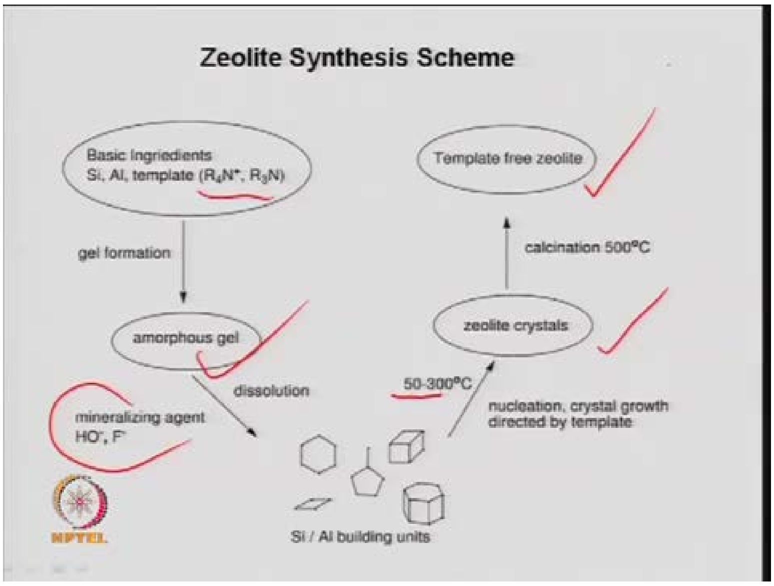
Heterogeneous Catalysis and Catalytic Processes
Prof. K. K. Pant
Department of Chemical Engineering
Indian Institute of Technology, Delhi

Lecture – 20

Good morning, so last time I was talking about synthesis of zeolite, so I will continue it today also.

(Refer Slide Time: 00:37)



Zeolite Synthesis Scheme

Basic Ingriedients
Si, Al, template (R_4N^+, R_3N)

gel formation

amorphous gel

mineralizing agent
HO^-, F^-

dissolution

Si / Al building units

50-300°C

nucleation, crystal growth directed by template

zeolite crystals

calcination 500°C

Template free zeolite

Zeolite synthesis scheme, what I told that, it is based on hydro thermal synthesis, so hydro thermal synthesis under the condition of temperature, pressure, in the presence of some templating agent. Look at the flow sheet for zeolite synthesis, at typical flow sheet I will say, the basic ingredients, you need some silica source, some aluminum source and some templating agents, which may be quaternary amines, propyl amines, isopropyl amine groups, so this can be the templating or structure building agents.

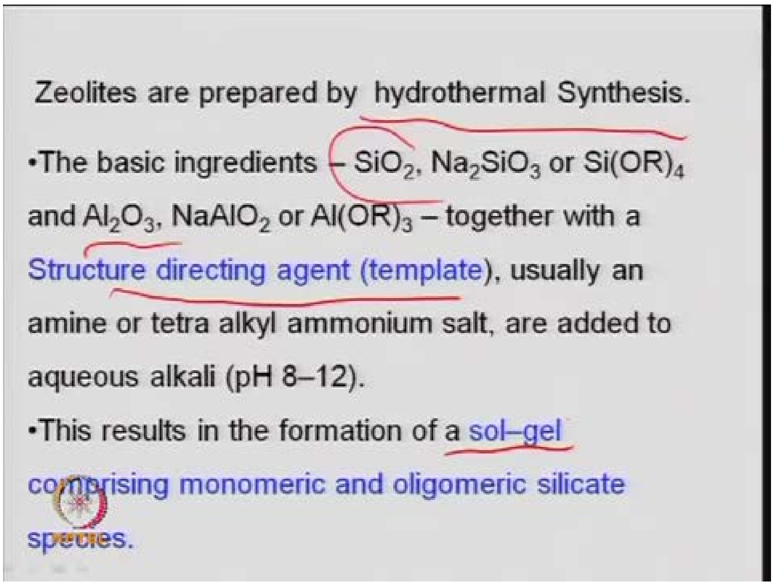
Under certain condition of temperature and the presence of hydroxyl ions, a gel forms and this gel structure formation will be very crucial, because it is a kind of primary building, the structure or a foundation of the zeolite matrix. So, matrix formation will come based on this gel structure, amorphous gel. So now, you may at some mineralizing agent, because the hydroxyl ions, which will provide some kind of hydrated H into the group and also control the PH during the reaction.

So, depending upon these and the type of gel, the dissolution takes place here and you get the different kind of silicon to aluminum building blocks. So, different six membered, five membered, four membered, so the control is very crucial in this stage and that will depend on the several parameters, which I will talk. So, water content then, your raw material, that templating agent, OH radicals, temperature, time. So, based on this, the structure building and now, this depending up on again temperature between 15 and 300 degree Centigrade, the nucleation takes place.

So that, is the step, when the crystal grown, the growth of the crystal is again very crucial and the structure it may be just like a ((Refer Time: 02:39)) type or a zeolite A type material and there may be the difference. So, you have to do the X ray diffraction patterns in between here, so you get the zeolite crystal and that will be once and half time like aging time. And finally, so once the structure, the template has to be removed, the material has to be calcined accordingly.

So, calcination is generally done at around 500 degree Centigrade and you will have ultimately a template free zeolite and which can be further protonated. So, this is the basic of the zeolite synthesis and depending upon the type of the raw material, it is amount different silicon to aluminum ratio zeolites can be rewarded or prepared or you can later on do the impregnation or ion exchange technique for adding these cations to the groups, gallium, barium, boron, all this kind of calcium, ammonium zeolite, so this forms can be formed.

(Refer Slide Time: 03:40)



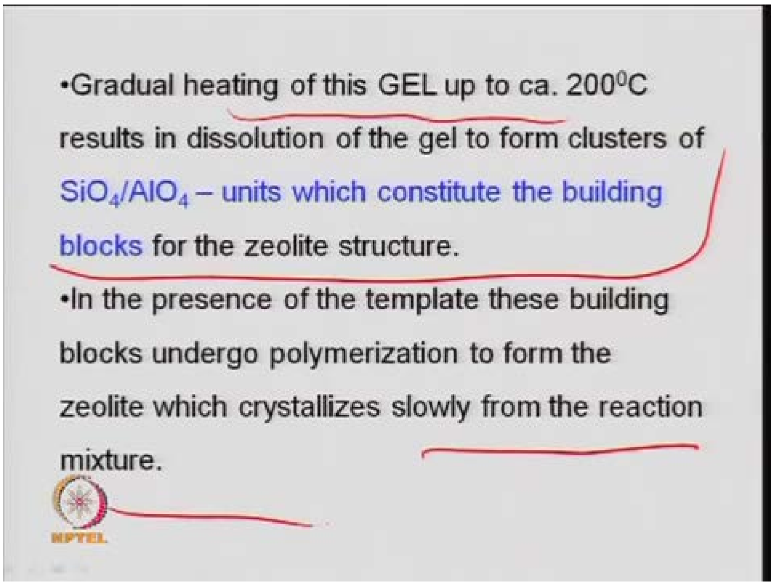
Zeolites are prepared by hydrothermal Synthesis.

- The basic ingredients – SiO_2, Na_2SiO_3 or $Si(OR)_4$ and Al_2O_3, $NaAlO_2$ or $Al(OR)_3$ – together with a Structure directing agent (template), usually an amine or tetra alkyl ammonium salt, are added to aqueous alkali (pH 8–12).
- This results in the formation of a sol–gel comprising monomeric and oligomeric silicate species.

So, I said that, the zeolites are formed by hydro thermal synthesis and the basic ingredients, which are very crucial for the zeolite synthesis is silica, sodium silicate, Si OR whole 4. So, these kind of organic materials can be selected, alkyl groups, alumina, alumina source, sodium aluminate can be taken or again some form of Al OR whole thrice can be taken. Together with some structure directing agent, which is a template and they are usually amines or tetra alkyl ammonium salt.

So, these can be used as a templating or structure building agent, PH change because, the hydroxyl ions, so PH usually depends on the requirement of the type of the zeolite, so between 8 to 12. So, basically they may required for the gel formation, so the results is in the formation of sol gel comprising monomeric and oligomeric silicate species. So, here the kind of polymerization, a kind of condensation reaction takes place, where you get the primary or secondary building blocks during the synthesis.

(Refer Slide Time: 05:03)

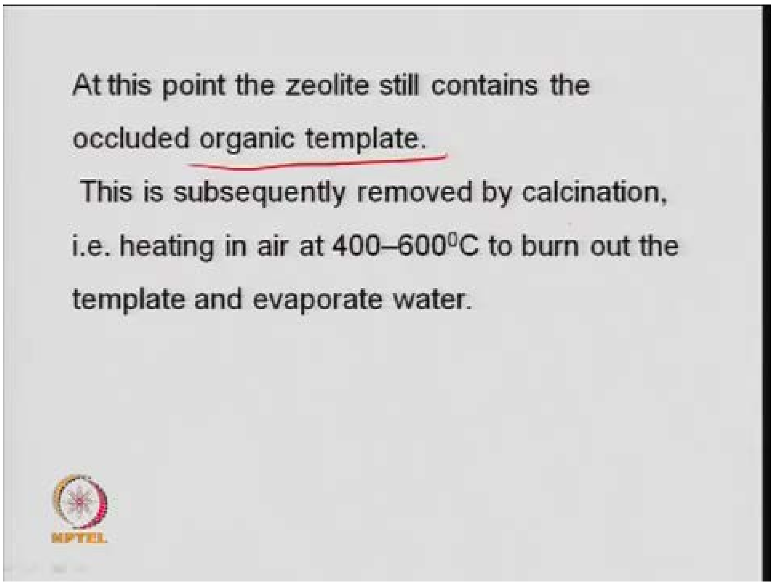


- Gradual heating of this GEL up to ca. 200^0C results in dissolution of the gel to form clusters of SiO_4/AlO_4 – units which constitute the building blocks for the zeolite structure.
- In the presence of the template these building blocks undergo polymerization to form the zeolite which crystallizes slowly from the reaction mixture.

So now, when you heat this gel at approximately 200 degree centigrade, that gives you the dissolution of the gel, which I just discussed in the flow soon. So, dissolution of the gel, which forms the SiO4 AlO 4 a structure, a building that is what we have seen, the four membered, six membered, five membered. So, that will depend on here that, time verses temperature and the amount of water present in the zeolite. So, this constitutes the building block for the zeolite structure, so that is the and now, the further crystallization has start localization or nucleation has to be done.

So, in the presence of template, so this building blocks or zeolites undergo polymerization and that will form the a zeolite and that crystallizes slowly from the reaction mixture. So now, how the crystal grows that is important, the crystals grow during this nucleus semester and the temperature time and finally, you have the definite structure of the zeolite.

(Refer Slide Time: 06:05)

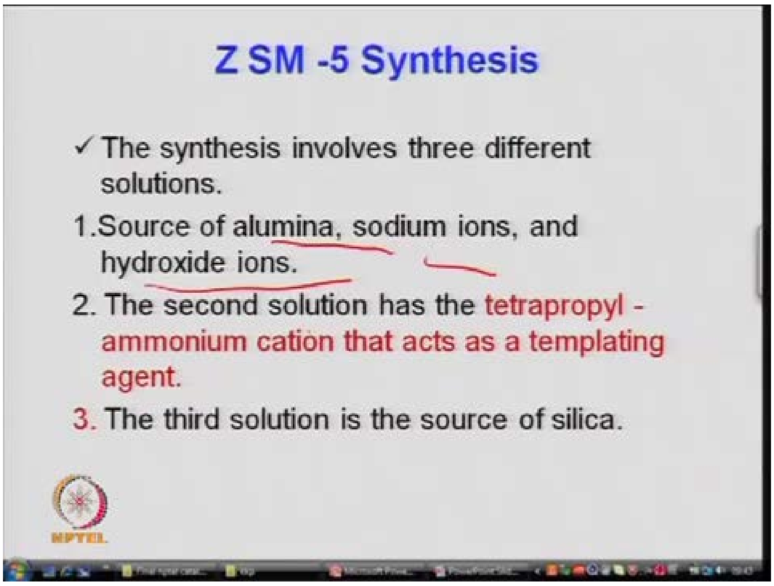


At this point the zeolite still contains the occluded organic template.

