Nanostructured Materials-Synthesis, Properties, Self Assembly and Applications

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Module - 2
Lecture - 3
Synthetic Methodologies

Welcome back to this course on nanostructured materials, synthesis, properties, self assembly and applications. Today, we will start the first lecture of the second module basically one the synthetic methodologies of obtaining nanostructures. In the previous two lectures, we introduced you to the basics of nanoscience and nanotechnology, what are nanomaterials, what properties they may have which are different than bulk properties. Some idea of where nanotechnology can take us some applications very briefly we went through that and we also gave you some idea about the two basic methodologies that people use.

One is the top down approach and the other is the bottom up approach, so we would be now discussing more in detail about each of these synthetic methodologies. So, in the first two lectures of module two that is this lecture and the next lecture we will be studying one particular method of synthesis.

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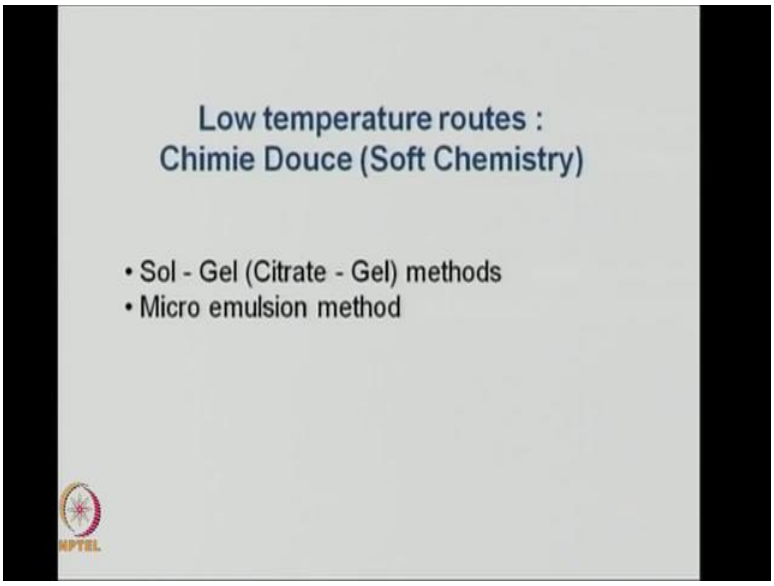

Low temperature routes :
Chimie Douce (Soft Chemistry)

- Sol - Gel (Citrate - Gel) methods
- Micro emulsion method

So, let me tell you that low temperature methods are basically bottom of approaches, so another word which is used for low temperature methods is Chimie Douce which in French means soft chemistry. So, the first two methods which I will discuss in this course are the Sol Gel, which is also can be a citrate Gel method depending on if your using citric acid as one of the poly hydroxy acids for the formation of the Sol Gel is a general term for many of these processes.

Low temperature processes which form one of the methodologies of the bottom up approach is to obtain nanostructures. The other methodology that I will discuss after Sol Gel in the micro emulsion method, so we will have two lectures on the Sol Gel method. Then, we will have two lectures on the micro emulsion method, so what is this Sol Gel technique.

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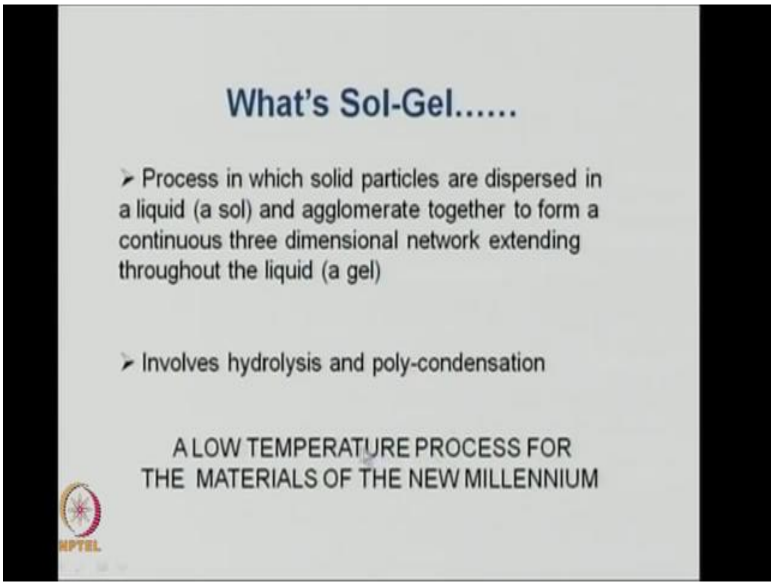

What's Sol-Gel......

- Process in which solid particles are dispersed in a liquid (a sol) and agglomerate together to form a continuous three dimensional network extending throughout the liquid (a gel)
- Involves hydrolysis and poly-condensation

A LOW TEMPERATURE PROCESS FOR
THE MATERIALS OF THE NEW MILLENNIUM

So, in this Sol Gel technique, we have a process in which solid particles are dispersed in a liquid, so you this is called a Sol when your very fine particles dispersed in a liquid and then they agglomerate together to form a three dimensional network. Then, it is called a Gel so in a Gel you still have some liquid within it so from a Sol which yields particles in a liquid to a Gel which is an inter interconnected system three dimensional network structure which still has some liquid is a gel. So, this Sol to Gel transition involves hydrolysis and poly condensation, this is a low temperature process. Many new materials are being synthesized, which are called blast materials for the new millennium by this low temperature root, which is called Sol Gel root.

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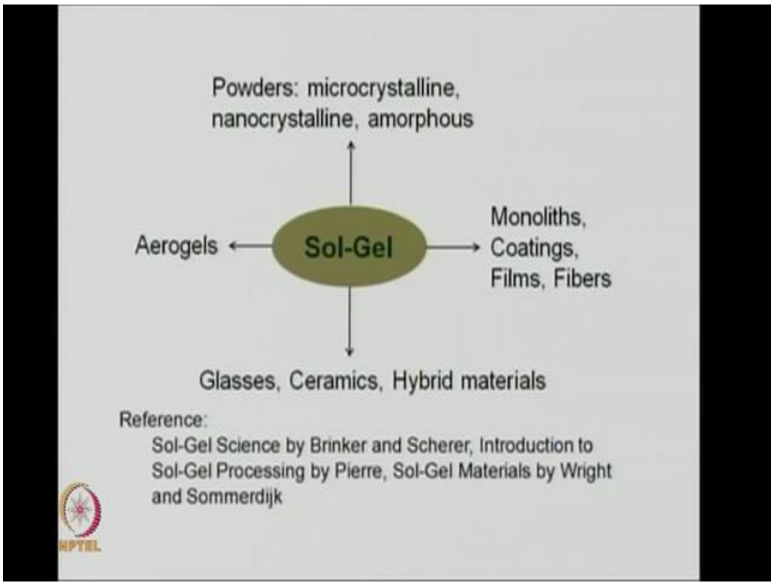

Powders: microcrystalline, nanocrystalline, amorphous

Aerogels

Sol-Gel

Monoliths, Coatings, Films, Fibers

Glasses, Ceramics, Hybrid materials

Reference:
Sol-Gel Science by Brinker and Scherer, Introduction to Sol-Gel Processing by Pierre, Sol-Gel Materials by Wright and Sommerdijk

Now, you can get from Sol Gel method powders which are microcrystalline or nanocrystalline, you can get amorphous powders that means they do not have any crystallinity. So, they lack the long range order which is there in crystalline substances, you can make a aerogels that means you can have a porous network structure. If you remove from the Gel, the liquid without destroying the structure, you get a porous structure which is called a aerogel, you can also get a monolithic structure by the Sol Gel route and many compounds are made by this method.

You can make coatings you can make films, you can also make glasses and other ceramics by the Sol Gel method. So, this is a very popular method or making crystalline materials as well as other forms of materials with either high surface area very small particle size and crystalline as well as glasses which are amorphous materials. These are two references, one is Sol Gel science by Brinker and Scherer, then introduction to Sol Gel processing by Pierre.

You can also look at this book on Sol Gel materials by Wright and Sommerdijk, so these are all classic books on Sol Gel science and technology, which tell you how to synthesize or how to choose a starting material to make a particular Sol. Then, what you do with that Sol to get a Gel and how from the Gel you can get an aerogel or a 0 Gel or coatings or films, etcetera.

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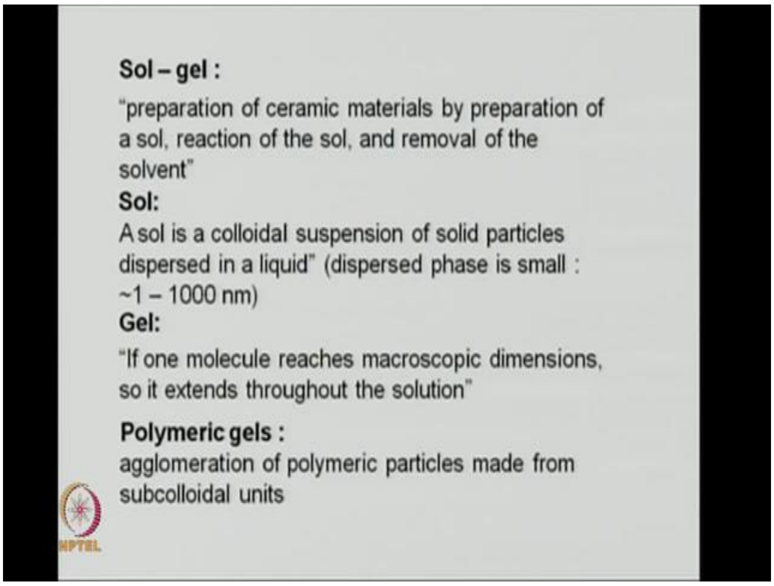

Sol – gel :

"preparation of ceramic materials by preparation of a sol, reaction of the sol, and removal of the solvent"

Sol:

A sol is a colloidal suspension of solid particles dispersed in a liquid" (dispersed phase is small : ~1 – 1000 nm)

Gel:

"If one molecule reaches macroscopic dimensions, so it extends throughout the solution"

Polymeric gels :

agglomeration of polymeric particles made from subcolloidal units

So, in a typical Sol Gel process, we are preparing making a Sol, then reaction of the Sol to get the Gel and finally, we remove the solvent. So, in a Sol you have a colloidal suspension of solid particles and the dispersed phase that is solid phase is small particles of the order of 1 to 1000 nanometers. When we react this Sol and it forms an interconnected network structure, we get this, so this reaches macroscopic dimensions and it extends throughout the solution. You can get polymeric gels by the agglomeration of polymeric particles made from subcolloidal units. So, from the Sol we get which is particles in a liquid to a Gel which is a three dimensional network structure, so you get this Sol to Gel transition.

