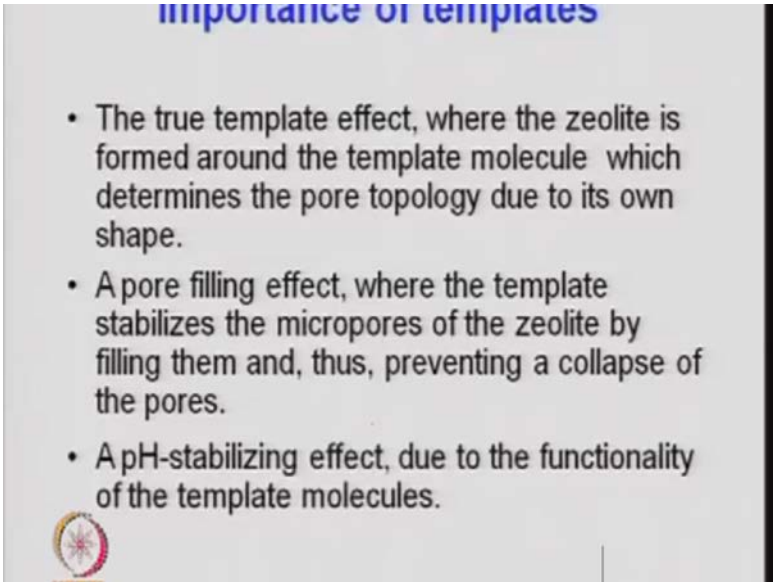

So, template is very important as I said because it builds the structure so, the true template effect where the zeolite is formed around the template molecule, which determines the pore topology due to its own shape so, template has a definite structure so, depending upon the structure of the template you will get the framework of the zeolite so that, that is very important the pour filling effect so, pore size will be depending upon the type of the template which has been taken.

So, the pour filling effect where the template stabilize the Micro pores of the zeolite by filling them and thus preventing the collapse of the pores because, when the structure builds, it is a then the pore structure may collapse also, template may provide a support to that. So, just like a die when you prepare the skeletons and you use that some polymeric material or some and then you heat that polymer materials goes away or the material goes away and then you have a structure so, here also we are doing same thing a masking agent is required. So, that is a kind of mask.

So, what type of mask you have taken that builds the structure p H stabilizing effect so, due to the functionality of the template molecules again they have some role in stabilizing the p H besides the regular hydroxyl ions.

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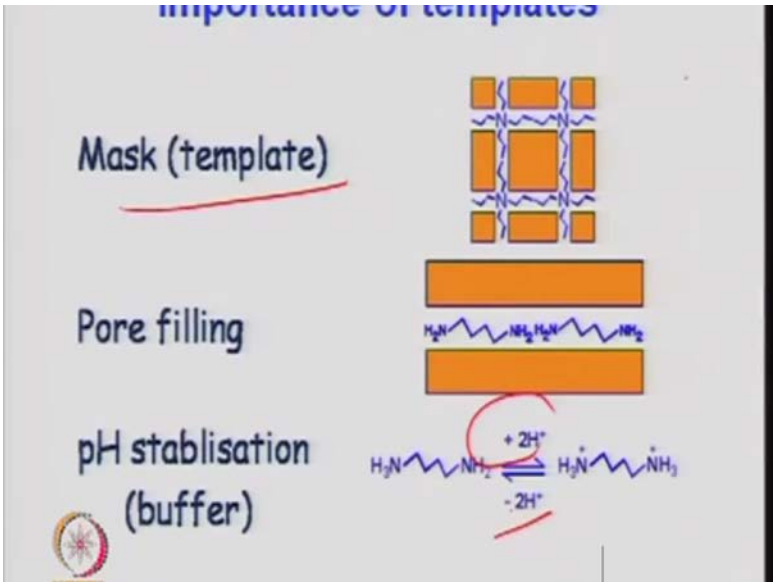

So, this is what the template structure so, this is a you look this is the template and your zeolite material goes into that like this and this also adds so, this is a masking so, a structure will build depending upon the type of template same thing for pour filling also, material just goes inside and it fills back and p H stabilization because, it provides some kind of this protons or hydroxyl ions. So, it can stabilize the p H also of the solution so, all these can be used as that the organic templates, they are very crucial the selection of the type of template is important, when you look at the type of the zeolite.