This is subsequently removed by calcination, i.e. heating in air at 400–600^{0}C to burn out the template and evaporate water.

So, at this point, the zeolite will have some organic template, which I said that, calcination is required, so this is removed by calcination. So, calcination is just a heating in the presence of oxygen or air in a temperature range 400 to 600 degree Centigrade and that can be checked from the TGA analysis, Thermo Gravimetric Analysis. So, you can find out, what is the temperature required to remove the template.

(Refer Slide Time: 06:35)



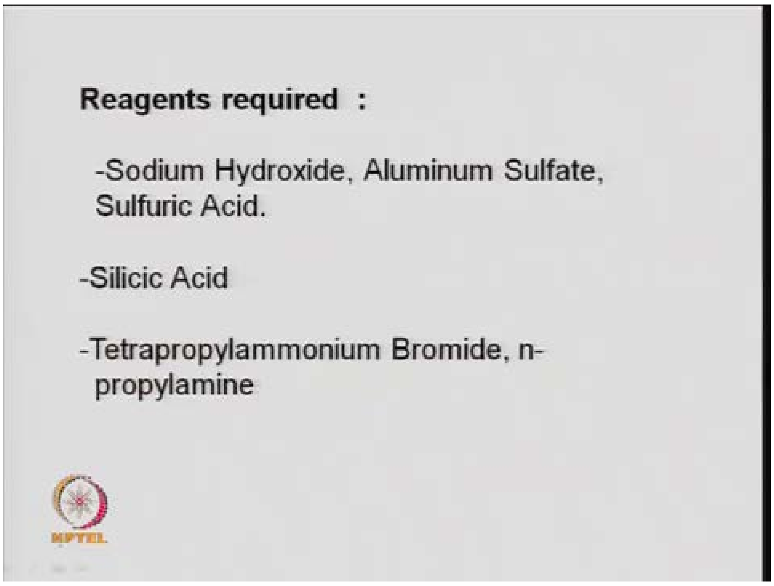
Z SM -5 Synthesis

✓ The synthesis involves three different solutions.

1. Source of alumina, sodium ions, and hydroxide ions.
2. The second solution has the tetrapropyl - ammonium cation that acts as a templating agent.
3. The third solution is the source of silica.

This typical recipe for Z SM 5 very quickly I will go through that for the preparation, that the source of shell alumina, sodium ions are required, hydroxide ions are required, so these are the raw material. Then, the second solution which is your templating agents, so this templating agents are again as I said, isopropyl ammonium cation are used as templating agent. And the third solution is the source of silica, so this tetrapropyl ammonium cation can be any group. And depending upon the organic material, so isopropyl is one, there can be other templating agents also, just EDTA can also be used just like in a sol gel process or some alcohol groups can also be taken, other alcohols, any alcoholic groups can be taken, which in the presence of the ammonium cations.

(Refer Slide Time: 07:44)



Reagents required :

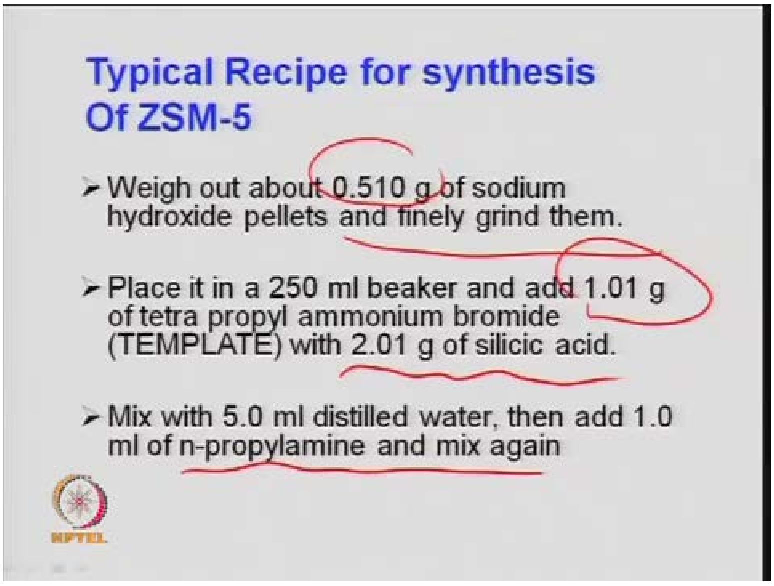
-Sodium Hydroxide, Aluminum Sulfate, Sulfuric Acid.

-Silicic Acid

-Tetrapropylammonium Bromide, n-propylamine

So, the reagents required we have discussed.

(Refer Slide Time: 07:45)



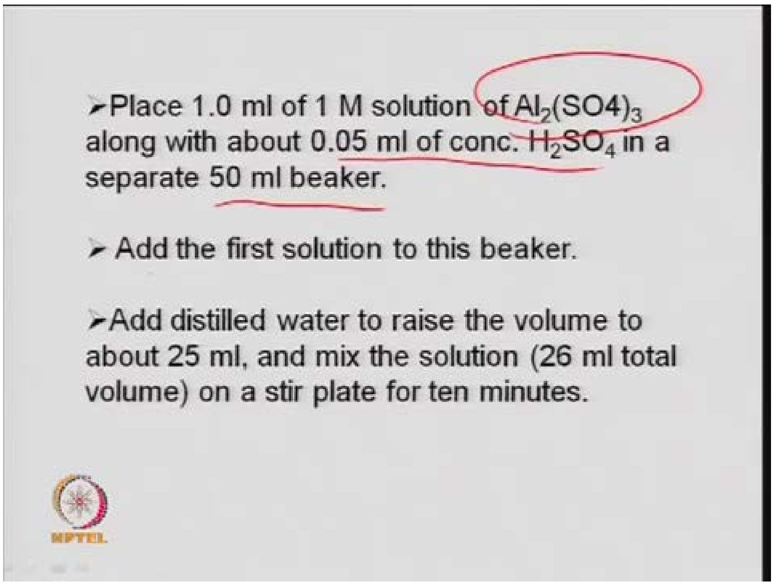
Typical Recipe for synthesis Of ZSM-5

- Weigh out about 0.510 g of sodium hydroxide pellets and finely grind them.
- Place it in a 250 ml beaker and add 1.01 g of tetra propyl ammonium bromide (TEMPLATE) with 2.01 g of silicic acid.
- Mix with 5.0 ml distilled water, then add 1.0 ml of n-propylamine and mix again

So, typical recipe is just for Z SM 5 preparation, so just for a 10 gram of this final solid material, at that which you get, so just 0.510 gram of the sodium hydroxide pellets are required and just finely grind them. That is, the size the particles should be in the smaller form just to dissolve them properly and place them in a 250 ml of beaker and add 1.01 gram of tetra propyl ammonium bromide, which is a TEM templating agent here.

So, any other type of templating agent can also be used as I said before and with 2.01 gram of silicic acid, a source of silica, so this is the reagents or these are the reagents required for the zeolite synthesis and took this 5 ml of distilled water. So, water is again important, quantity of water very important, so 5 ml distilled water and add 1 ml of the normal propyl amine and mix again. So, these are the kind of materials, which are generally required to provide the zeolite structure or primary group to form a gel.

(Refer Slide Time: 09:02)

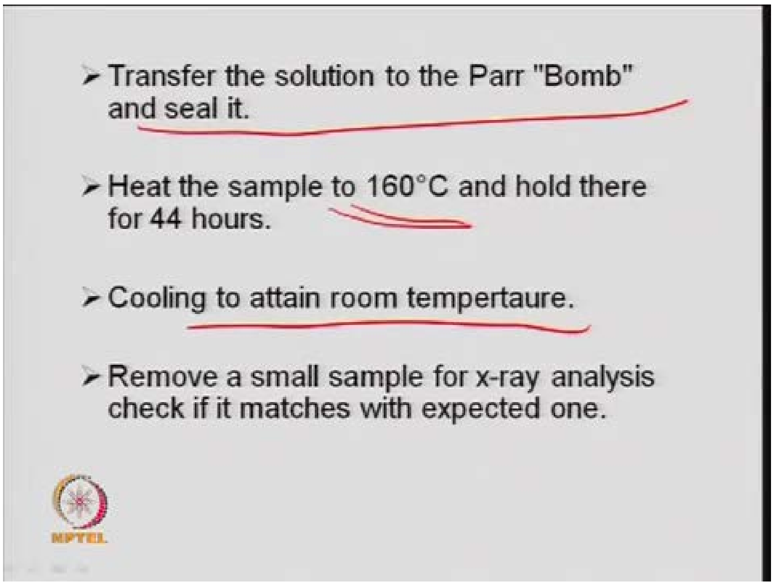


- Place 1.0 ml of 1 M solution of $Al_2(SO4)_3$ along with about 0.05 ml of conc. H_2SO_4 in a separate 50 ml beaker.
- Add the first solution to this beaker.
- Add distilled water to raise the volume to about 25 ml, and mix the solution (26 ml total volume) on a stir plate for ten minutes.

So, 1 ml of 1 M solution of aluminum sulfate again another, so one backs there, another backs is here now in the form of alumina source and then, mix them. So, 1 ml of 1 M solution of aluminum silicate, this will depend on the requirement of the silicon to aluminum ration in the zeolite frame work. So, one can calculate from the initial calculation, how much amount of silicon is required, how much amount of aluminum is required and based on that, decide the mass of these materials.

So, with this, add 0.05 ml of concentrate sulfuric acid, some protonated acid in a separate 50 ml beaker, so now you have two solutions. So, first solution is mixed into the second, so one is the source of silica and another source of alumina and then, mix them together and add distilled water to raise the volume to approximately 25 ml and then, mix it. So, this will be roughly 26 ml of the total volume and stir it in a under some temperature conditions for 10 minutes, just to have a lean from mixing.

(Refer Slide Time: 10:15)

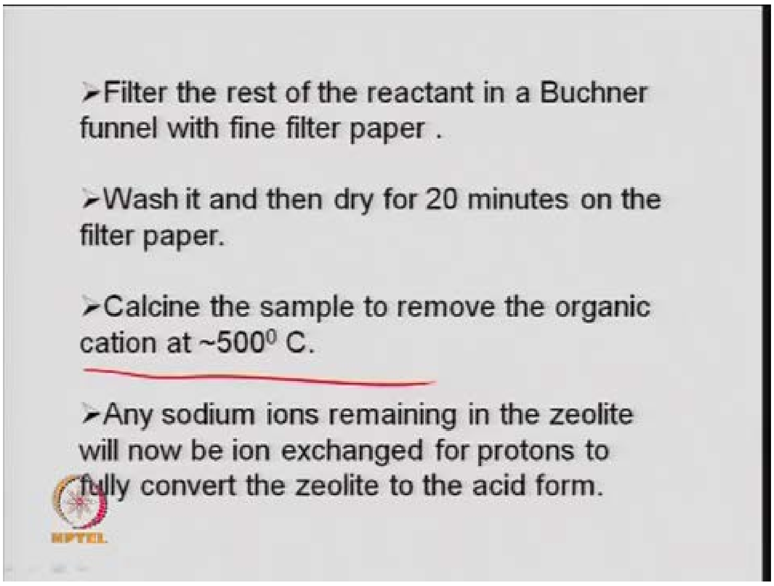


- ➢ Transfer the solution to the Parr "Bomb" and seal it.
- ➢ Heat the sample to 160°C and hold there for 44 hours.
- ➢ Cooling to attain room tempertaure.
- ➢ Remove a small sample for x-ray analysis check if it matches with expected one.

Then, transfer this into a bomb Parr reactor, which is a high pressure reactor, because now this silica source, aluminum source in the presence of templating agents, some minerals, some acid, hydroxyl group, so all these are mixed together and kept in a bomb, because it is a hydro thermal synthesis. So now, depends that is the requirement, so 160 degree Centigrade for the Z SM 5 and time is referring 44 hour, but this can vary from 3 days to 4 days also, it depends, so 36 to 44 hour also.