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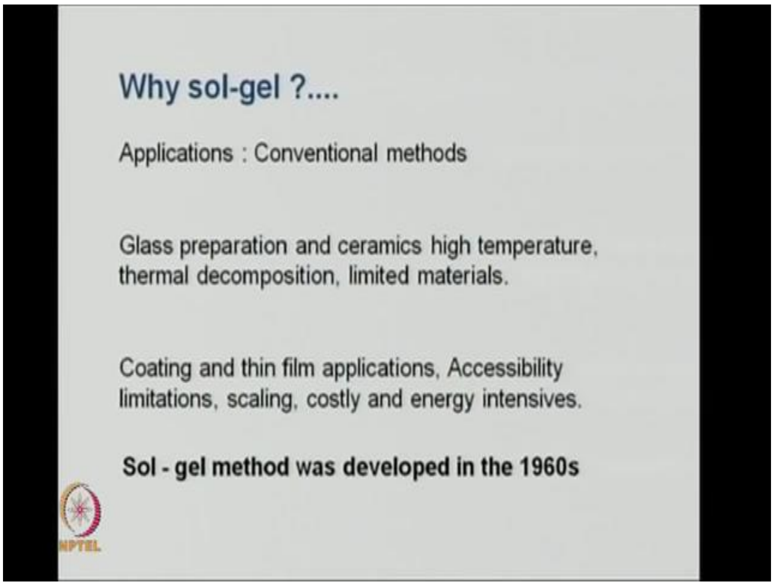

Why sol-gel ?....

Applications : Conventional methods

Glass preparation and ceramics high temperature, thermal decomposition, limited materials.

Coating and thin film applications, Accessibility limitations, scaling, costly and energy intensives.

Sol - gel method was developed in the 1960s

Why one needs to use this Sol Gel method apart from the conventional method since you can make lot of new materials, which have lot of applications. So, you can make coatings and thin film applications the convention methods have limited materials. They can synthesize they cannot synthesize the porous materials and nanocrystalline materials, whereas in the Sol Gel method, you can make nano crystalline materials.

You can make coatings, thin films and the cost is quite low because it is a bottom up approach it is a low temperature method and it is not energy intensive as the conventional methods. The Sol Gel method was developed in the 1960s and it has been improved over the last fifty years to apply to several new materials, which are being discovered in the recent past.

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Steps involved in a typical sol-gel process

Hydrolysis

Condensation

Gelation

Ageing

Drying

Densification

Now, the steps which are involved in a typical Sol Gel process, you have first the hydrolysis step, then you have the condensation step and in after the condensation step you have the Gelation. You may get the Gel and then the Gel is allowed to age that means it is kept for some time and during aging and some solvent may go away and after that you have to dry the gel and then densify it depending on your applications.

You would like to densify or you may not like to densify an it depends on the kind of application that your looking for… So, these are the main or the key steps in a typical Sol Gel process, so you go from hydrolysis condensation Gelation ageing drying and then you get a dense solid by densifying the dried Gel.

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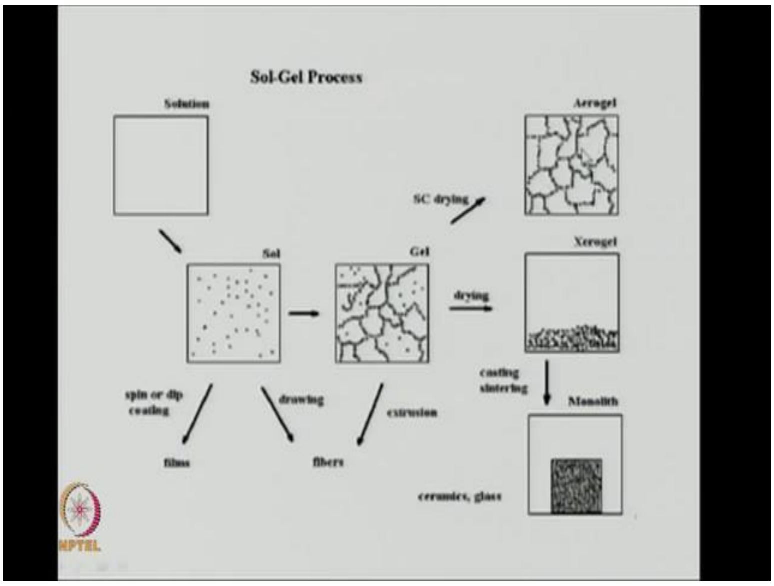

Sol-Gel Process

Solution

Sol

Gel

SC drying

Aerogel

drying

Xerogel

casting
sintering

Monolith

spin or dip
coating

films

drawing

extrusion

fibers

ceramics, glass

So, in a pictorial view you can look at you have a solution, then you get a Sol where you have these particles which are dispersed in this liquid and then depending on what you want to do you can get several products. You can take this dispersed solid in a liquid which is a Sol you can spin coat or dip coat it. You get films, this one application you can pass it through some mould and draw fibers out of it. So, you can get fibers of oxides or metal fibers depending on what kind of particle are there you can allow these particles to condense and form a network like this to form which is a Gel. Then, that Gel you can dry in different methods if you dry it simply and allow this structure to collapse, then it will form what is called a 0 gel.

So, in a 0 Gel, the structure collapses and you do not get this kind of a network structure anymore however there is something called super critical drying, you do that you can remove the liquid in between these network structure to get this porous Gel. This is called a aerogel, it is like a very porous structure, where the liquid has been removed and the structure still remains. So, you can get the aerogel or the zero Gel depending on how you dry the Gel and this will have a very high surface area, it will be catalytically very active, however this will have a low surface area.

Now, you can also get a monolith, so if you take this zero Gel and heat it at high temperature that means sintering, it you will get a monolithic structure which you can use like you want to use a ceramic or class monolith. They can be made like this you can make fibers not only by drying from the Sol, you can also draw fibers by extruding from the Gel. So, various end products are possible depending on the application you have to treat the Gel in appropriate manner to yield either the aerogel the zero Gel the monolithic structure or fibers or films.

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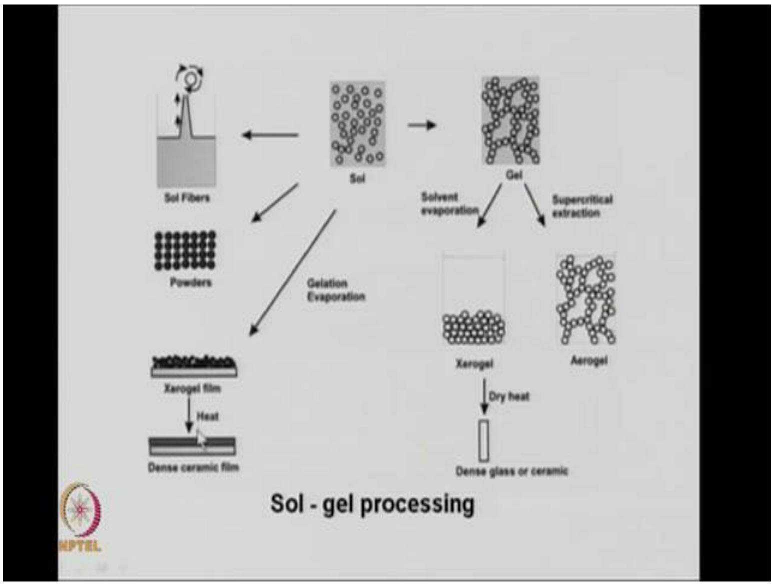

Sol - gel processing

Now, in a typical Sol Gel processing like to discuss what I just mentioned in little bit more detail. So, you have the Sol the particles are there in a liquid and you want to make a Gel, so you allow them to interconnect. So, when they interconnect they form kind of a 3 D structure which still has some liquid inside. Then, you can get the zero Gel or on normal drying and under super critical extraction, you can take out the liquid without disturbing the three dimensional porous structure and you get the aerogel. You can heat the zero Gel into the dense solid or you can make a film like from the Sol, you can make a film which is called a zero Gel film and you can make a dense film. After heating this, you can just get powders if you dry the Sol, you will get the powders which may be nanocrystalline. So, you get a nanocrystalline powders, you can make nanocrystalline films depends on what is your application.

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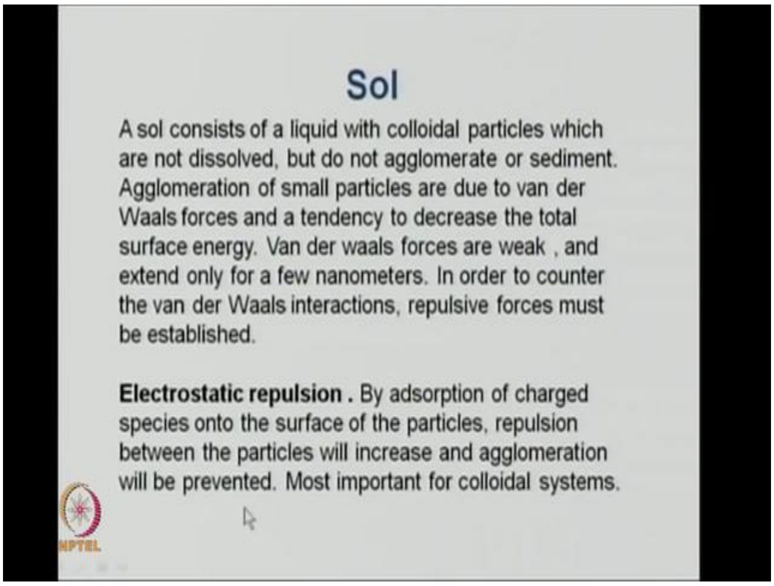

Sol

A sol consists of a liquid with colloidal particles which are not dissolved, but do not agglomerate or sediment. Agglomeration of small particles are due to van der Waals forces and a tendency to decrease the total surface energy. Van der waals forces are weak , and extend only for a few nanometers. In order to counter the van der Waals interactions, repulsive forces must be established.