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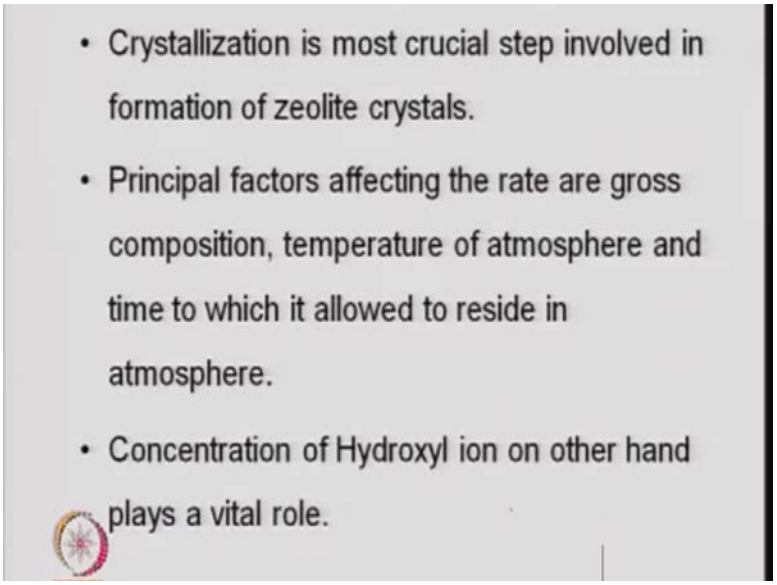

And crystallization as I said is a most crucial step that is involved in the formation of the zeolite crystal. So, the crystallization is the crucial step in terms of the size of the crystal which generally required for the given catalytic activity, the principle factor affecting the rate are gross composition temperature of atmosphere and time to which it is allowed to reside in the atmosphere. So that, crystallization as I said is the time is important because. the crystal will grow if the temperature is high and time is high so, it is a kind of centering growth of the crystal so, a definite crystal size is required and the concentration of hydroxyl ion on the other hand also plays a very important role because, the gel formation depends on this and that gel is over which the which further nuclides and gives you the crystal so that, is related to your hydroxyl ion concentration.

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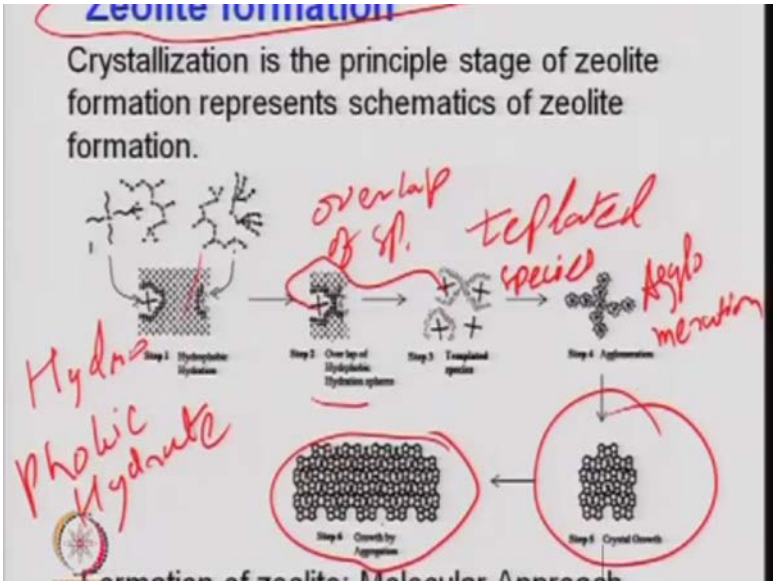

So, this is just a picture so, basically the zeolite formation is related to the crystallization and that is the principle step in the case of zeolite formation and this you see that nuclide formation here so, first is the hydrophobic hydration. So that, is the removal of the water the crystal when you see the nuclide formation or crystal formation so, it is a kind the water has to be removed so, this is first that is the hydrophobic hydration so, first step is your hydrophobic hydration here so, removal of the water from the crystals.