So, different time, you have to just look at and check the type or the resultant product then, cool it, so here in this form, the generalized form, that is what the primary as I said, four membered ring, six membered ring, so that has formed and started crystallization. So, remove the sample for X ray analysis and check if it matches with the expected one, so this is what the as I said that, after different time intervals, you have to check through XRD, whether reacted phase of zeolite has formed or not. And then, you can decide the or you can optimize the process condition for the hydro thermal synthesis.

(Refer Slide Time: 11:30)



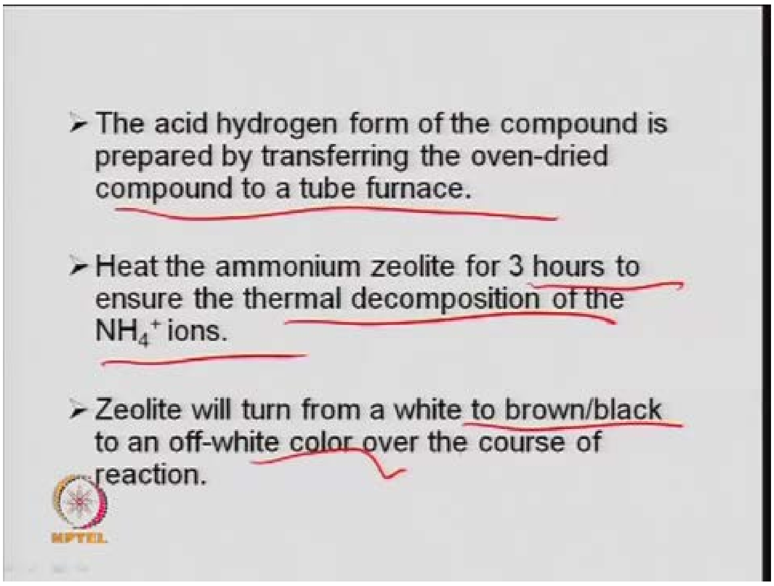
- Filter the rest of the reactant in a Buchner funnel with fine filter paper .
- Wash it and then dry for 20 minutes on the filter paper.
- Calcine the sample to remove the organic cation at ~500^0 C.
- Any sodium ions remaining in the zeolite will now be ion exchanged for protons to fully convert the zeolite to the acid form.

So now, filter the rest of the reactant using some final or in a presence of some filter paper, because that zeolites this fine particle. So, you need a fine filter paper and wash it for 20 minutes, so gel which is dried gel, you wash it just under water and reflects condition, continuously wash it till you get a constant PH of water. So, complete removal of these hydroxyl or protonyl or the sulfuric ions, so calcine the sample to remove the organic cations.

So now, it is a zeolite material, but contains the alcoholic group that is, templating agent, so heat it around 500 degree Centigrade, so that is templates will go out or any undesired thus nitrate oxides, nitrate, sulphates, so this will also removed during the heating. And again calcination time and calcination temperature is very crucial, because the particle may get sintered. When you are looking for a nano zeolite synthesis, so you have to grind it, finally again at the liter end to get the nano particles of the zeolites, because external surface area is also important.

So, any sodium ions remaining in the zeolite will now be ion exchange for protons to fully converts zeolite into the acid form. So, you can exchange it with any other cation exchange on zeolite. So, depending upon the requirement, if sodium is present then, treated with some acid, so that can be a kind of protonated zeolites, different kind and depending upon the CTT required in the zeolite.

(Refer Slide Time: 13:14)

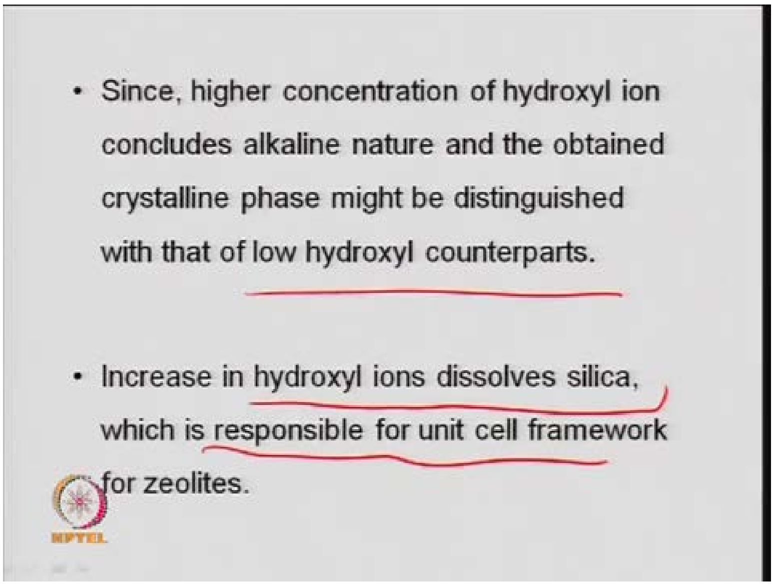


- The acid hydrogen form of the compound is prepared by transferring the oven-dried compound to a tube furnace.
- Heat the ammonium zeolite for 3 hours to ensure the thermal decomposition of the NH_4^+ ions.
- Zeolite will turn from a white to brown/black to an off-white color over the course of reaction.

So, acid hydrogen form of the compound is prepared by transferring the oven dried compound in a tube furnace. So, that is again the zeolite material, which contains the sodium ion, that is to be removed, so the next further treatment is based on the acid treatment. So, heat the ammonium zeolite for 3 hours, to ensure the thermal decomposition of the ammonium ions.

So, these are kind of exchange of this sodium ion with ammonium and then, heat it for the thermal decomposition of this ammonium ion and zeolite will turn from a white to the brown black, brown or black to an off white color over a course of reaction. So finally, you get the zeolite material, which is now ammonium exchange zeolite, so likewise the different kind of zeolites with different actions can be meet.

(Refer Slide Time: 14:02)

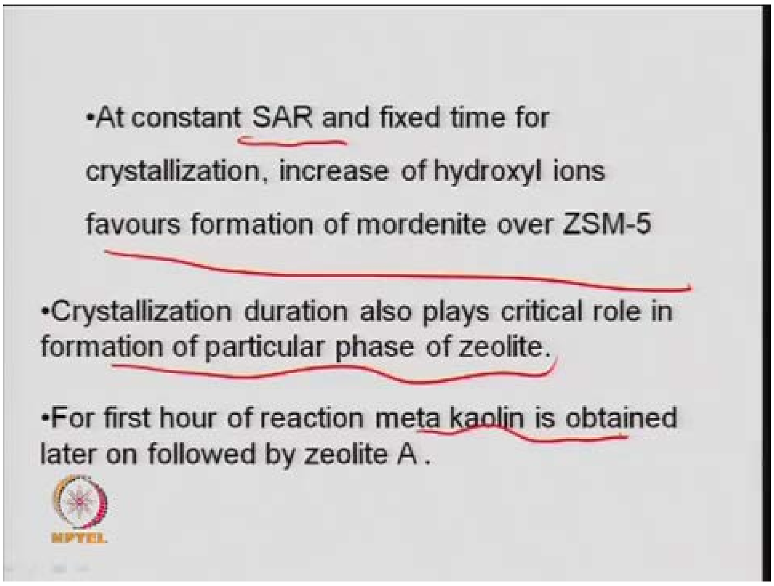


- Since, higher concentration of hydroxyl ion concludes alkaline nature and the obtained crystalline phase might be distinguished with that of low hydroxyl counterparts.
- Increase in hydroxyl ions dissolves silica, which is responsible for unit cell framework for zeolites.

So, since higher concentration of hydroxyl ion concludes alkaline nature and the obtained crystalline phase might be distinguished with that of the low hydroxyl counterparts. So, I will just talk this later, I mean to say here is that, the presence of hydroxyl ion is important, but it definite concentration of hydroxyl ion that is, a kind of PH type, that is important for making a definite kind of gel structure. And then, further crystal growth also, nucleation of that primary block, primary building unit of the zeolite, so that is also important.

So, I will talk on that little later, effect of process variable, so increase in hydroxyl ion that dissolve the silica material, the higher concentration of the hydroxyl ion or higher PH in the solution dissolves the alumina and that is responsible for the unit cell frame work for zeolite. Because, the frame work of the zeolite is because of the t atoms, silicon atom especially when you are looking MCF type of material or high siliceous material, Z SM 5 material, where the silica alumina ratio may be 500. So, the structures become, because the structure of a zeolite depends on the presence of silicon in the frame work. So that, if the hydroxyl ions, they can heat that siliceous material and then, structure may damage in one way.

(Refer Slide Time: 15:33)



- At constant SAR and fixed time for crystallization, increase of hydroxyl ions favours formation of mordenite over ZSM-5
- Crystallization duration also plays critical role in formation of particular phase of zeolite.
- For first hour of reaction meta kaolin is obtained later on followed by zeolite A .

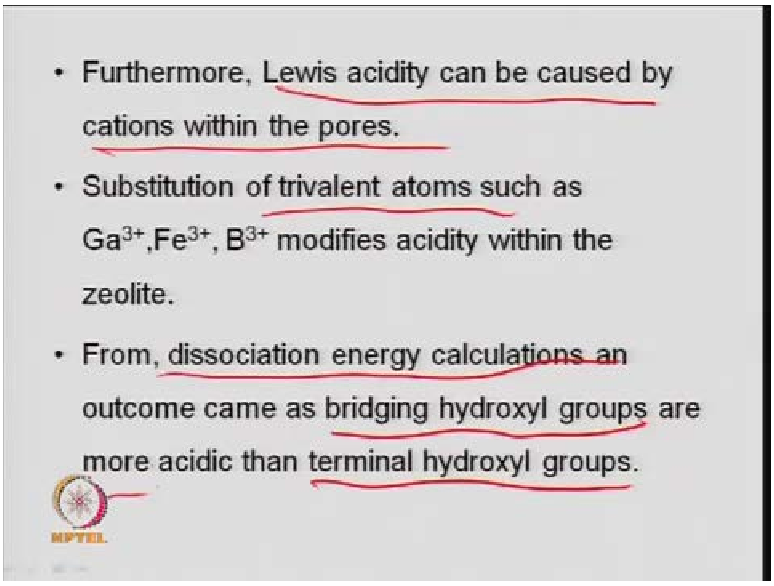
At constant silicon to aluminum ratio or silica alumina ratio and fixed time for crystallization, increase of hydroxyl ion favors the formation of mordenite over Z SM 5. So, these are some typical results from some different research based on the literature and it has been observed that, if you want to fix some silicon to alumina ratio in the zeolite, for a given time of crystallization, because when you study the parameter, a kind of design of experiment has to be done.

And then, you have to keep other parameter constant and vary one parameter, so keeping all as constant, if the hydroxyl ion concentration is increased then, the mordenite formation may be higher compared to the zeolite 5 formation. It means, one has to controlled this hydroxyl ion concentration, so amount of this hydroxyl ion presents or PH is a decisive factor, whether mordenite will form or Z SM 5 will form. Again crystallization duration also plays a very critical role in formation of particular phase of zeolite.

Because, crystallization when you start from nuclear formation, the step which I have discussed and then, these growth of the crystal, depending upon the aging time and temperature. So, at a given temperature, if your time is higher then, the crystal may grow in size, plays different kind of zeolite form, so phase transformation is a function of the time of crystallization also. For a first hour of reaction, meta kaolin which is basically kaolin is a natural type of zeolites, so that can be amorphous in nature also.

Or we have different kind of natural zeolites available, natural clay materials, mordenite which are again acidic. If you give some acid treatment, you can get good kind of acidity from these kind of clay materials, laminar structures of the zeolites and these materials can also be used as a source of a zeolite or molecular sieve. So, that is the, this kind of structure can be obtained and then, when you increase it further second hour, third hour then, the zeolite may form and so on, so again the time is important, the reaction time.

(Refer Slide Time: 17:58)



- Furthermore, Lewis acidity can be caused by cations within the pores.
- Substitution of trivalent atoms such as Ga^{3+},Fe^{3+}, B^{3+} modifies acidity within the zeolite.
- From, dissociation energy calculations an outcome came as bridging hydroxyl groups are more acidic than terminal hydroxyl groups.