Electrostatic repulsion . By adsorption of charged species onto the surface of the particles, repulsion between the particles will increase and agglomeration will be prevented. Most important for colloidal systems.

So, what a Sol consists of, liquid with colloidal particles which are not dissolved, but do not agglomerate or sediment, they have particles, which are not going to come down and sediment. So, that is a Sol and the agglomeration is due to Van der waals forces and in order to counter the Van der waals forces, because you want to keep the particles separate there must be repulsive forces. These repulsive forces are important in a Sol to keep it highly, you know the particles to be highly separated and mono disperse this repulsive force can be due to electrostatic repulsion.

This electrostatic repulsion is caused due to the absorption of charged species on the surface of the particles. So, when you have charges on the surface of the particles there will be repulsion between the particles and agglomeration will be prevented. This is very important for colloidal systems, where you have particles and these particles have a surface charge. These surface charges prevent the particle from agglomerating and in turn keep the size of the particles small. That is what you want when you want to synthesize nanomaterials, the other way or one method as I said is using charge the other way is using some steric hindrance.

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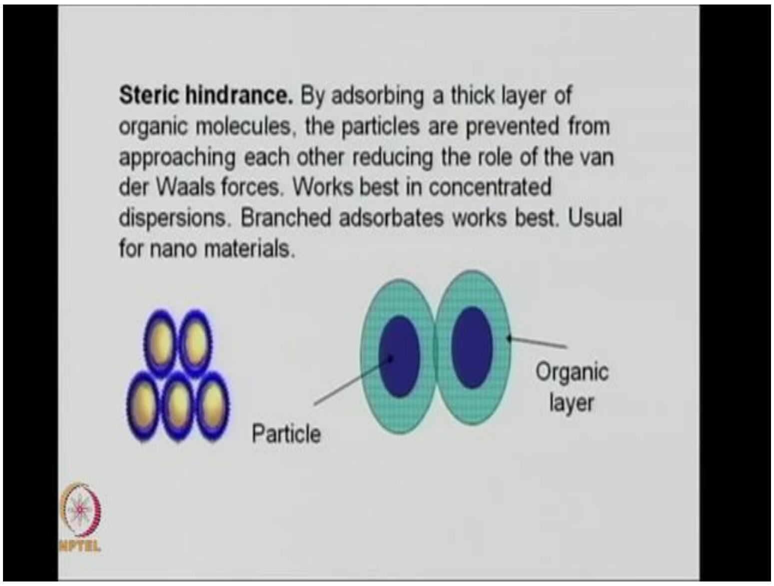

Steric hindrance. By adsorbing a thick layer of organic molecules, the particles are prevented from approaching each other reducing the role of the van der Waals forces. Works best in concentrated dispersions. Branched adsorbates works best. Usual for nano materials.

So, you have a particle on which you can coat some organic layer, so this organic layer and that organic layer will prevent these two particles from coming close. So, this works well when you have concentrated solution or dispersions and this is also used for synthesizing nanomaterials. So, you if you have a nanoparticle and you want to keep them separate not coalescing with each other, then you coat each nanoparticle with some organic molecule or surfactant molecule. Then, they form a shell kind of thing and they keep these two particles apart, so this is sterically your keeping the particles apart. So, you can use either charge to keep particles apart or you can use these kind of organic layers to keep the particles apart.

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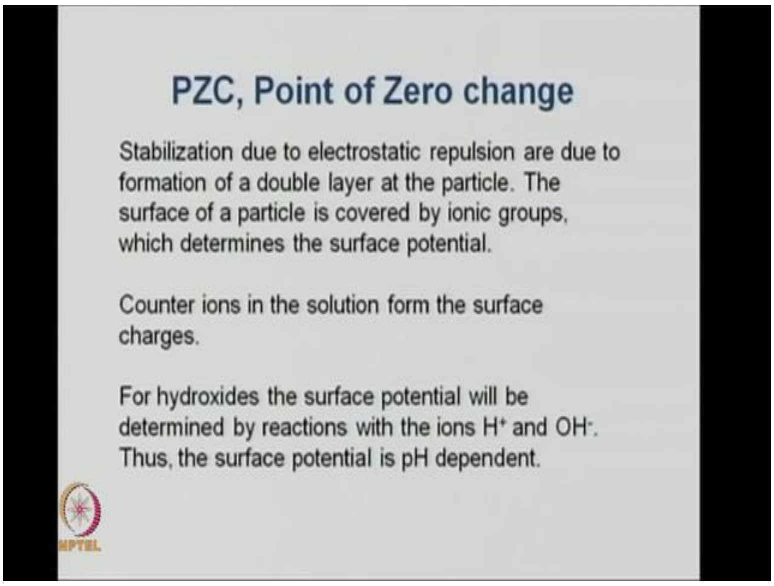

PZC, Point of Zero change

Stabilization due to electrostatic repulsion are due to formation of a double layer at the particle. The surface of a particle is covered by ionic groups, which determines the surface potential.

Counter ions in the solution form the surface charges.

For hydroxides the surface potential will be determined by reactions with the ions H^+ and OH^-. Thus, the surface potential is pH dependent.

Now, there is a concept in when you study Sol Gel science, there is something called point of zero charge P Z C as it is called it is this point of zero charge when there is stabilization. Then, you have electrostatic repulsion because you have charges and so the particles are not agglomerating and then you have this double layer at the particles. So, there is a charge on the surface and there is a charge in the liquid or on the other particle, which keeps the particles away. Now, the charge on the surface of the particle will determine what is its surfaces potential and the counter ions in the solution will form the surface charges.

So, for example, if you have hydroxides the surface potential will be determined by reactions with the ions like H plus ions and OH minus ions. So, basically it will depend if you have this particle in a solution what is the p H of the solution. So, this surface potential will be p H dependent because depending on your p H you will have a concentration of hydrogen ions in solution. That concentration of hydrogen ions in solution will affect the kind of charges on the surface of this particle and hence will affect the surface potential of this particle.

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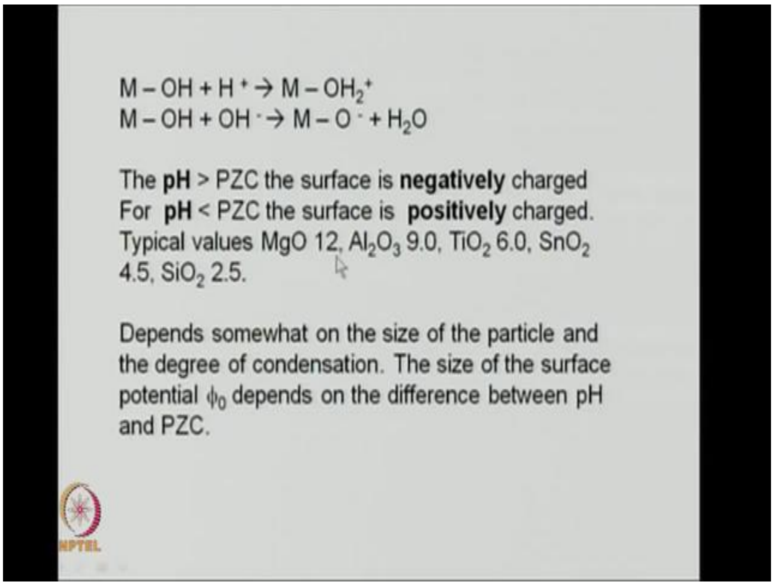

$M-OH + H^+ \rightarrow M-OH_2^+$
$M-OH + OH^- \rightarrow M-O^- + H_2O$

The **pH** > PZC the surface is **negatively** charged
For **pH** < PZC the surface is **positively** charged.
Typical values MgO 12, Al_2O_3 9.0, TiO_2 6.0, SnO_2 4.5, SiO_2 2.5.

Depends somewhat on the size of the particle and the degree of condensation. The size of the surface potential ψ_0 depends on the difference between pH and PZC.

So, you can have reactions like this hydrosilanes is on the surface and if you add this protons or hydrogen ions in a solution. That means the p H of the solution is less than 7, then you can form this kind of reactions, if your p H of the solution is more than 7 that means you have hydrosilanes in solution. Then, you can generate of minus ions on the surface, so depending on the p H whether it is less than 7 or more than 7, you will have positive charges on the surface or negative charges on the surface.

So, that is what is mentioned here if the p H is greater than P Z C, the surface is negatively charged if the p H is less than P Z C. There is a point of zero charge the surface is positively charged, so typical values are like or magnesium oxide, you have to have a p H of 12. So, if your p H solution this point of zero charge for magnesium oxide is 12, so if you have a p H of solution which is more than 12, then only the surface will be negatively charged. So, I you have a very strongly basic solution, then only magnesium oxide surface will be negatively charged, otherwise it will be positively charged.

However, if you have silica for example, silica will be positively or negatively charged that will depend on its P Z C which is f2.5, which is very low. So, if you have even water which has a p H of 7, so it is greater than the P Z C, so even water will give rise to positive ions on the surface of silica.

You have the p H 7 greater than P Z C, which is 2.5 for silica, however in water magnesium oxide whose P Z C is 12 will not have positive charge on the surface, but will have negative charge on the surface. So, depending on what is oxide what surfaces your using what is its P Z C, you have to use a p H of the solution to create the kind of charge that you need on the surface.

If you want to create positive charge, you must know that the p H should be less than the P Z C of the material. So, all this will control the degree of condensation and the size of the surface potential phi naught will depend on the difference between p H and P Z C and this P Z C will depend on the size of the particle and the degree of condensation.