So that, is the gel what you have then you step 2 is the overlap of hydrophobic hydration sphere, now this these are coming closer so, this water molecule which goes so and this is what now a they are coming closer so, overlap of hydrophobic hydration of spheres so,

I will write here overlap so, hydrophobic hydration sphere the step 3 which is related to the template so that, is very important here.

So, template species so, different kind of templates or see you can here this is the overlapping and the these two overlapped overlap of the hydrophobic layers and this is a kind of structure building here the templating because, of the templates and step 4 because they are now agglomerating because, the water has been removed so, this is what the agglomeration so, it increase in size growth of crystal and because of this you will have a crystal growth a framework has built now.

So, this is crystal growth step number 5 and finally, depending upon the time which you have given and the temperature the crystal continues to grow and that is what the aggregation of the crystals so, growth of the crystal by aggregation so, they are just now structure is building, it is a kind of condensation so, water is being removed and they are coming closer and closer so, the structure building that is what depending upon that so, you have a forth of the crystal so, this can be a very large crystal grow all growth also which may not be desired.

So, you have to control these steps of the because depending upon these step and this step and this step you get finally, this the that is the masking of the that is the structure builds and the depending upon the time which you have given the growth of the crystal will take place nucleation will be increasing nucleation will take place so that, is to be controlled in terms of the zeolite synthesis.

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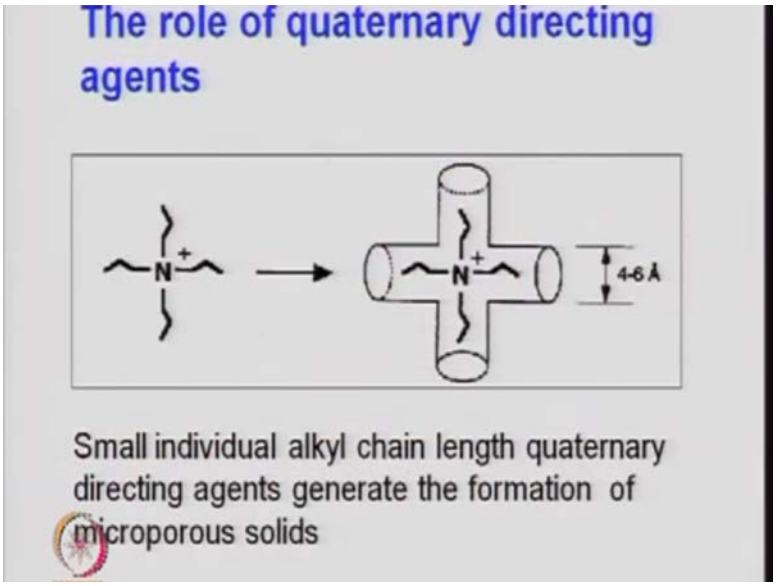

So, the quaternary directing agent whether I talked the templating agents which just we discussed here this one.

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So, the same thing is elaborated here the quaternary directing agent all these templating agents so, this is what the structure so, this is just what you look at here it has gone inside and gives you gave you some dimensions of that framework of the zeolite what I was talking 4.6 angstrom kind of k so, small individual alkyl chain length quaternary directing agent they generate the formation of Micro porous solids so, amount of the carbon which is present in that ring of that organic templating agent or quaternary compounds which you take as a templating agents so that, is important. So, what is shown here has gone like this and the structure is built like this.

So, this generates the formation of the Micro porous material if the individual alkyl chain length is small if the individual alkyl chain length is larger the size will be larger because, it is a kind of template on which the structure is build in or framework is forming.