Lewis acidity and Lewis acidity is caused by the cations within the pores, so presence of cations in the pore will give you a kind of Lewis acidity. So, basically Lewis type of acidity as I say aluminum chloride, earlier Friedel craft reaction the AlCO 3 used as the catalyst. But, this can be used, because they reacts, so separation may be a problem, because this is liquid phase of this. When you have a liquid phase reaction then, there is a difficulty, the catalyst separation is a problem.

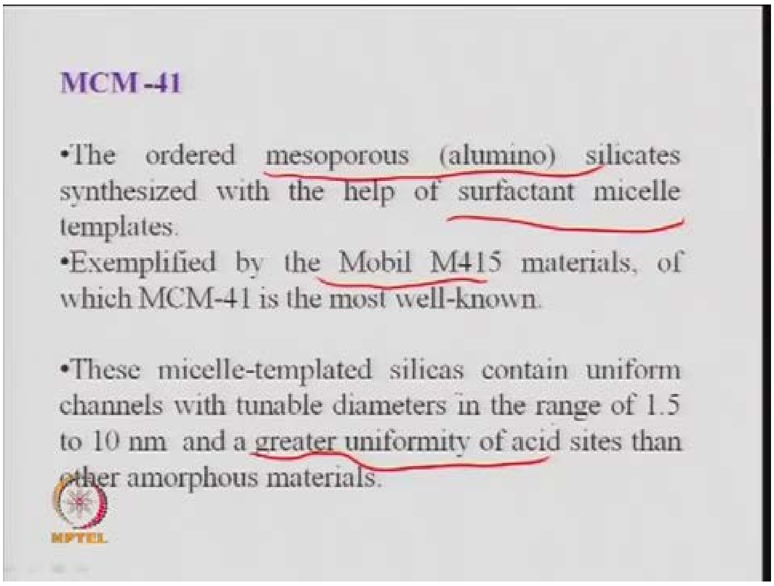
So, and you wish to a lot of catalyst comes as a waste liquid catalyst, sulfuric acid which is a Bronner's type acid catalyst can be substituted for Z SM 5, but undesired. So, as I said, during the alkylation reaction, the sulfuric acid or hydrofluoric acid or S3 PO 4, these are used for polymerization alkalization kind of reaction in petrochemical industry. But, if you have solid catalyst then, separation may not a problem, so that is why, the zeolite type catalyst may be preferred.

But, that kind of strong acidity is desired, so again during the formation, the acidity can be controlled, so one thing is that, acidity is controlled by silicon to aluminum ratio in the frame work, that is the first thing. So, higher content of silica, more acidic concentration, more strength of the acidic side. So, the second thing is that, depending upon the type of frame work and the cations, which are present inside the pore of the zeolite, so which are present in the age of the zeolite, so there is a difference in term, so the acidity.

So, these are weaker kind of acid, which are present in the pore of a zeolite and substitution of trivalent atoms such as gallium, iron, boron, they modifies the acidity within the zeolite. So, some time you give a treatment to the zeolite that, protonated zeolite or ammonia exchange zeolite, sodium zeolite and these cations can be replaced by some other cations like gallium, iron, boron and again that gives you the acidity in the zeolite.

So, from dissociation energy calculations, it has been observed that, the bridging in hydroxyl group are more acidic than terminal hydroxyl group. So, that is what the proton which you get in the form of hydroxyl groups H, when you have a Bronner's type acidity in the zeolite structure and when you heat that, the water removes from the zeolite and you get a least type of acidity. So, that is the meaning here that, bridging the hydroxyl groups, which comes in the form of bridge, they are more acidic than the hydroxyl groups, which are attached to the terminals of that. So, that is another important aspect of preparing the zeolite or providing a kind of acidity to the zeolite.

(Refer Slide Time: 20:45)



MCM-41

- The ordered mesoporous (alumino) silicates synthesized with the help of surfactant micelle templates.
- Exemplified by the Mobil M415 materials, of which MCM-41 is the most well-known.

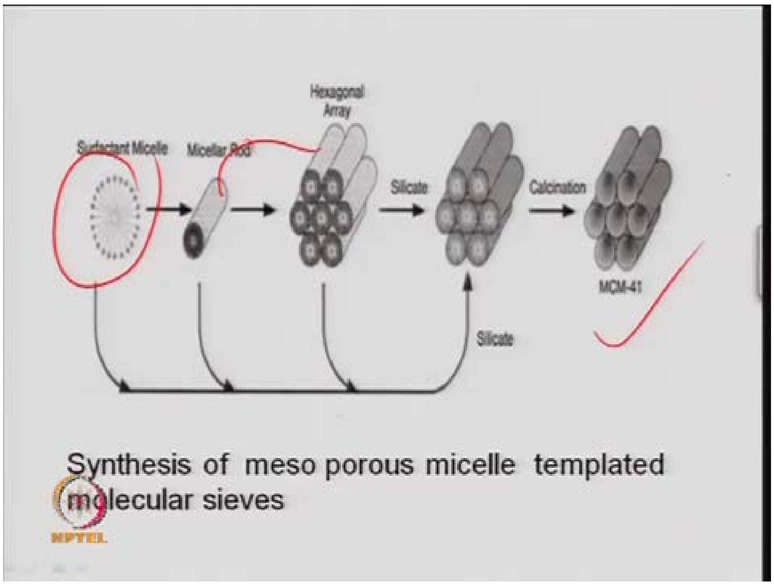
- These micelle-templated silicas contain uniform channels with tunable diameters in the range of 1.5 to 10 nm and a greater uniformity of acid sites than other amorphous materials.

MCM 41 is a different kind of mesoporous material basically and has been used widely for the different kind of reactions and molecular sieving action, so they are different basically and the preparation is little bit different. So, and they may some time the silica more siliceous based material also, so again it is a kind of mesoporous material of alumina silicate and synthesized with the help of surfactant micelle templates. So, instead of using those alkylated or quaternary groups of alcohols, here the same kind of surfactant are used, so detergent type materials, so that is the template here.

So, you get a lamellar kind of structure here or 2 D kind of structure, instead of that cage type of structure what you got in the earlier case for Z SM 5 or further size zeolite A, they have a cage type of a structure. So, here if you look at the Mobil has developed M 415 type material and MCM 41 is the one of the well known material, so there are different kind of MCM 22, MCM 41. So, different kind of materials of these kind of mesoporous material are available, so the micelle templated silica contain some uniform channels with tunable diameters, which are in the range of 1.5 to 10 nanometer.

So, they are basically 15 angstrom to 100 angstrom in mesoporous range, because less than 20 angstrom is a microporous material. This is the definition of IUPAC that, if the pore size is less than 20 angstrom then, it is a kind of microporous material, between 20 to 100, it can be considered as mesoporous and above 100 angstrom pore, they are macroporous material. So, basically these are the mesoporous and has a greater uniformity of acid sides then, other amorphous material, because the same material can be an amorphous natural clay materials. So, different kind of say raw materials, natural clay raw material, they can also be used as zeolite metal, but their acidity, there is not controlled, they are amorphous in nature basically, here you get a kind of crystalline material.

(Refer Slide Time: 23:12)



Synthesis of meso porous micelle templated molecular sieves

So, this is just one recipe that, any surfactant micelle that is converted to a micellar rod just like the structure of building agent, what we are talking during the formation of gel. So, depending upon the condition of a reaction, temperature time and other parameters, which I told before, the ph is dissuasive factor, So you get a kind of this micellar rod and then, they are poly condensed. the building blocks structure, the secondary building blocks from these primary building blocks.

So, in an arranged way, you can see a lamellar kind of structure can also be formed from this, so hexagonal array. So, they are arranged in some hexagonal array and they just mixed the structure and this structure that is during the edging, you get this kind of a structure and when you calcine it, template gets removed or all the surfactant micelle gets removed and finally, you have a kind of MCM metal. So, silicate source is added along with this, so this can be a kind of silica type of zeolite material, highly acidic in nature. So, different kind of mesoporous materials can be made by using the different kind of raw materials of silicate sources.

(Refer Slide Time: 24:30)

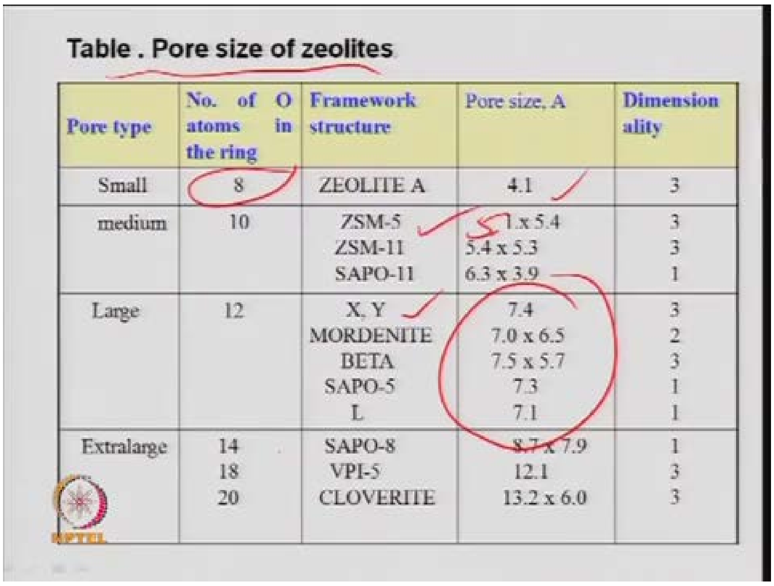


Table . Pore size of zeolites

Pore type	No. of O atoms in the ring	Framework structure	Pore size, A	Dimensionality
Small	8	ZEOLITE A	4.1	3
medium	10	ZSM-5	5.1 x 5.4	3
		ZSM-11	5.4 x 5.3	3
		SAPO-11	6.3 x 3.9	1
Large	12	X, Y	7.4	3
		MORDENITE	7.0 x 6.5	2
		BETA	7.5 x 5.7	3
		SAPO-5	7.3	1
		L	7.1	1
Extralarge	14	SAPO-8	8.7 x 7.9	1
	18	VPI-5	12.1	3
	20	CLOVERITE	13.2 x 6.0	3

So, during this preparation as I said, the way parameter is important and you get different kind of zeolites, so that I have already discussed earlier. So, depending upon the time, temperature, templates agent, you get in the hydroxyl ion concentration, amount of water, so different pores size of the zeolites can be obtained or different type of zeolite. So, when you say zeolite material, basically it has a narrower pore size distribution compared to the other material, which are non zeolytic in nature or amorphous material.

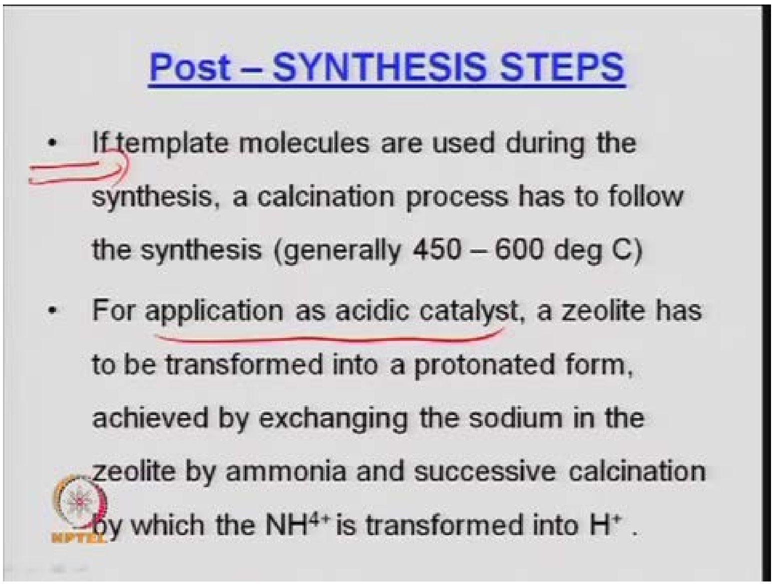
So, the one thing is important in the zeolite that, they are crystalline in nature, they have a definite pore size or very narrower pore size distribution. So, you can get different kind of these zeolite materials, based on the controlling the parameters of the reaction during the synthesis or hydrothermal synthesis. So, small pore zeolites, which are eight membered ring, because as I said when the gel forms, you get these kind of rings. The oxygen in the frame work of the zeolite that is, your primary building block for that zeolite formation.