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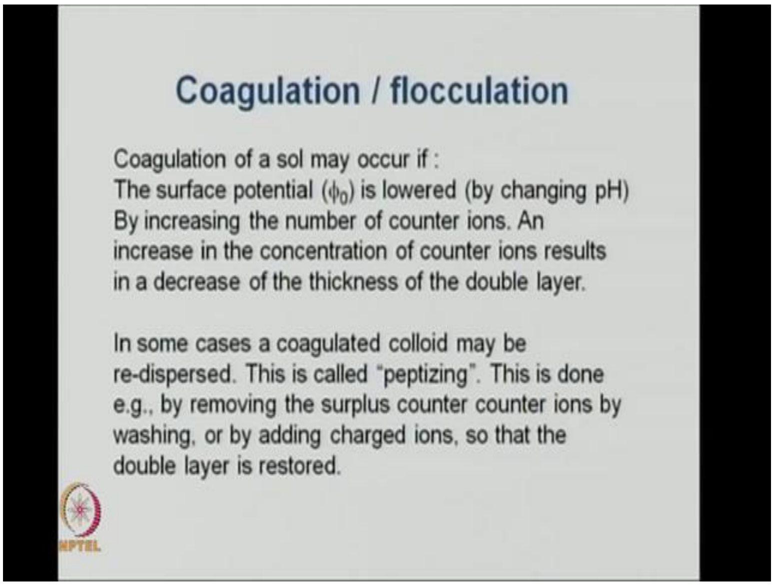

Coagulation / flocculation

Coagulation of a sol may occur if :
The surface potential (ϕ_0) is lowered (by changing pH)
By increasing the number of counter ions. An increase in the concentration of counter ions results in a decrease of the thickness of the double layer.

In some cases a coagulated colloid may be re-dispersed. This is called "peptizing". This is done e.g., by removing the surplus counter counter ions by washing, or by adding charged ions, so that the double layer is restored.

So, this is a very important property in Sol Gel sign to understand the nature if the charge surface on the particles, and to understand the charges which will develop in a particular kind of solution whose p H can be varied. Now, after that if suppose you have a Sol, you can get coagulation that means the Sol the particles are trying to aggregate if the surface potential is lower. If you change the p H, then you can start getting agglomeration which is like coagulation or flocculation it is called. So, you can do that by changing the surface potential by changing the counter ions, for example an increase in the counter ion concentration will result in a decrease in the thickness of the double layer.

You can also call this kind of coagulation of a colloid as peptization, so this done by removing counter ions by washing or by adding charged ions so that the double layer is restored. So, this kind of process is very important in industries most of the pharmaceutical industries oil industries etcetera, use all these techniques of coagulation and flocculation and is also important in our course. Here, we are discussing how we want to synthesize mono dispersed nano particles using the Sol Gel method that is to control the size of the particle from the Sol to the Gel using various charges or p H around the ions.

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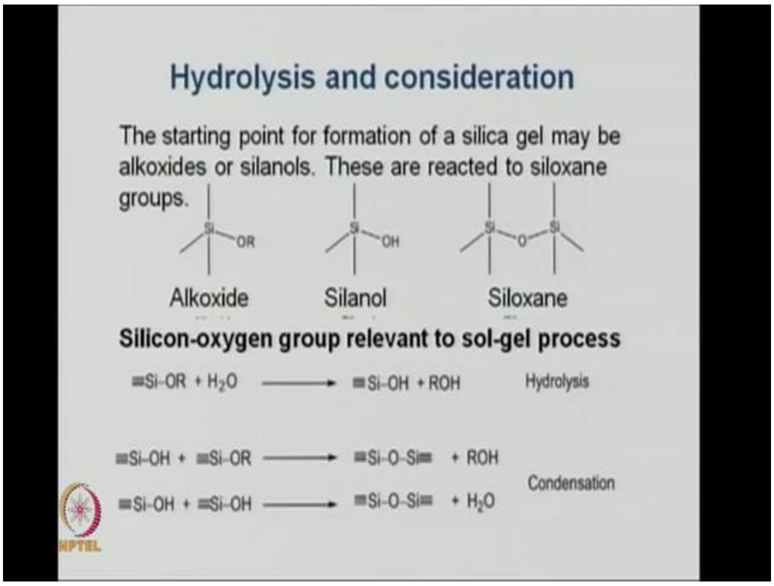

Hydrolysis and consideration

The starting point for formation of a silica gel may be alkoxides or silanols. These are reacted to siloxane groups.

Silicon-oxygen group relevant to sol-gel process

$\equiv Si{-}OR + H_2O \longrightarrow \equiv Si{-}OH + ROH$ Hydrolysis

$\equiv Si{-}OH + \equiv Si{-}OR \longrightarrow \equiv Si{-}O{-}Si\equiv + ROH$

$\equiv Si{-}OH + \equiv Si{-}OH \longrightarrow \equiv Si{-}O{-}Si\equiv + H_2O$

Condensation

So, if you look at hydrolysis and condensation the starting point for formation of a silica Gel can be an alkoxide like this is a typical silicon alkoxide this R group. If it is methyl, then it is a methoxide and if you can have mono alkyl derivates or mono alkoxy groups or di alkoxzy groups or tetra alkoxy groups. Now, if you instead of the alkyl group here if you have a high region or a proton, then you have a what are called the silanol groups. So, you can have the alkoxide groups the silanol groups and if two of these silanols come together, then they can condense and one water molecule will be released.

So, when one water molecule is released they form what is called the siloxane, so these are terms which will occur very commonly in Sol Gel chemistry, where your using alkoxy groups or silanol groups and siloxanes are formed for alkoxide. You go to silanol by hydrolysis from silanol to siloxane using condensation reactions, so you can these are given below also. So, you have this alkoxide and you get hydrolyzed with water and you form the silanol groups the silanol group can react with another alkoxy group to get give you a siloxane group or a silanol can react with another silanol to form a siloxane rule. These are the condensation reactions, this is a typical hydrolysis reactions, so most of Sol Gel chemistry involves hydrolysis and condensation.

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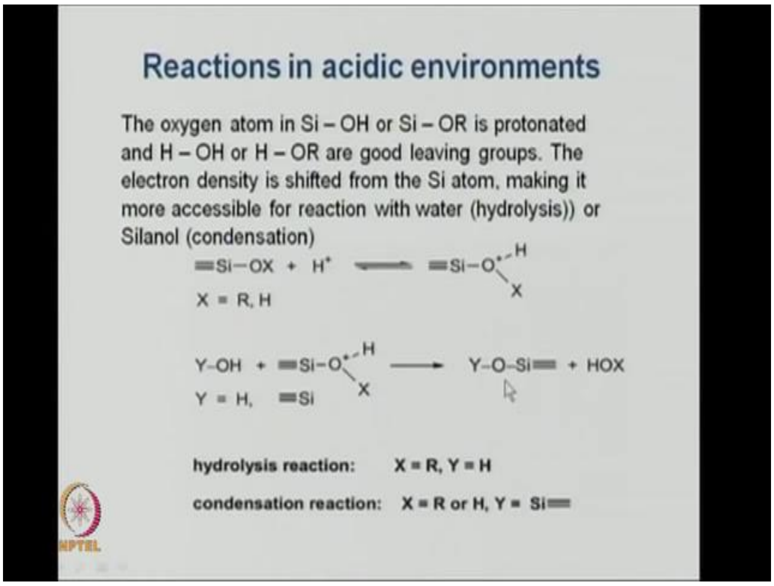

Reactions in acidic environments

The oxygen atom in Si – OH or Si – OR is protonated and H – OH or H – OR are good leaving groups. The electron density is shifted from the Si atom, making it more accessible for reaction with water (hydrolysis)) or Silanol (condensation)

$$\equiv Si-OX + H^{+} \rightleftharpoons \equiv Si-\overset{+}{O}(H)(X)$$

$X = R, H$

$$Y-OH + \equiv Si-\overset{+}{O}(H)(X) \longrightarrow Y-O-Si\equiv + HOX$$

$Y = H, \equiv Si$

hydrolysis reaction: **$X = R, Y = H$**

condensation reaction: **$X = R$ or H, $Y = Si\equiv$**

Now, in reactions depend on whether you are doing them in acidic environment or in basic environment. So, in an acidic environment the oxygen atom in the silanol group or the alkoxy group, if you have a alkyl group here is protonated in an acidic medium and water or alcohol are known to be good living groups. So, the electron density is shifted from the silicon atom and that makes the reaction easier for or the hydrolysis to be easier and you can form this kind of groups.

So, this is the first step the proton in a acidic environment reacts with this alkoxy group to form this OH plus group. Then, it reacts with the another hydrosil group to form a water molecule or a alcohol molecule, which leaves and giving you back a siloxane type moiety. So, if this is silicon you have silicon of siloxane moiety or if this is a methyl group, then you will have a methyl oxysilicon moiety.

So, it depends on what kind of agents they are, so if your y can be silicon right like this, so you will have silicon oxygen silicon which is a siloxane moiety. So, the first step in an acidic environment is the protonation and the second step is the condensation, where the water or alcoholic group will leave leaving you behind chain of silicon oxygen silicon which is a siloxane ring. So, from two independent silicon containing molecules, you get one new molecule, where two silicons are breached with a oxygen, so this is a condensation reaction.

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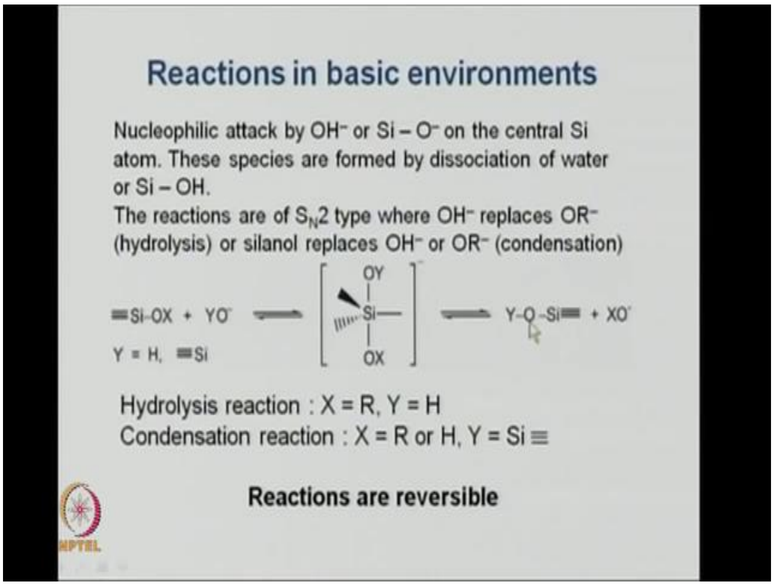

Reactions in basic environments

Nucleophilic attack by OH^- or $Si-O^-$ on the central Si atom. These species are formed by dissociation of water or Si – OH.