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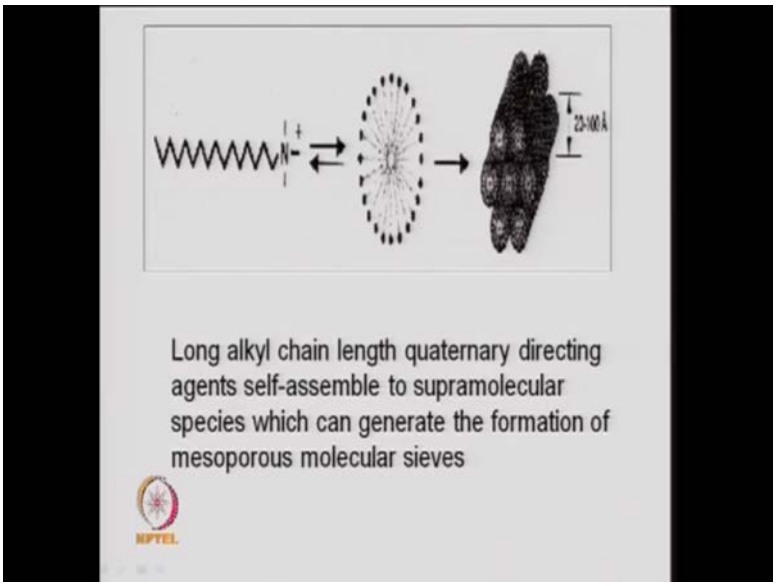

So, same thing for this here, if you need laminar or 1d structure like in MCM type materials MCM forty 1 MCM 48 what I was talking earlier. So, large alkyl chain length quaternary directing agents self assemble to supramolecular species, which can generate the formation of Meso porous molecular sieves so, here you, can see the size is between 20 and 100 angstrom.

So, you that is the selection of the templating agent or structure building agents so, kind of alkyl chain length which you select that is important whether it is a smaller chain length or larger chain length so, accordingly your structure will built.

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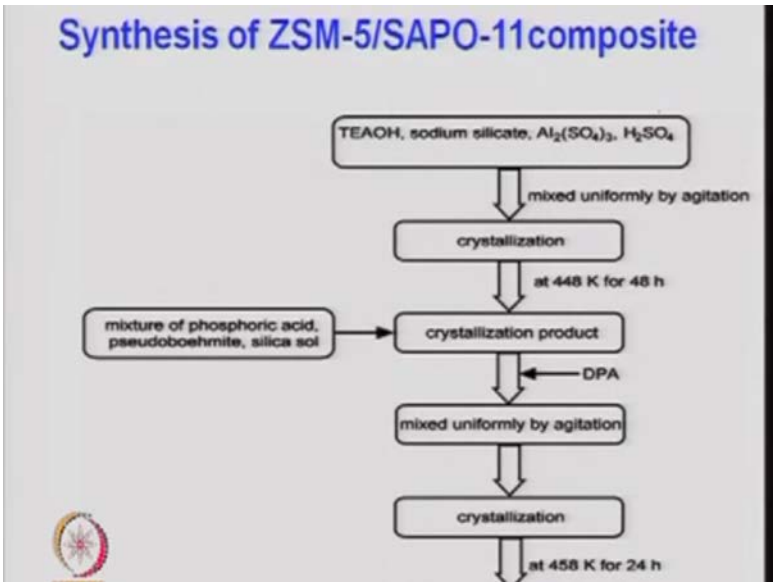

So, just a typical if you look at flow sheet form of the either it is ZSM 5 or SAPO composite a simple AZS M 5 is separate appear and then phosphorous SAPO is to be added so, it is mixture of these 2 kind combination because, you need to control the acidity in certain cases. So, just some say you have some alcohol wood, structure building or this your templating agents sodium silicate, some silicate source some alumina source acid sulphuric acid so, these are mixed and agitated then you need crystallization.