So, it is a just sodalite as we said truncated, so octahedral hexagonal, so these are truncated and over that, the structure builds. So, you will see that, four membered ring when I said, six membered ring, depending upon the orientation of that crystalline phase, the crystal orientation. So, zeolite A, pore size is roughly 4.1 angstrom and three dimensional. So, all are k type structures here, same thing for medium pore zeolite, you would have Z SM 5, Z SM 11, SAPO 11, silica alumina phosphate, which you have added the phosphetic material then, you get a SAPO type of zeolite what I was discussing yesterday.

So, they have the channels like this variation in the two axis, if you look at the size may vary, say like this in this case, it is 1 into 5.4, so longer in one direction and smaller in other direction Z SM 5 type of material. But, Z SM 5 this is basically 5.1, 5.4 type of materials, which are generally for Z SM 5, so this is a basically, here it is 5.1 in for Z SM 5. So, and again a k type structure three dimensional structure, same thing for SAPO, SAPO is one dimensional basically and 6.3 to 3.9, which has the channel opening.

So, large pore zeolite, you have X type zeolite, Y type zeolite, MODERNITE, BETA zeolite, again SAPO 5 and L type of zeolite, Linde type zeolite. So, they have the large pore opening of the order of 7.4 angstrom and above and dimensions again can vary 3 D, 2 D, 1 D, 1 D like that. So, different kind of structure, lamellar layers in the structure of the zeolite, extra large which have 14, 18 and 20 oxygen in the ring. So, they are considered as a extra large zeolite and pores can be of the order of say 12 to 13 angstrom in size and again they can be 3 D type or 1 D zeolite.

(Refer Slide Time: 27:51)



Post – SYNTHESIS STEPS

- If template molecules are used during the synthesis, a calcination process has to follow the synthesis (generally 450 – 600 deg C)
- For application as acidic catalyst, a zeolite has to be transformed into a protonated form, achieved by exchanging the sodium in the zeolite by ammonia and successive calcination by which the NH^{4+} is transformed into H^+ .

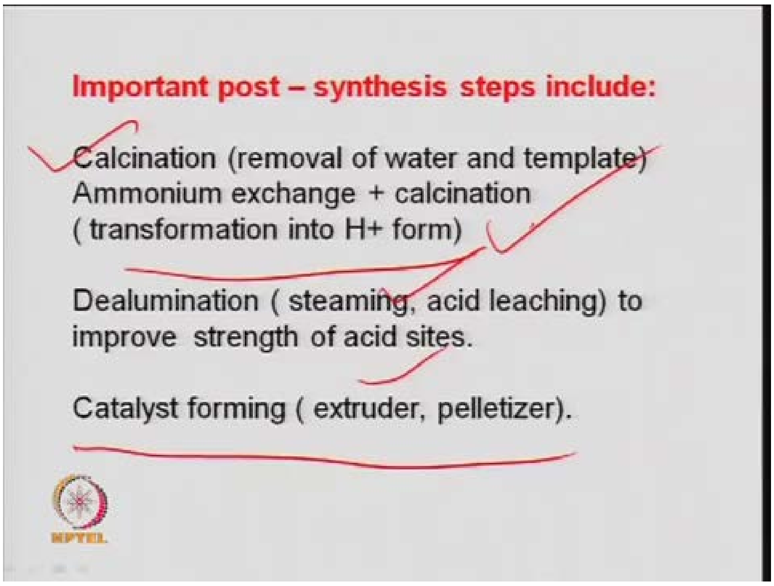
So, once the zeolite is synthesized, you need to look several other steps, so what we call the post synthesis steps. So, first thing is that, type of template which have been used, if the template molecules are used during this synthesis and generally used for the zeolite, the calcination process has to be done. So, calcination is generally done between 450 to

600 degree Centigrade for the removal of this template, because it is a mask and that has to be removed, it does not have any catalytic activity basically.

So, for the application as acidic catalyst, the zeolite has to be transformed into a protonated form, because that is very important, the concentration of H positive ions in the zeolite. Because, the Bronner's acid when we say, so it has the ability to donate a proton. Lewis acidity has the ability to accept an electron, so that gives them the kind of electro negativity in the group and that is the basic of the zeolite material that, when you have added aluminum in the group, it provides the kind of electro negativity.

So, the application of acidic catalyst, the zeolite has to transformed into a protonated form and that can be achieved by exchanging this sodium in the zeolite by ammonia and successive calcination, by which the ammonium ion is transformed into H positive. So, generally as I said, sodium form of zeolite, ammonium form of the zeolite and you give them the treatment and you converted it into the H form of the zeolite. So, you must to add H Z SM 5, which is a protonated kind of zeolite and this H can be replaced by gallium. H can replaced by molybdenum by ion exchange, cation exchange of process, so that is a different preparation from this kind of zeolite materials.

(Refer Slide Time: 29:51)



Important post – synthesis steps include:

Calcination (removal of water and template)
Ammonium exchange + calcination
(transformation into H+ form)

Dealumination (steaming, acid leaching) to improve strength of acid sites.

Catalyst forming (extruder, pelletizer).

So, the important post synthesis step if you look at, so calcinations is one, the removal of water and the template that is, excess water and template growth and ammonium exchange plus calcinations and that transform into the H plus form. As I said, when the zeolite contains sodium, you have to give the treatment with ammonia and then, you get the ammonia form of the zeolite. And when you heat it, the ammonia will be released and you get the H plus zeolite, so that is again an important step here.

Sometime dealumination is done, so dealumination is required sometime as I said that, higher silicon to aluminum ratio in the frame work of zeolite provides the strength to the acid side. So, the dealumination is generally done with the mild acid treatments or as I discussed last time also that, you can give the treatment with some sulfuric acid, small very dilute concentration sulfuric acid, that will leach out some of the aluminum from the frame work of the zeolite rate.

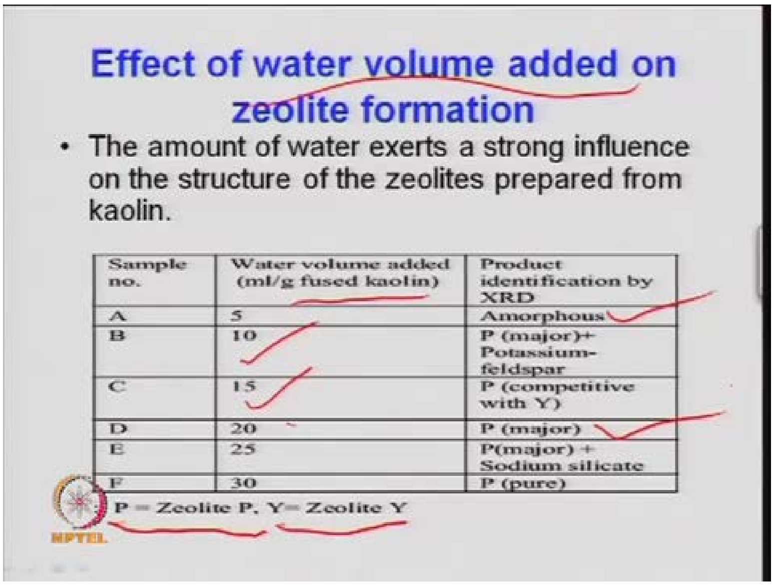
So, their silicon to aluminum ratio will increase, this can also be done by steaming, so that is another method, so steaming or acid leaching can be done to improve the strength of the acid site and that process is known as dealumination. Then, pelletizer, you need the powder during the process you have the powder material and when you look at the reactor application then, the catalyst need a definite shape and size. Because, the smaller or fine powder may have the pressure drop problem during the reactor, which I will take separately later, but these need to be formed in the form of exudates.

So, most of the time zeolites are available in the form of exudates, you can make a tablet also, but when you have a exudates, they are more porous material. But, the only thing that, the strength is poor, in the form of exudates means, you are passing the dou, the material is in the form of dou and you pass it through some dye, you are just making the, you get the noodles. So, it is a kind of the process, where you get different size or of the exudates.

Second thing is that, you have a kind of pelettizing, where you are applying certain kind of high pressure, may be of the order of the 6 ton to 10 ton, so very high pressure. And depending upon the pressure, so the porous may just, the structure may crumble, that is one issue in the case of zeolite. And the second thing is that, you may have a lower porosity, because the pores between the particles when you look at for the reaction, so the pressure drop that is, when the particles are applied prepared under high pressure, the pellet porosity is low.

Particle porosity is not changing, but the pellet porosity may be, so but your strength increase in that case. Because, you have the particles are well binded, because in the presence of binder, this has been just done, the pelletizer. Pellet verses exudates, that is another issue during the catalytic activity and that we will see later.

(Refer Slide Time: 33:05)



Effect of water volume added on zeolite formation

- The amount of water exerts a strong influence on the structure of the zeolites prepared from kaolin.

Sample no.	Water volume added (ml/g fused kaolin)	Product identification by XRD
A	5	Amorphous
B	10	P (major)+ Potassium-feldspar
C	15	P (competitive with Y)
D	20	P (major)
E	25	P(major) + Sodium silicate
F	30	P (pure)

P = Zeolite P, Y= Zeolite Y

So, the process variables which is said, they have an important consideration, important effects on the property of the zeolite and that is to be considered during the synthesis. So, just if you look at here, effect of water volume added on zeolite formation. So, I said that, very low water may not be good and very high water also may not be good, so these are just the research outputs that has been done or data produced by using the amount of water.

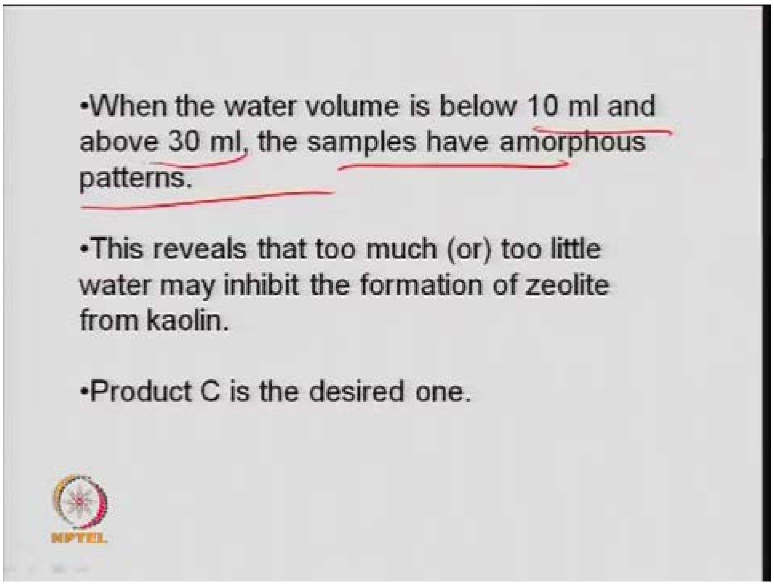
And it has been observed that, amount of water exerts a strong influence on the structure of zeolites, which is prepared from the kaolin, natural clay type materials. So, there are different samples named as A B C D E F and P is the zeolite P, so P here refers to the P type zeolite and Y refers a Y type zeolite. Just some experiment have been carried out with different kaolin material or same kaolin material, but different amount of water loading, other parameters were kept constant.

So, the products were characterized by X ray diffraction that is, the final crystalline structure of the zeolite material and the volume of water, here per ml of the volume of water added in milliliter of per gram of fused kaolin. So, for per gram, the water added 5 ml, 10 ml, 15, 20, 25 and 30 ml, when the water and volume was too low 5 ml, it was just amorphous in nature, no crystalline P was seen. So, low volume of water was not favorable and when the volume was 10 then, P a major form, major P was obtained.

XRD peak shows that, major is the P type of edge, which is good for the desired that is, the P type of zeolite, there was some potassium feldspar, because it is present in the kaolin, so that is from the kaolin. And when the volume of water was 15, again it is a P type and the Y type, in this case there was no Y, here a combination of P zeolite and the Y type zeolite when the water was 15. Because, water goes into the frame work channel of the zeolite and also it helps in the forming the hydroxyl cations, so that is important.