The reactions are of S_N2 type where OH^- replaces OR^- (hydrolysis) or silanol replaces OH^- or OR^- (condensation)

Hydrolysis reaction : X = R, Y = H

Condensation reaction : X = R or H, Y = Si ≡

Reactions are reversible

Now, in basic environment, you will have nucleophilic attack by hydroxyl group or SiO minus either hydroxyl group or SiO minus on the central silicon atom. These species are found by disassociation of water or silanol groups and these are the bimolecular type of reactions S N 2 type of reactions, where OH minus replaces OR minus, so that are a typical hydrolysis or it can be condensation reactions.

So, if you look at this reaction silicon OX and reacting with either OH minus or O, Si minus, then this reacts at the silicon site. So, silicon here is has got our bonds tetrahedral and that it forms a intermediate with these species, so the O, I attaches here and then the OX minus will leave leaving you behind this Y O Si unit. So, this is in a environment, so you can have hydrolysis followed by condensation in this manner. Ultimately, here also you get two silicons or one hydrogen and silicon breached with an oxygen, so this is a condensation reaction.

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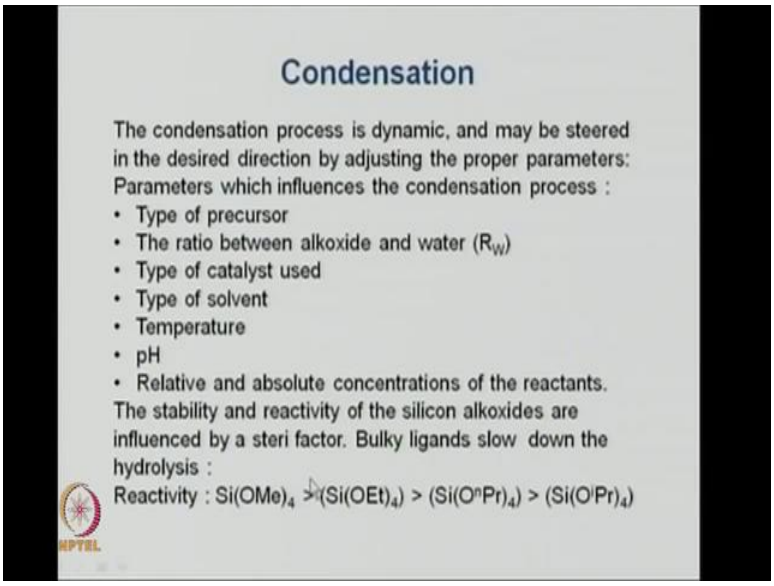

Condensation

The condensation process is dynamic, and may be steered in the desired direction by adjusting the proper parameters:
Parameters which influences the condensation process :

- Type of precursor
- The ratio between alkoxide and water (R_W)
- Type of catalyst used
- Type of solvent
- Temperature
- pH
- Relative and absolute concentrations of the reactants.

The stability and reactivity of the silicon alkoxides are influenced by a steri factor. Bulky ligands slow down the hydrolysis :
Reactivity : $Si(OMe)_4$ > $(Si(OEt)_4)$ > $(Si(O^nPr)_4)$ > $(Si(O^iPr)_4)$

So, condensation processes are dynamic processes and will depend on several parameters now these parameters are can be the type o precursor that you have chosen the amount of water in your system. The amount of alkoxide in your system the type of catalyst that your using the solvent the temperature the p H, which is very important. The concentrations of the reactants, all these will affect the condensation process and the stability and reactivity of silicon alkoxides. They are also influenced by steric factors, so if you have a bulky ligand, it will slow down the hydrolysis.

So, if you have for example, silicon with four methoxy groups, which are small groups its reaction will be much faster compared to a bulky group like isopropoxy group. So, its reaction will be much smaller, so this is how the reactivity decreases, this will be having the highest reactivity because you have less steric hindrances. As you increase the carbon chain length from methyl to ethyl to propyl to normal propyl to isopropyl, you your reactivity is decreasing along this series. This is a typical for condensation reactions were not only all these parameters temperature solvent p H, but steric factors also play a very important role.

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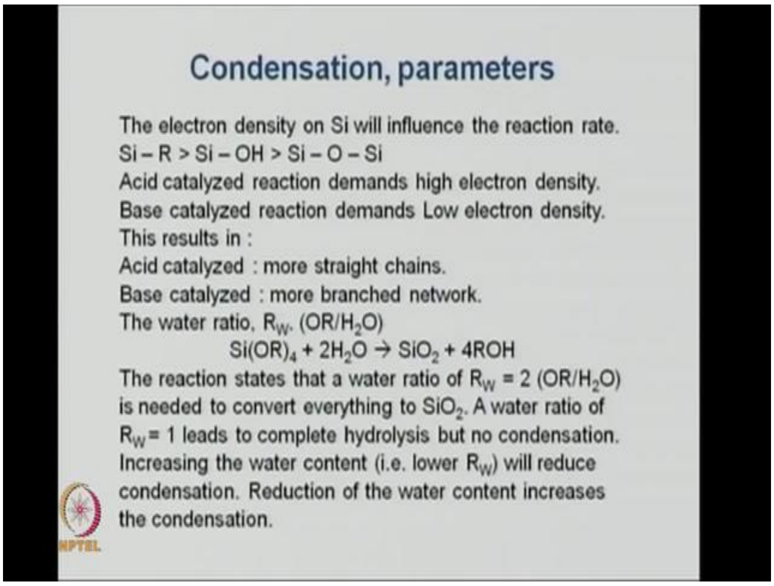

Condensation, parameters

The electron density on Si will influence the reaction rate.
Si – R > Si – OH > Si – O – Si
Acid catalyzed reaction demands high electron density.
Base catalyzed reaction demands Low electron density.
This results in :
Acid catalyzed : more straight chains.
Base catalyzed : more branched network.
The water ratio, R_W, (OR/H_2O)

$$Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4ROH$$

The reaction states that a water ratio of $R_W = 2$ (OR/H_2O) is needed to convert everything to SiO_2. A water ratio of $R_W = 1$ leads to complete hydrolysis but no condensation. Increasing the water content (i.e. lower R_W) will reduce condensation. Reduction of the water content increases the condensation.

So, the other parameters like electron density and the silicon will influence the reaction rate of condensation. So, the electron density and the silicon will depend on what are the groups attached to silicon whether you have an alkyl group which is an electron donating group. So, you will have more electron density if it is attached to alkyl group, if you have a hydroxyl group it has less electron donating capability than an alkyl group. So, this system will have less electron density on the silicon, so this series in this series this moiety will have the highest electron density on silicon compared to this moiety, where the electron density on silicon will be very low.

Now, depending on electron density you will have is in acid catalysis or basic catalysis or example acid catalysis or acid catalyzed reaction demands high electron density on the silicon. So, in this kind of situation, it will prefer or acid catalyzed reactions will be preferred base catalyzed reaction demands low electron density so that those reactions will lead to more branched networks acid catalyzed reactions will lead to more straight chains. Here, base catalyzed reactions will lead to more branched chains in these siloxane, which form at the end now the water ratio how much alkoxide you have and how much water you have this ratio is called R W that also matters a lot.

For example, if you have a water ratio of 2, that means you have OR to water is equal to 2, then the reaction converts everything to silica. So, you start with this tetra alkyl silane and after hydrolysis, if you have this ratio of the silane and water then you this reaction will go to silica. Now, if you have a water ratio of 1, it leads to hydrolysis, but not to condensation here you see that you have a water ratio of this is 4 time, this is 4 and this is 2.

So, this is twice the number of alkoxy groups are there or the number of OH groups and hence as you see you have everything to convert to silica, which is that means you have SiO, SI network all through the solid. If you have only 1, that means half the amount of SiO R 4 compared to what you have here, then you will have hydrolysis, but you will not have condensation. So, increasing the water content will reduce condensation and reduction in the water content increase the condensation.

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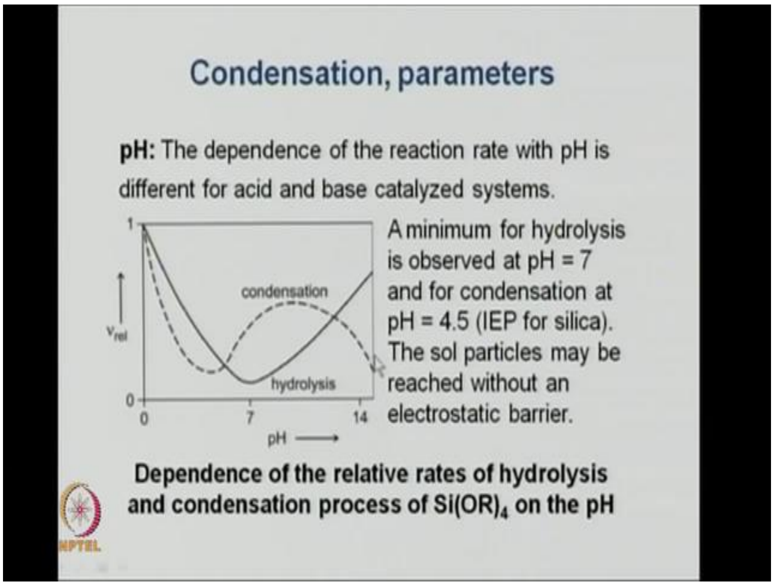

Condensation, parameters

pH: The dependence of the reaction rate with pH is different for acid and base catalyzed systems.

A minimum for hydrolysis is observed at pH = 7 and for condensation at pH = 4.5 (IEP for silica). The sol particles may be reached without an electrostatic barrier.

Dependence of the relative rates of hydrolysis and condensation process of $Si(OR)_4$ on the pH

Now, the dependence of p H as I said is very important and it is very different for acid and base catalyzed systems. So, if you look at this plot, this is kind of the rate of reaction with plotted with p H, so the hydrolysis rate is minimum around p H 7 whereas the condensation rate is minimum around much lower p H say around 5.5 or something. The rate is maximum around 8.5 or 9, so this is of course for silica and at p H, this is around 4.5, which is the isoelectric point for silica.

You have the minimum condensation minimum for hydrolysis is at 7 and minimum for condensation for silica is at p H equal to 4.5, which is the isoelectric point for silica. So, the dependence of the reaction rate with p H is a very dramatic and it depends a lot on whether it is a acid or base catalyzed system.