So that, what we were discussing a definite temperature is required so, here it is around 448 degree Kelvin so, temperature is higher and time is 48 hour for aging so, the crystal forms so, crystalline product is here then you may add some d p amines groups and then if required because SAPO so, this is 1 step for just ZSM 5 but, if SAPO is required so, you have to add the mixture of phosphoric acid some psuedobomide which is again a kind of aluminous powder fine alumna powder and silica solution so, its it may be the some tetra ethyl ortho silicate or some silica in the dissolved form solution form.

So, this can be added during this process along with some amines and then you mix them uniformly again agitated crystallized and we will have a composite ZSM 5 SAPO element so, it is a kind of reacted species of ZSM 5 and this silica alumino phosphate instead of just you have ZSM 5 1 SAPO another side and do the dry mixing. So, the property here the phosphorous is attached to the ZSM5 and it is kind of a composite

material so, different approaches can be used for the preparation of different kind of catalyst.

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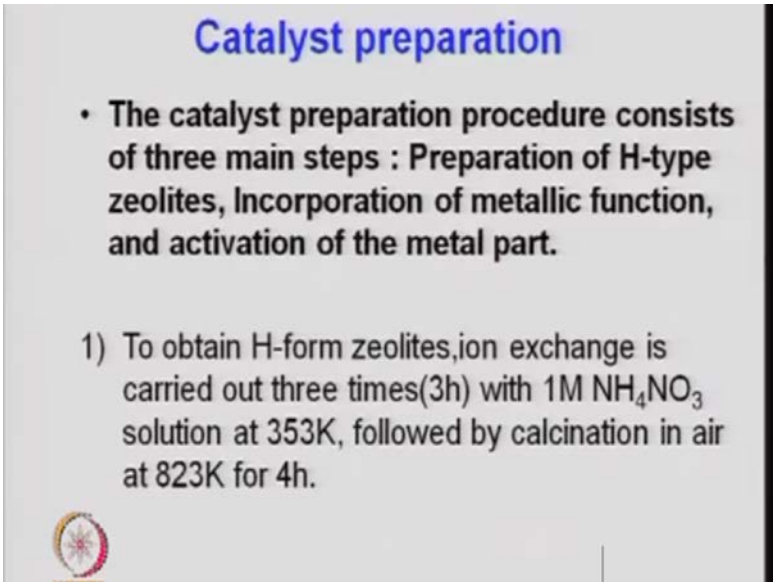

So, just quickly I will go through this recipe because, we have already done the discussion on this so, the catalyst preparation or zeolite catalyst preparation so, basically the process is preparation of some proton type zeolites which are prorogated zeolites incorporation of metallic function to them that is replace the proton by some ammonia zeolites gallium boron whatever and then activation of the metal part. So, calcinations are desired in that case reduction may be required then you get a complete catalyst.

So, first part is just the zeolite preparation and now you metal precursor if required. so that, can be just like our impugnation method once the zeolite you already prepared it can be some ion exchange process so that, depends on the type of the zeolite materials.

So, to obtain the hydrogen form of zeolite the ion exchange is carried out ion exchange is slow process as I said earlier also, you need to do repeatedly 3 times 3 hours for 3 hour continuation and with say just this one method of 1 m ammonium nitrate solution the temperature around 353 Kelvin followed by calcinations in air at 823 Kelvin for 4 hour so, this is 1 recipe as I said so, in order from zeolite material, now you need to prepare something like gallium as ZSM 5 you have the as ZSM 5 so, replace use the gallium on that or moly as ZSM 5.

So, these means the molybdenum is to be attached to the zeolite frameworks so, zeolites the kinetic diameter molybdenum and zeolite pore diameter is one so, whether it can diffuse into the pore or not that is equation issue so, it is good to replace the h positive part of that zeolite by metal species. So, it is a kind of ion exchange so, ion exchange processes are very slow process so, you need to give enough time you need to give a definite temperature proper agitation and then you can get this type of zeolite. So, I stop here I will continue quickly in the next term.