And 20 volume, the major phase were P type zeolite, 25 it is P plus, again sodium silicate and 30 is just P pure. So, means the depending upon the volume of water added, the different type of zeolite or mixture of two type of zeolite may form. So therefore, the amount of water is important, the volume of water added per gram of the material.

(Refer Slide Time: 36:12)

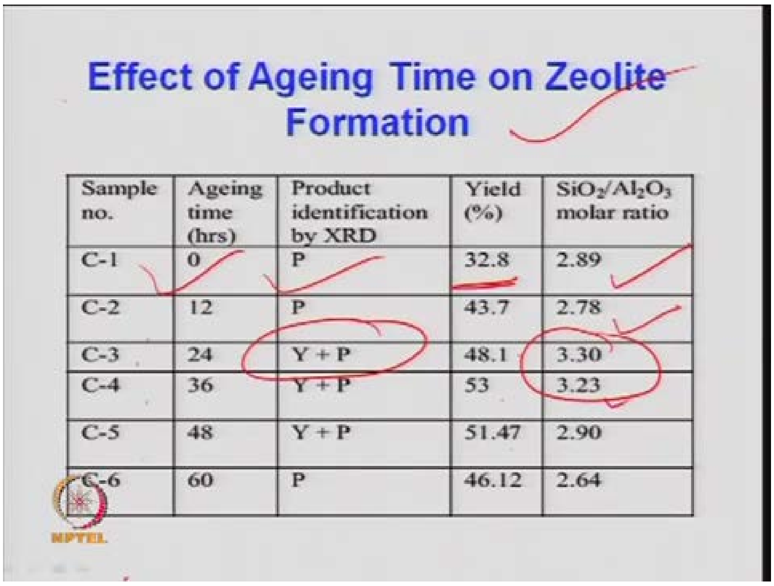


- When the water volume is below 10 ml and above 30 ml, the samples have amorphous patterns.
- This reveals that too much (or) too little water may inhibit the formation of zeolite from kaolin.
- Product C is the desired one.

So, when water volume is below 10 ml and above 30 ml, the samples have amorphous patterns, no crystalline P, so that is what the observation from here that, very high and very low. Above 30 also, it was amorphous in nature, this revels that too much or too little water may inhabit the formation of zeolite from kaolin material. So, this is just the output of one research, which has been carried out by some researcher and they reported that, if the kaolin zeolite is produced from the kaolin type of material then, too much water and too low water may not be favorable.

So, means the depending upon a given process, depending upon the type of the material which has been taken for the synthesis, the amount of water may vary and one has to check the optimum condition for synthesis. So, in this case, say product C, which is this one, so 15 ml water give this P, which is competitive with Y, so both type of zeolite formation, so that is the favorable result.

(Refer Slide Time: 37:24)



Effect of Ageing Time on Zeolite Formation

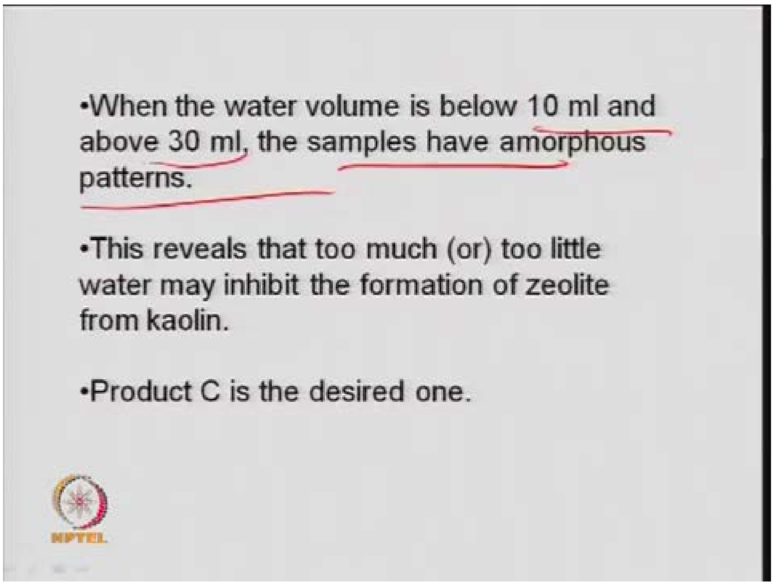
Sample no.	Ageing time (hrs)	Product identification by XRD	Yield (%)	SiO_2/Al_2O_3 molar ratio
C-1	0	P	32.8	2.89
C-2	12	P	43.7	2.78
C-3	24	Y + P	48.1	3.30
C-4	36	Y + P	53	3.23
C-5	48	Y + P	51.47	2.90
C-6	60	P	46.12	2.64

They have also carried out experiment of ageing time, effect of ageing time on zeolite formation. So, as I said that, the crystallization will depend on this, degree of crystalline T, which you confirm from the X ray diffraction pattern. So, again here, the different sample C 1 C 2 C 3 C 4 C 5 C 6, ageing time this was just 0, no time was given for ageing, this is for 12 hours, this is 24, 36, 48 and 60. So, the product identification was done by X ray diffraction pattern and no, it is just a pure type material.

When 12 hour it is again P, but the yield wise if you look at here and silicon to alumina ratio or silica to alumina ratio, so this is 2.89. For 12 hour it is 2.78, 24 hour the phase was Y plus P. So, because the acidity is depending on this, yield of crystal that is measured phase on the intensity of the X ray diffraction pattern and then, counted the count rate, so that compared. So, P type 32.8 percent here, it is 43.7 so increasing, 24 hour it became 48.1, 36 43 and this is also silica to alumina ratio is now some where tuned.

So now, what is the silica to alumina ratio desired in your final one, suppose if take 3.3 is the desired then, I will fix this time, where you have Y plus P with yield of this type of zeolite 48.1 percent yield of Y plus P in total and same thing, here it is 53 with acidity on it depends, they gone down. So, it means, again you can see that, ageing time has a very crucial effect or yield, the yield is also showing some sort of maxima in terms of the Y and P type of zeolite. And silica to alumina ratio, which is very crucial for the given time of zeolite, given type of zeolite that becomes the important.

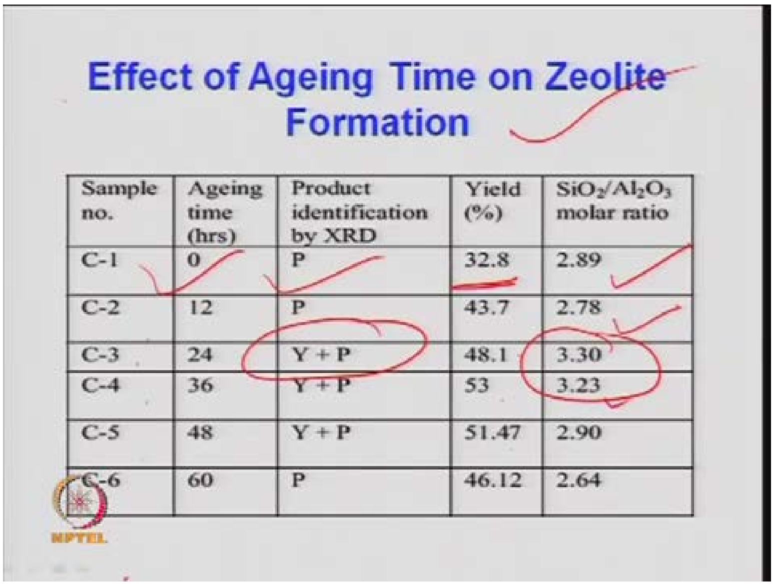
(Refer Slide Time: 39:26)



- When the water volume is below 10 ml and above 30 ml, the samples have amorphous patterns.
- This reveals that too much (or) too little water may inhibit the formation of zeolite from kaolin.
- Product C is the desired one.

So, here again the influence if you see, the proper ageing time for this kind of study, they desired was 3.3 silica to alumina ratio, so 24 was the better one. For the formation of zeolite Y with higher intensity, so at 24 hour, the zeolite Y percentage was higher and silica to alumina ratio was 3.3. At the optimum point, the yield percent of the product was 48 percent and silica to alumina molar ratio was 3.3. So therefore, this C 3 was considered as a desired product in this case.

(Refer Slide Time: 40:08)



Effect of Ageing Time on Zeolite Formation

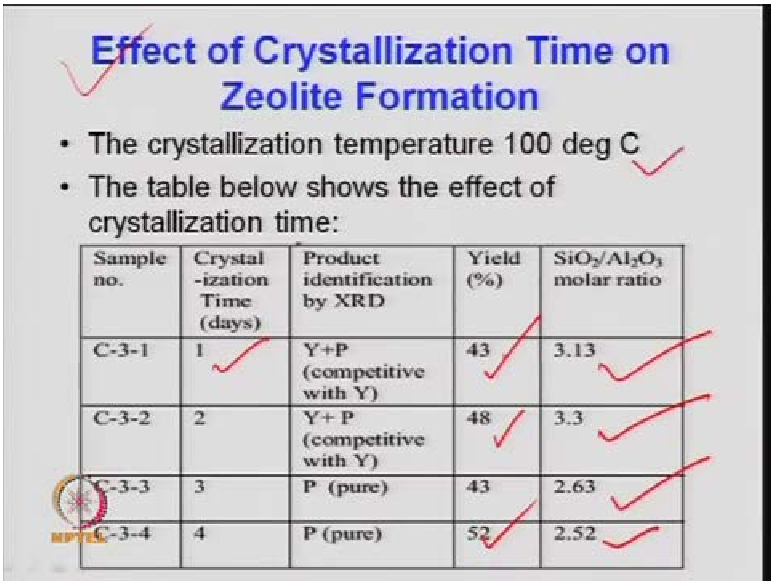
Sample no.	Ageing time (hrs)	Product identification by XRD	Yield (%)	SiO_2/Al_2O_3 molar ratio
C-1	0	P	32.8	2.89
C-2	12	P	43.7	2.78
C-3	24	Y + P	48.1	3.30
C-4	36	Y + P	53	3.23
C-5	48	Y + P	51.47	2.90
C-6	60	P	46.12	2.64

Then, crystallization time, so crystallization time again is important in the zeolite synthesis. So, one is the ageing which has been done when the nucleate form before that, the gel has formed and then, you age the gel, dissolution has been done there and now, the growth of the crystal which is nucleation, so that is again important. So, here again if you look at the different experiment which have been carried out, crystallization time varied from 1 2 3 and 4, so between 1 and 4 days.

The product identification was done by XRD and the peaks of Y and P type zeolites were identified, so competitions with Y. Yield wise if you see here, it varied from 43 48, 43 to 52, when the time was varied from 1 to 4, so yield varied from 43 to 52 in terms of the Y, the zeolites. And silicon to ammonium ratio here it is 3.13, it is 3.3 2.63 2.52, so decreased, because the degree of crystallinity is very important when the nucleate forms and the crystal growths, the crystal will grow.

And it is a condensation also, because the building a kind of sodalite cage, which has formed. The first thing in the ageing, where the six membered ring, so eight membered, five membered rings have formed, that is the first step and then, it is converting into a cage, just truncated octahedron, pentagon structure or hexagonal structure. So now, one buckyball structure forms and when you are talking a crystallization then, these are connecting together, building together and making a frame work of the zeolite.