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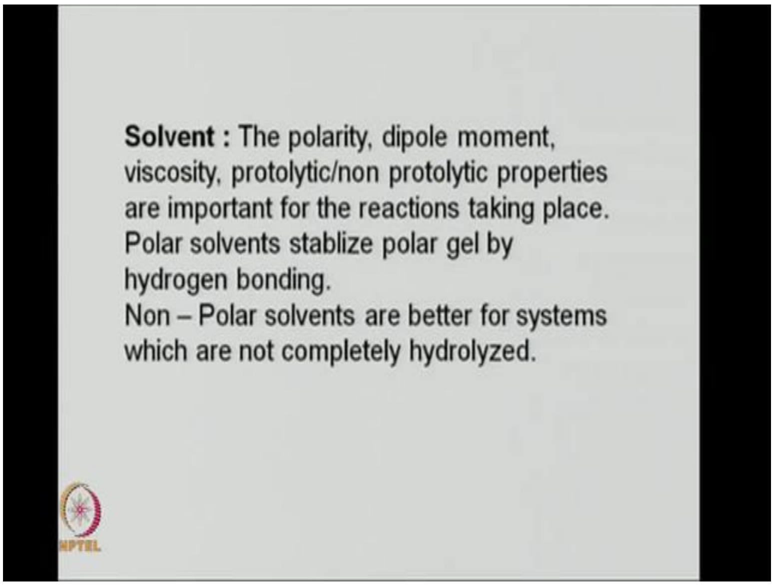

Solvent : The polarity, dipole moment, viscosity, protolytic/non protolytic properties are important for the reactions taking place.
Polar solvents stablize polar gel by hydrogen bonding.
Non – Polar solvents are better for systems which are not completely hydrolyzed.

Now, if you look at the solvent, the solvent will also affect the rates of these reactions the polarity of the solvent the dipole moment of the solvent, which is related to the dielectric constant of the solvent. For example, water has a very high dielectric constant of 80, you know will be this solvent will be very different. If you take benzene, which has a much lower dielectric constant, the polarity the dipole moment, the viscosity of the solvent and other properties, which can break the hydrogen OH bond. The hydrolysis or proteolysis are important for the reactions which take part in the Sol Gel process.

So, polar solvents will stabilize the Gel by hydrogen bonding that is very important. So, when the Gel is formed from the Sol if you have a polar solvent because the solvent is still present in the Gel the polar solvents will stabilize the Gel through hydrogen bonding. Non polar solvents are better for systems, which are not completely hydrolyzed so depending on your kind of system this solvent has to be chosen to give you the right kind of mechanical strength or the Gel.

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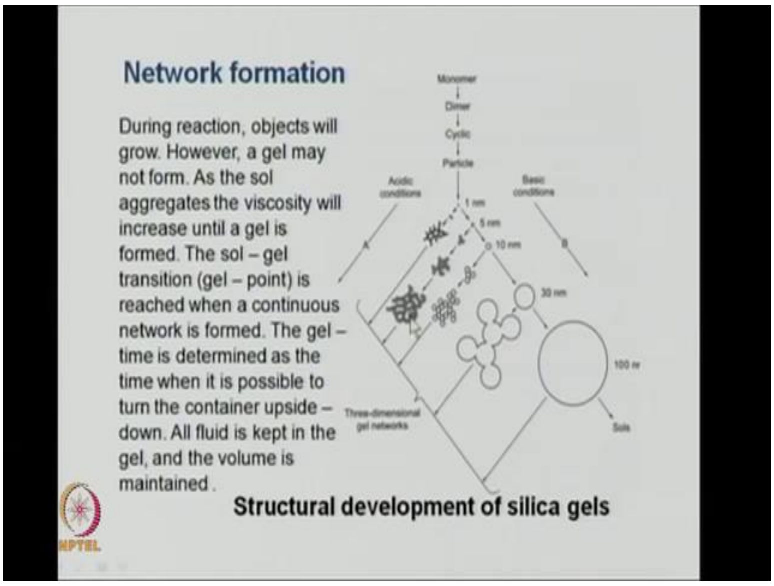

Network formation

During reaction, objects will grow. However, a gel may not form. As the sol aggregates the viscosity will increase until a gel is formed. The sol – gel transition (gel – point) is reached when a continuous network is formed. The gel – time is determined as the time when it is possible to turn the container upside – down. All fluid is kept in the gel, and the volume is maintained .

Structural development of silica gels

Now, during network formation the objects will grow, so a Gel may not form these Sol particles or the aggregates of the sol particles may grow the as the viscosity increases until a Gel is formed. So, as you are going from a Sol to Gel, if you evaluate the viscosity the viscosity is increasing till it forms a Gel and that is the Sol Gel transition that is called the Gel point, when the Sol turns into the Gel. That is dependent on the kind of solvent, because the viscosity is important and it the Sol Gel transition is reached when a continuous network is formed. So, when all the particles are connected interconnected to form one network structure through this hydrolysis and condensation.

Then, that is called the Gel point and that is when the continuous network is formed the Gel time is determined as the time, when you can after forming the Sol how much time does it take before the Gel is formed. Now, how do you know when the Gel is formed is very simple, if you take a Sol and you look at it till when you turn the fluid upside down and it does not flow that is when the Gel has formed. So, all the fluid is within the Gel and it does not fall even when the container is turned upside down. So, that is when your Gel has formed, so this is a simple, but method of finding the Gel point, there are other methods of course, by which you can study the Sol Gel transition.

So, if you look at this diagram on one axis, you have the increase in acidic conditions or another axis, you have an increase in basic conditions and what you start with this a monomer. That means one simple molecule and then it forms a dimmer, it may form a cyclic polymer a particle a small particle say a 1 nanometer particle or a 2 nanometer particle. Then, what happens, if you have acidic conditions and what happens when it you have basic conditions. So, when you have basic conditions, you can see that this particle is growing to larger and larger size and you can get a very large particle dispersed in the liquid.

So, that is the Sol, however I you increase the acidic conditions, then you can get this interconnected particles and which can form three dimensional Gel networks. So, that is caused as you are increasing the acidic conditions and you are encouraging hydrolysis and condensation at the same time. So, you can have this kind of particle formation which are interconnected or you can have growth of these particles from small size to larger size as your increasing the basic conditions.

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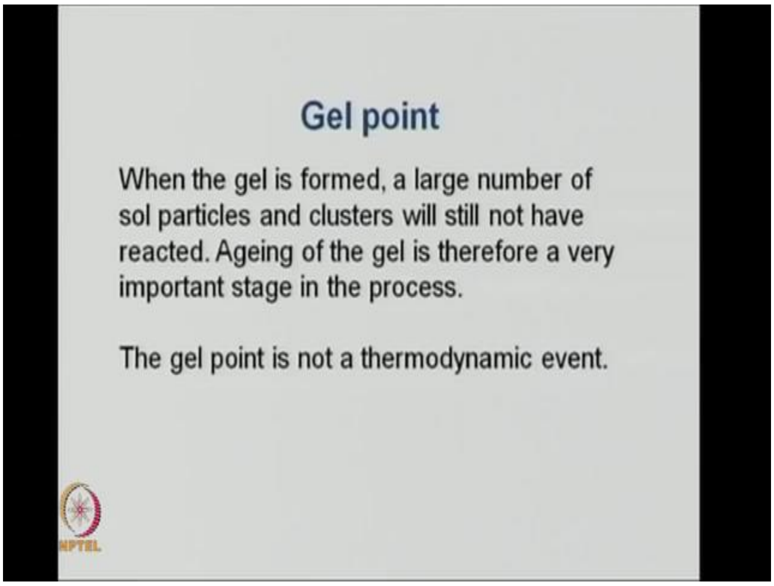

Gel point

When the gel is formed, a large number of sol particles and clusters will still not have reacted. Ageing of the gel is therefore a very important stage in the process.

The gel point is not a thermodynamic event.

So, the Gel point is a point where a large number of Sol particles and clusters are still have not reacted the aging of the Gel is therefore, a very important stage. So, although from Sol to Gel a you have a transition this is not a at the Gel point which is not a thermodynamic event.

Now, you have to age the Gel because there are still more Sol particles there and more clusters have to take part. So, the entire Gel has to get connected see the Gel point is the point, where you form a single interconnect that is all through you the liquid, you have one interconnect. That does not mean that all the particles have hydrolyzed, there are still particles, which need to be hydrolyzed, and so you need to do ageing.

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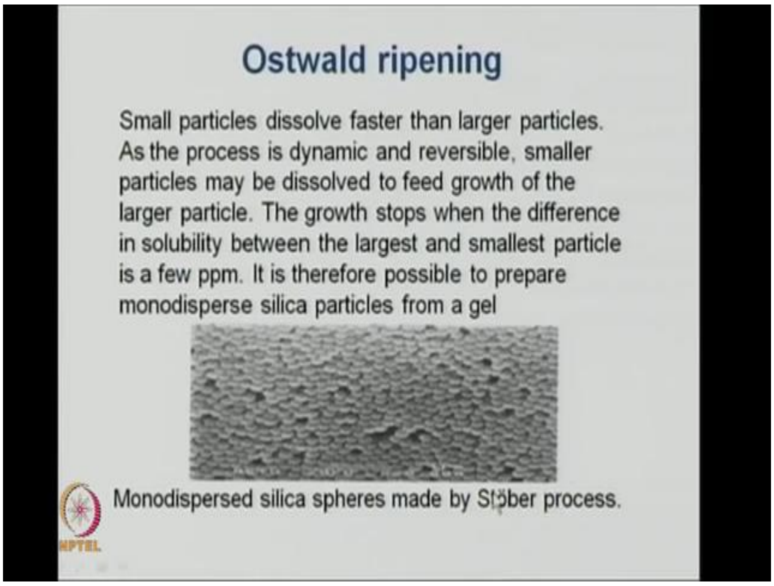

Ostwald ripening

Small particles dissolve faster than larger particles. As the process is dynamic and reversible, smaller particles may be dissolved to feed growth of the larger particle. The growth stops when the difference in solubility between the largest and smallest particle is a few ppm. It is therefore possible to prepare monodisperse silica particles from a gel

Monodispersed silica spheres made by Stöber process.

What happens in ageing, you have small particles, which dissolve faster than larger particles, this is also called Ostwald ripening. So, you will have small particles which are dissolving or which are joining with larger particles to grow bigger and bigger particles. So, as time proceeds, the smaller particles will disappear away and the larger particles will grow, so the growth will stop when the difference in solubility between the largest and smallest particle is a very few parts per million. So, it is therefore, possible to prepare mono disperse silica particles from a Gel because you through this process which is a natural process which is called Ostwald ripening.