(Refer Slide Time: 42:22)



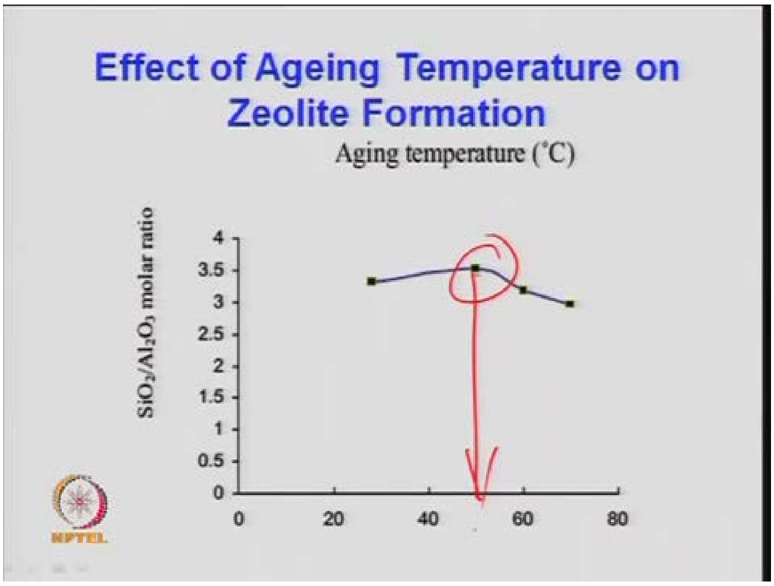
Effect of Crystallization Time on Zeolite Formation

- The crystallization temperature 100 deg C
- The table below shows the effect of crystallization time:

Sample no.	Crystal -ization Time (days)	Product identification by XRD	Yield (%)	SiO_2/Al_2O_3 molar ratio
C-3-1	1	Y+P (competitive with Y)	43	3.13
C-3-2	2	Y+ P (competitive with Y)	48	3.3
C-3-3	3	P (pure)	43	2.63
C-3-4	4	P (pure)	52	2.52

So, that is during this period, the crystals when they are growing, so then this again the definite requirement depending upon the conditions or the final catalyst or zeolite desired, one has to identify. So, crystallization temperature was kept 100 degree for comparison and time was varied ((Refer Time: 42:24)). And here again, because as a desired was a silica to alumina ratio of 3.3 with some yield percent of 48, so that is what the optimal point, which is desired for the given catalytic reaction. The crystallization time was roughly 2 days, so our requirement was this 48 that is, yield and this acidity silicon to alumina ratio rather, so for that, this 2 days were found effective or optimal. So, this is the desired sample here in this case and beyond this point the molar ratio has decreased, so silica to alumina ratio went down, so not favored.

(Refer Slide Time: 43:09)

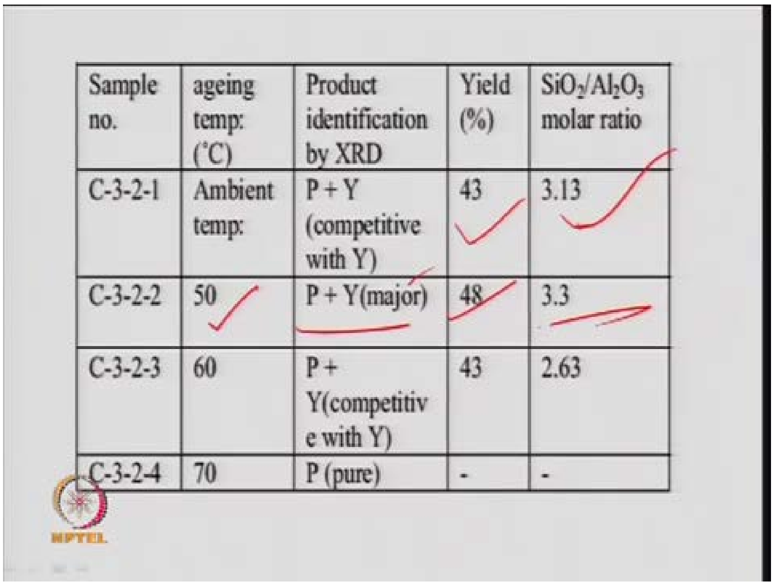


Effect of Ageing Temperature on Zeolite Formation

So, this is just a effect of ageing temperature again on zeolite formation, so the ageing temperature, so in that, it was kept 100 degree Centigrade, at 100 that time is important. So now, once time is optimized, so that is what the sometimes the design of experiments, which is a kind of factorial design. If you have n number of parameters then, 2 to the power n number of experiments may be required that is, to identify the most suitable condition.

So, one can identify the maximum limit and the minimum limit of the parameter, so minimum to maximum and then, identify the most suitable parameter and conduct the experiment at those conditions. So, that is the better way to identify or short list the number of variables of the design or design parameters for the experiment. So, here also again if you see here, the silicon to alumina ratio was maximum here at around this temperature. So, it means, the temperature also plays a very important role, so ageing temperature is very important for the crystallization or nucleate formation, this is the dissolution when the gel is forming.

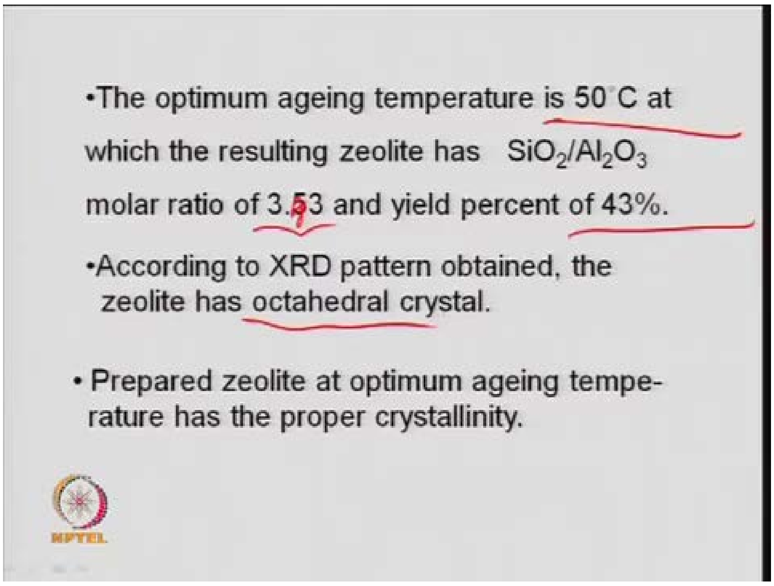
(Refer Slide Time: 44:19)



Sample no.	ageing temp: (°C)	Product identification by XRD	Yield (%)	SiO_2/Al_2O_3 molar ratio
C-3-2-1	Ambient temp:	P + Y (competitive with Y)	43	3.13
C-3-2-2	50	P + Y(major)	48	3.3
C-3-2-3	60	P + Y(competitive with Y)	43	2.63
C-3-2-4	70	P (pure)	-	-

So, you can see again that ambient temperature ageing goes down, so 43 percent yield, silica to alumina ratio 3.13. 50 degree centigrade P plus Y, Y is the major here and 48 percent yield of Y and that is 3.3 with the silica to alumina ratio. So, again the 50 degree Centigrade ageing is better for this case.

(Refer Slide Time: 44:44)



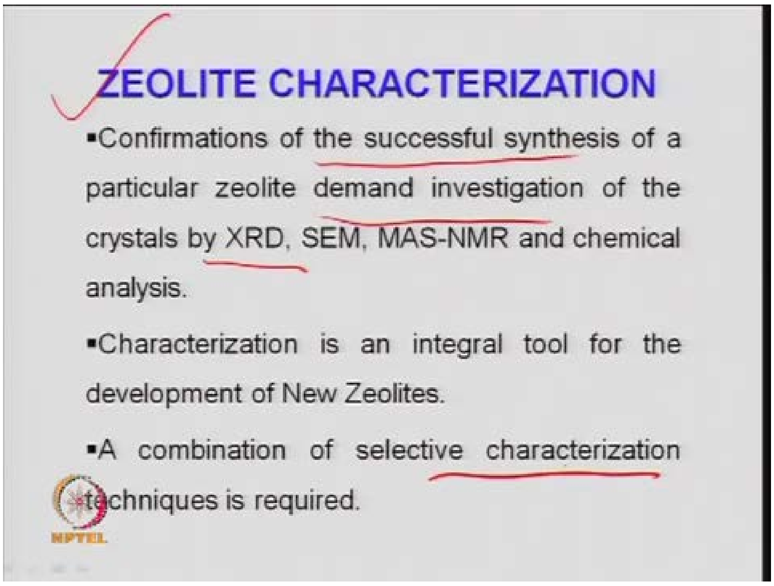
- The optimum ageing temperature is 50°C at which the resulting zeolite has SiO_2/Al_2O_3 molar ratio of 3.53 and yield percent of 43%.
- According to XRD pattern obtained, the zeolite has octahedral crystal.
- Prepared zeolite at optimum ageing temperature has the proper crystallinity.

So, optimum ageing temperature at around 50 degree Centigrade, at which resulting zeolite has silica to alumina ratio roughly 3.3 basically. In this case, 50 degree Centigrade, so 3.3 this is, not 3.53 and the yield percentage 43 percent. So, according to

XRD pattern, whatever the region observed, the zeolite has the octahedral crystal. So, one can do the details of these crystal morphology then, and look at the surface topology.

So, X ray diffraction is the one, by which the phases can be identified and then, other morphology or other characterization tools can be done to identify the crystal size and shape. So, prepared zeolites at optimum ageing temperature has proper crystallinity, so that is just the ageing temperature, time then, nucleation or crystallization temperature, crystallization time, so all are important for the synthesis of the zeolite.

(Refer Slide Time: 45:48)



ZEOLITE CHARACTERIZATION

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

So, what I mean to say that, when you have to prepare a definite kind of zeolite, the conditions for synthesis of preparation are to be identified first. And then, for those conditions based on the available raw materials or raw materials taken, you have to optimize the conditions for formation. So, there may be some initial heat and trial required, because the preparation of zeolite is not an easy job, it is an hydrothermal synthesis required high pressure, temperature and time.

And then, you have to take out the sample at different intervals, where you expect the results may be good based on some primary analysis and then, do the XRD analysis and then, identify the yield of the zeolite. So, one can prepare different kind of zeolite materials and then, look at their stability, selectivity for a given reaction and that can be a one type of zeolite. So, all the zeolites which are available are in the form of patents, they are just a proprietary items for a given vendor or given manufacturer.

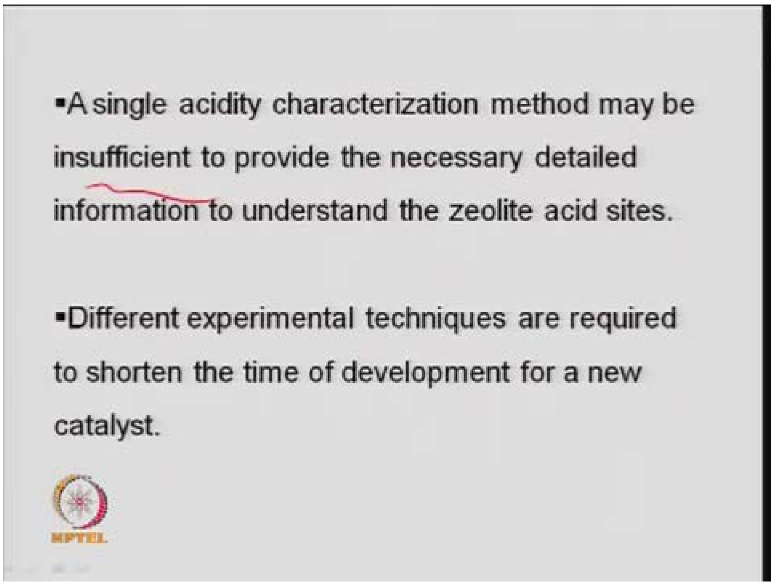
So, one has to look at or match the, tune the property of the prepared zeolite and then, compare with the available zeolite materials, so that is the important aspect in the zeolite synthesis. So, once prepared the characterization is again important, the zeolite characterization, so as usual the BT, TPD, TPR, XRD, SEM, TEM, FTIR, IR proton NMR, all these kind of characterization technique, which we have discussed earlier can be used for the characterization of the zeolite.

Because, these are the basic property or basic materials, analytical instruments to characterize any catalytic material or just to look at the surface characterization or demystify the surface analysis, so this can be used. So, here again the confirmation of successful synthesis of a particular zeolite, you are naming a zeolite, because they are prepared in a different hydrothermal conditions, different type of material.

So, they demand the investigation of the X ray diffraction, their crystals, type of the crystal, a scanning electron micrographs to look at the particle size, topology of the particle and the mass NMR. So, nuclear magnetic resonance to find out the bond oxide oxidation states of the zeolite material, that is important. And IR is used basically to find out the acidity of the zeolite, so this mass NMR can be used to find silicon to aluminum ratio of the zeolite also.