This is a thermodynamic process, if you have a statistical distribution of large particles and small particles this small particles dissolve and add on to the large particles. So, the large particles keep growing and this process of making silica using this Ostwald ripening process to give you a mono disperse silica spheres from a Gel is also called Stober’s process.

So, as we were discussing ageing, we continue on that as the viscosity increases rapidly the solvent is trapped in the Gel and these structure may change with time depending on p H, the temperature and solvent, but the Gel is still alive. There is liquid inside the Gel and it will also have Sol particles and agglomerates which will continue to react and contains as the Gel is drying. So, originally the Gel is flexible as more and more branches will condense the Gel will become viscous this will squeeze out the liquid from the interior.

The flexibility of the Gel will not be there anymore, so the hydrolysis and condensation are reversible processes and material from thermodynamically unfavorable points will dissolve and precipitate at more favorable points. So, thermodynamics will basically guide that which are unfavorable and which are favorable and guide the particles which are favorable. They will remain and the unfavorable particle from the thermo dynamical point of view will dissolve and disappear. Now, after aging when you have interconnected the entire Gel network you have to remove the liquid, which is still in the Gel and this requires drying.

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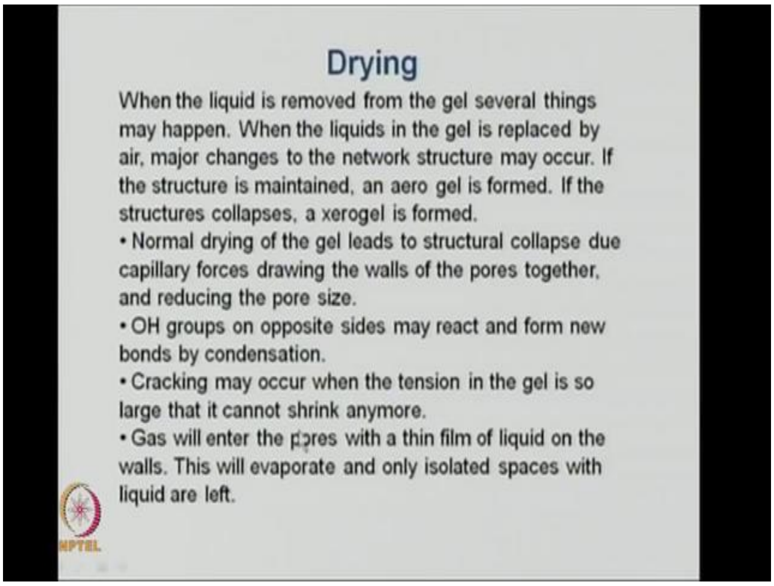

Drying

When the liquid is removed from the gel several things may happen. When the liquids in the gel is replaced by air, major changes to the network structure may occur. If the structure is maintained, an aero gel is formed. If the structures collapses, a xerogel is formed.

- Normal drying of the gel leads to structural collapse due capillary forces drawing the walls of the pores together, and reducing the pore size.
- OH groups on opposite sides may react and form new bonds by condensation.
- Cracking may occur when the tension in the gel is so large that it cannot shrink anymore.
- Gas will enter the pores with a thin film of liquid on the walls. This will evaporate and only isolated spaces with liquid are left.

So, when the liquid is dried it the Gel the pores in the Gel may be replaced by air and some changes in the network structure may occur. So, if you can maintain the structure, we get a Gel which has got air inside that is structure intact like it was when the liquid was there and this is called a aerogel, because there is no liquid. Now, the porous structure network structure is there and this is called as aerogel, however while taking out the liquid if the structure collapses and you do not have the network structure anymore it is a zero Gel and it is a much more condensed form the Gel.

So, normal drying of the Gel leads to structural collapse and reduces the pore size the hydroxyl groups on opposite sides may react and form new bonds by condensation cracking may occur when the tension in the Gel is large. It cannot shrink anymore and gas will enter the pores with a thin film and liquid on the walls, this will evaporate and only isolated spaces with liquid may be left. So, the drying process is very crucial whether you want an aero Gel or a zero Gel.

So, if you want high surface area you want porous structure then you have to remove the liquid very carefully. Then, you can get a aerogel if you want a more condensed structure higher density small pore size, then normal drying or quick drying is possible which will lead to the zero Gel.

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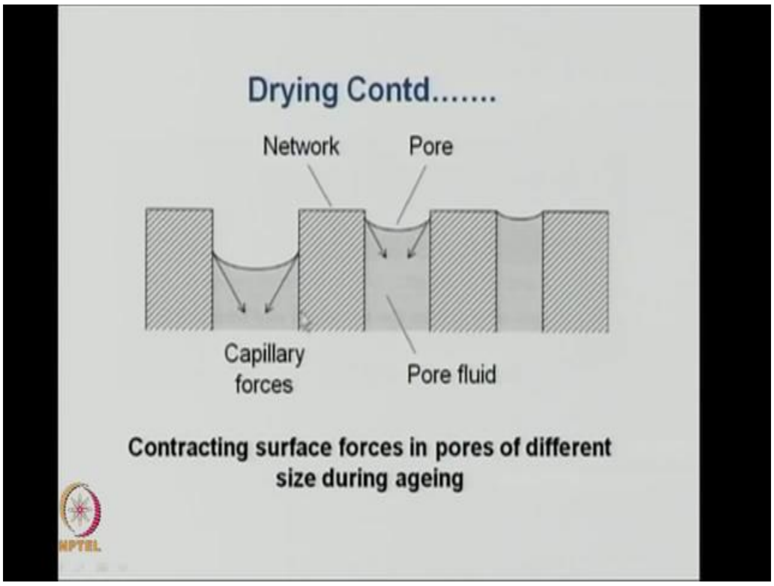

Drying Contd.......

Contracting surface forces in pores of different size during ageing

So, if you see the drying process, so this is your network structure in between the two networks, there is this pore and the capillary forces will be acting in the pores. You will have the fluids in the pores and they will be contracting as liquids are going the surface forces in these pores will be acting during this aging period, when slowly the drying is taking place.

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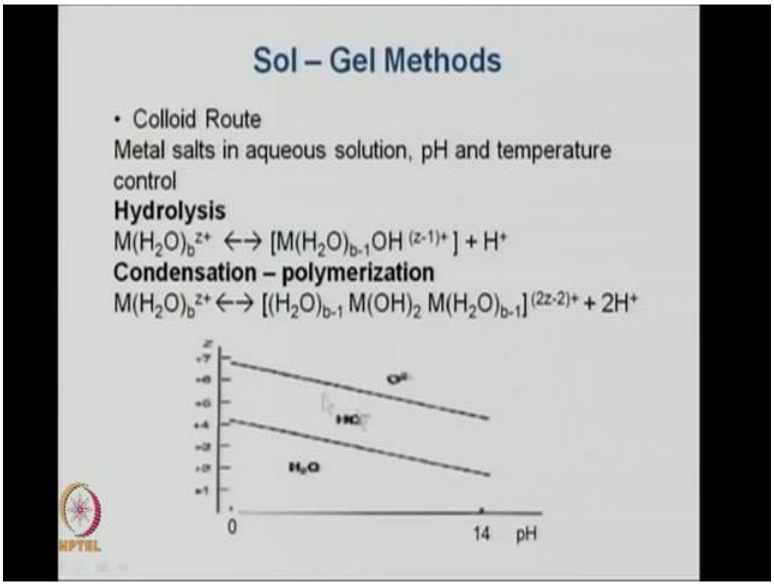

Sol – Gel Methods

- Colloid Route

Metal salts in aqueous solution, pH and temperature control

Hydrolysis

$M(H_2O)_b^{z+} \leftrightarrow [M(H_2O)_{b-1}OH^{(z-1)+}] + H^+$

Condensation – polymerization

$M(H_2O)_b^{z+} \leftrightarrow [(H_2O)_{b-1}M(OH)_2M(H_2O)_{b-1}]^{(2z-2)+} + 2H^+$

Now, in this colloidal Sol Gel route, the metal salts in the solution the p H and temperature control is very important and the two steps, which we discussed earlier the hydrolysis and the condensation polymerization are very important. Typically, they are shown here that if you have a metal with b number of water molecules it may be 4, 6 with z plus charge when it there is hydrolysis, you have one of the water molecules has splits up and you get a hydroxyl group and one proton is liberated.

Now, when you have this unit and it combines with another unit of this, so you have condensation and now from this you get two metal atoms with the water molecules which is 2, 1 less than what it should be and 2 water molecules go away to give you 2 hydroxyl groups and 2 protons. So, when you interact when you just hydrolyze you have this reaction one proton is liberated when you condense or polymerize, you will have 2 water molecules lost 1 from there, 1 from here and 2 protons are liberated. So, this processes are taking place all the time and if you see this z the charge as a function of p H, you can see how these vary as a function of p H.

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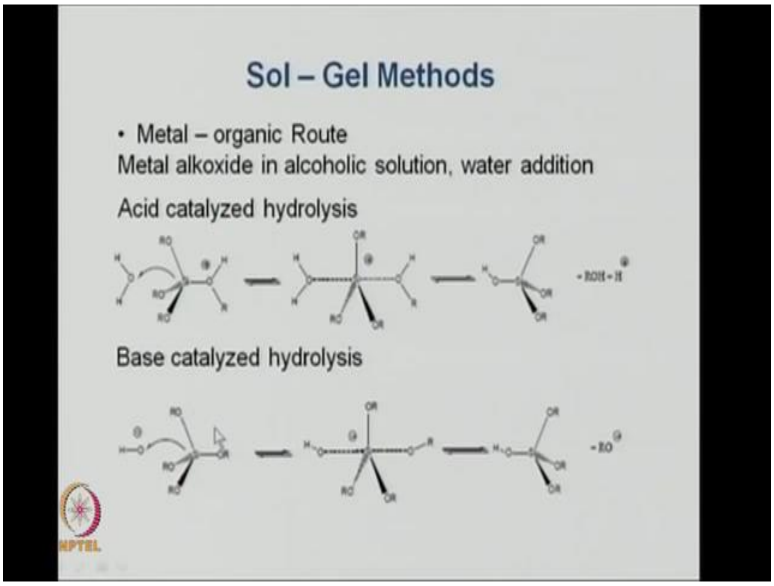

Sol – Gel Methods

- Metal – organic Route

Metal alkoxide in alcoholic solution, water addition

Acid catalyzed hydrolysis

Base catalyzed hydrolysis

Now, the Sol Gel method through the metal organic route this is the colloidal route, so the metal organic route you have metal alkoxide in alcoholic solution and you add water you can have the acid catalyzed hydrolysis little bit. We discussed earlier in the acid catalyzed hydrolysis, it is good to have a lot of electron density on the silicon, so if you have electron density on the silicon then this electron density can be attracted towards the electro negative oxygen ion. You form this kind of bond and the alcoholic group here can be a good leaving agent giving rise to a silanol group this is the acid hydrolysis.