So, all these are important beside that, the other usual tools as I said, the surface area, pore volume, pore size distribution, they are important. So, characterization becomes a very important for the development of a novel catalyst in general or in zeolite material. So, a combination selective characterization technique is required in order to characterize these kind of zeolite materials.

(Refer Slide Time: 49:07)



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

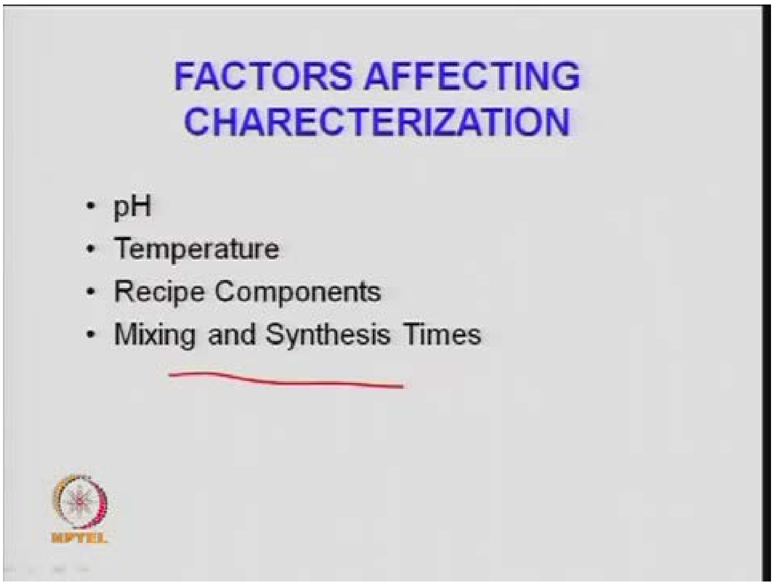
So, single acidity characterization, basically if you say the acidity, so it means, you are titrating with some base. So, basic simple thing is, the titration technique one can do and the only thing that the error analysis you have to confirm. Because, once you do by manual methods, there may be error or because the concentration of these acid sites when we say, they are reported either in terms of milli moles of the ammonia gas suppose if I use ammonia or pyridine base.

So, this is a low number basically and the determination of the concentration at these low concentration or low number value is not an easy job. So, basically one has to calculate based on titration technique, but the method should be much more sophisticated in order to determine, because the catalyst when I say, that it is protonated. The concentration of acid sites, Bronsted's type, Lewis type acid, so these are important to characterize. So, they can be measured, but more sophisticated, analytical equipments are required.

So, single acidity characterization method, this may not be sufficient to provide the necessary detail in the formation to understand the zeolite acid sites, because we have to say that, whether it is Lewis type acidity, Bronsted type acidity, at what temperature it gets disorp, the ammonia molecule which gets adsorbed and look at the desorption. So, through study is need to be done and the metals, which may be added, what is the effect of those metal which have been added as a cation exchanger.

So, again the acidity is affected, so one has to check those things. So, different experimental techniques are generally required to shorten the time of development of a new catalyst, so one has to characterize the catalyst thoroughly.

(Refer Slide Time: 50:56)

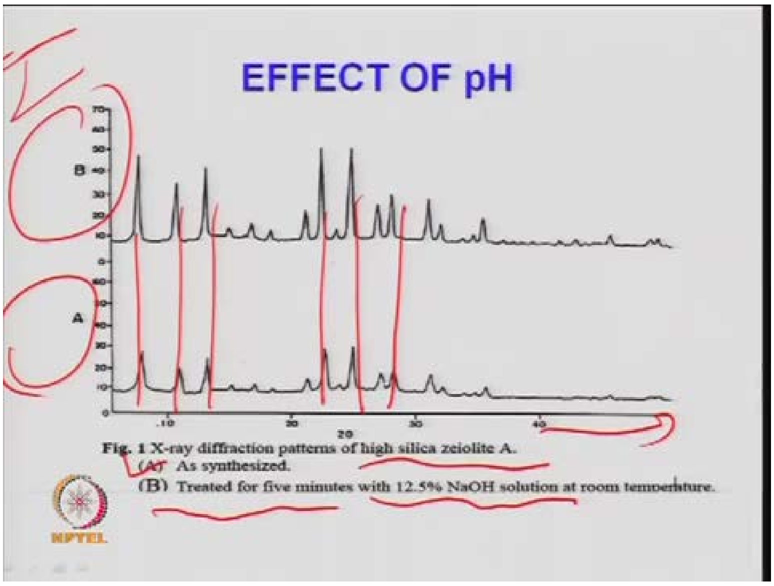


FACTORS AFFECTING CHARECTERIZATION

- pH
- Temperature
- Recipe Components
- Mixing and Synthesis Times

So, factors that may affect the characterization of a zeolite material again depends on the PH that, what I am talking during synthesis part, a synthesis, PH is different, different type of metal will be obtained. Temperature, recipe components, the type of silica to alumina materials have been taken, hydroxyl material, minerals which have been added, templating agents. So, all these will be crucial to impart the acidity or to develop a frame work or a silica to alumina ratio and accordingly, the property will differ, change. So, and mixing and synthesis times, so all these are very crucial.

(Refer Slide Time: 51:42)



EFFECT OF pH

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

So, just if you look at here, effect of PH, so this is A, so X ray diffraction patterns of high silica zeolite A, so this is a high silica zeolite material and the two type of methods have been used, which is a method A synthesis and this is the B, which is synthesis for 5 minutes with 12.5 percent sodium hydroxide solution at room temperature. That is, the zeolite has been treated for just 5 minutes with 12.5 percent sodium hydroxide and you see now the crystallinity.

So, effect what I mean to say the hydroxyl ions, which have been added to the zeolite material, just for 5 minutes the treatment was given and at room temperature, the property are differing in terms of the crystallinity. So, the peaks, you see the peaks can be similar if I just look at the major peak here, but the degree of crystallinity is different, intensity is different here. So, this side is your intensity, this can be some orbit unit or this can be something like 10 20 30 40 50 60 70 with say 100 percent is the top highest peak intensity and this is the diffraction angle 2 theta.

So, X ray diffraction pattern, so at a given wavelength, the peaks were reported and you can see here then, when the treatment has been done with some alkaline material, zeolite materials have been treated with some alkaline material, the peak intensity is now high. So, basically these peaks are some silicate, some aluminate, silica alumina, so all those are the numbers have not been mentioned, but here just for the sake of comparison I am saying that, the intensity of the peak change, when it was treated with some alkaline material, so this is the effect of PH.

(Refer Slide Time: 53:40)

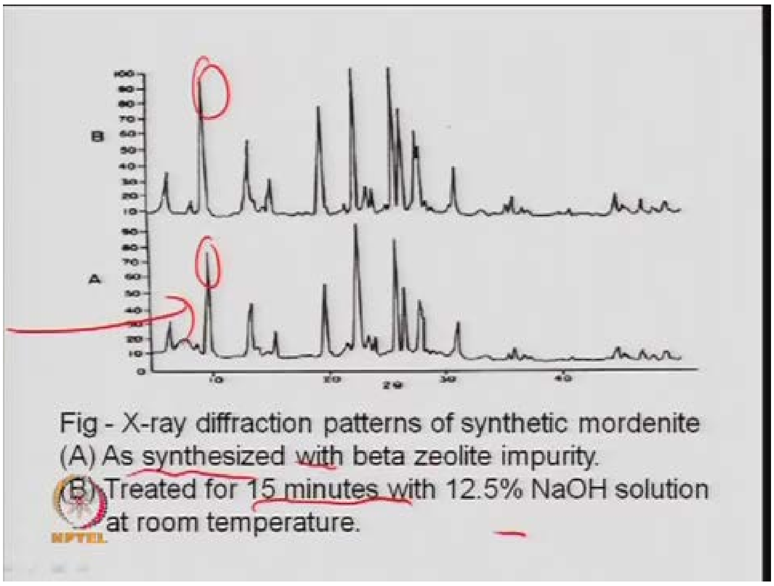


Fig - X-ray diffraction patterns of synthetic mordenite
(A) As synthesized with beta zeolite impurity.
(B) Treated for 15 minutes with 12.5% NaOH solution
at room temperature.

So, again here the zeolite material, X ray diffraction pattern of synthetic mordenite zeolite is synthesis with beta zeolite impurity. So, there are two kind of zeolite mixtures, so one is treated, so this A is just synthesis with beta zeolite. So, this is your A, just you are prepared the zeolite material with no treatment. In this case, after zeolite which have been obtained, is again treated for 15 minute with 12.5 percent NaOH. So, here also it has been observed that, the intensities are different here, say this is different type, this is different.

So, peak intensity is change although the degree of crystallinity if you look at, it is not changing, there is no significant change or no new peak has been reported. So, it means, no new phase has been formed or the phases have not been damaged also, but the intensity of those peaks have been reduced when there is no treatment. And when they are treated under certain that is, kept under certain PH then, the peak intensity is higher, so effect of PH has some role.

(Refer Slide Time: 55:01)

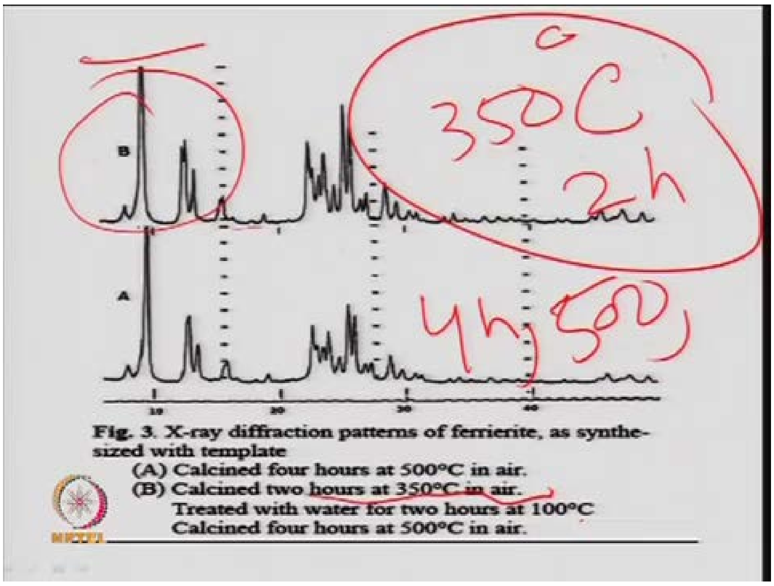


Fig. 3. X-ray diffraction patterns of ferrierite, as synthesized with template
(A) Calcined four hours at 500°C in air.
(B) Calcined two hours at 350°C in air.
Treated with water for two hours at 100°C
Calcined four hours at 500°C in air.

So, this is again a different which in for ferrite type material in the presence of some template. So, A calcine for 4 hour at 500 degree Centigrade and B is calcined for 2 hour at 350 degree Centigrade. So, here calcination temperature is 350 degree Centigrade, here the calcination temperature is 500 degree Centigrade. Time is also different, so 500 degree Centigrade 4 hour and this is just for 2 hour.

So, this again to check the effect of calcination, in this case if you see, this calcine catalyst which is for 2 hours at 350 degree Centigrade in presence of air, both are the treated with water for 2 hour at 100 and calcined for 4 hour at 500 degree Centigrade, again this sample B. So, first it is calcined for 2 hour to 300 and then, treated with water and again calcined for 500 degree Centigrade for 4 hour. So, retreatment was done means, just look at that what is the effect of calcination and what is the effect of water treatment on the zeolite.

So, here it can be seen that, not significant deference has been observed that is, when you are calcined for 350 degree Centigrade 2 hour and then, second case, the metal was treated with water for 2 hour at 100 degree Centigrade and then, again calcined for 500 for 4 hour. So, logically if you look at the structure wise in phase formation, no new phase has been formed and their order of crystallinity is also similar.

So, this observation says that, 350 degree Centigrade for 2 hour is sufficient for the calcination, no need to go to 500 and 4 hour. So, that is just to identify the temperature required or minimum temperature required for the treatment of the zeolite. So, not significant change, but it will depend on the type of zeolite to zeolite, so I will continue it next time ((Refer Time: 57:11)).