In the basic hydrolysis, you have this OH minus and it takes up a it binds to this silicon and the silicon gets a negative charge. Then, you will lose a OR minus group and gives rise to again a silanol group, so you have these two mechanisms for the acid catalysis and the base catalysis process.

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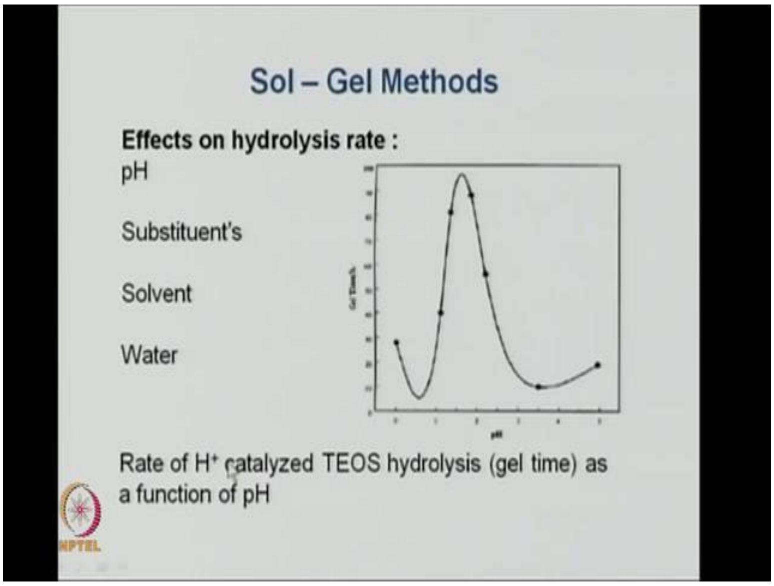

Sol – Gel Methods

Effects on hydrolysis rate :

pH

Substituent's

Solvent

Water

Rate of H⁺ catalyzed TEOS hydrolysis (gel time) as a function of pH

Now, you can see that the Sol Gel method the Gel time how much time it takes to Gel or the hydrolysis rate depends on p H substitutions the solvent and water and we plot this Gel time with p H. You can see that at a particular p H the Gel time is very high and then at some other p H the Gel time is very low. So, the rate at which the acid catalysis takes place is a function p H it depends on the p H how this acid catalysis is taking place. Now, the precursors effect as mentioned earlier, you can have a streic effects like if you have a very small groups the rate is very high if you have very large groups like the butyl group or the hexyl groups the weight will be very small.

So, this is very large and as you go along this their hydrolysis rate will be lowered, then electron density will affect what is electron density on the silicon and this electron density is related to the electron donating power of the alkyl groups or the alkoxy groups. Alkyl groups have high electron density donating capacity, they will be very high here and electron density will be very low there.

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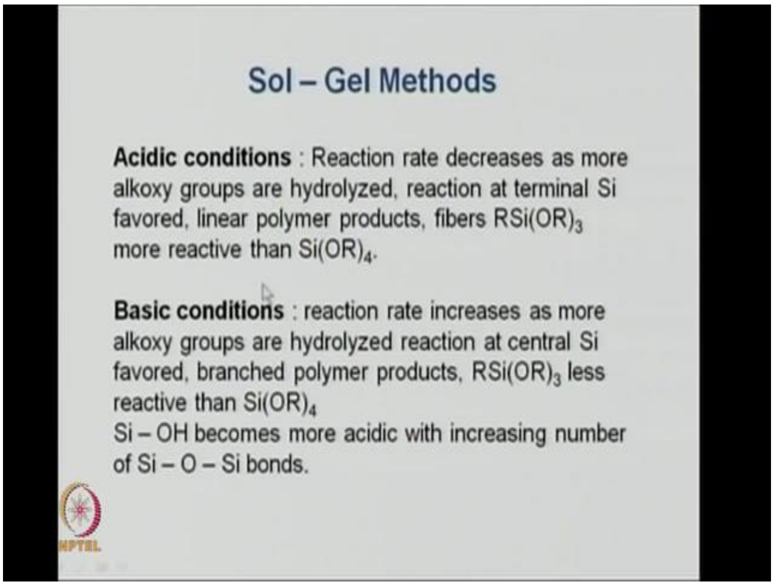

Sol – Gel Methods

Acidic conditions : Reaction rate decreases as more alkoxy groups are hydrolyzed, reaction at terminal Si favored, linear polymer products, fibers $RSi(OR)_3$ more reactive than $Si(OR)_4$.

Basic conditions : reaction rate increases as more alkoxy groups are hydrolyzed reaction at central Si favored, branched polymer products, $RSi(OR)_3$ less reactive than $Si(OR)_4$

Si – OH becomes more acidic with increasing number of Si – O – Si bonds.

So, to again kind of recapitulate that the Sol Gel method can be done in acidic conditions, where your hydrolyzing alkoxy groups and reaction at terminal silicon is favored. In basic conditions, the reactions are favor branched polymers products and the reaction rate increases as more alkoxy groups are hydrolyzed. In the acidic condition, reaction rate decreases as more alkoxy groups are hydrolyzed, so these are difference between the Sol Gel processes under acidic and basic conditions.

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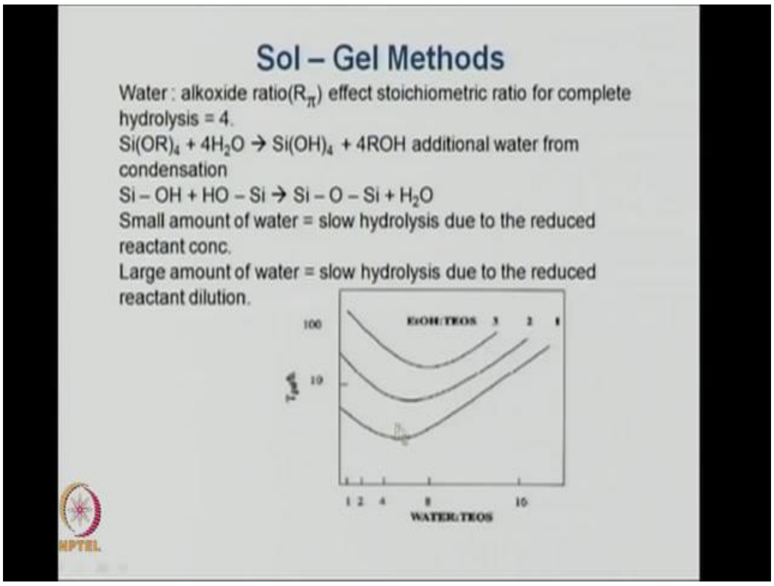

Sol – Gel Methods

Water : alkoxide ratio(R_π) effect stoichiometric ratio for complete hydrolysis = 4.

$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH$ additional water from condensation

$Si-OH + HO-Si \rightarrow Si-O-Si + H_2O$

Small amount of water = slow hydrolysis due to the reduced reactant conc.

Large amount of water = slow hydrolysis due to the reduced reactant dilution.

Now, this also we discussed that the amount of water and the alkoxide group, the rates depend on the ratio of the water is to the alkoxide group and you can see that it is a minimum at a certain concentration. So, you can have large rates of hydrolysis or slow rates of hydrolysis at very slow less concentration of water. You have a reasonable time right and very again very large amount of water this is reciprocated, so there is some optimal water is to silane concentration where this comes to a minimum.

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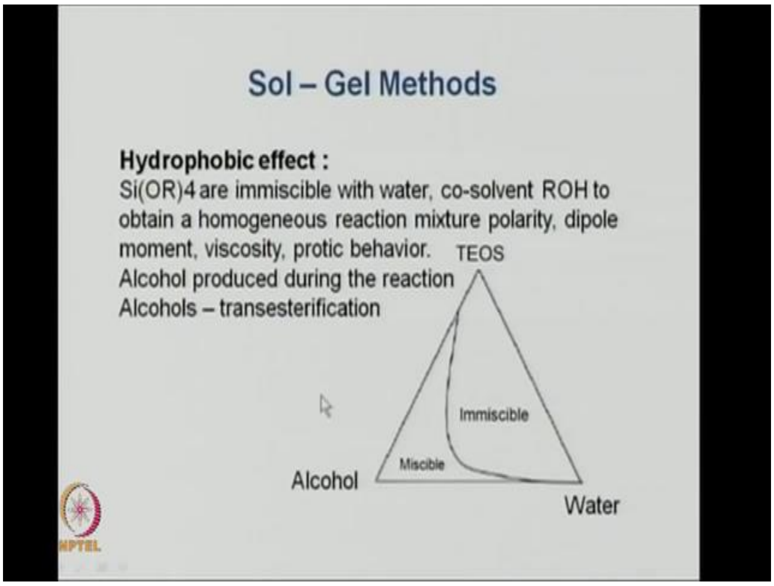

Sol – Gel Methods

Hydrophobic effect :

Si(OR)4 are immiscible with water, co-solvent ROH to obtain a homogeneous reaction mixture polarity, dipole moment, viscosity, protic behavior.

Alcohol produced during the reaction

Alcohols – transesterification

Now, there are other effects like hydrophobic effects which are important, so this is a phase diagram of the silane the alcohol and water these are the three things which are in your system. In some range of compositions, you have miscibility and in some other range it is immiscible. So, normally it is the silane as you see is immiscible with water only when you add an alcohol you come to the miscibility range. So, it is important to know the concentration of your silane and water and alcohol, for a particular alcohol you’ll have a particular phase diagram. So, knowledge of these ternary phase diagrams is important to design a particular system for a proceeding with your Sol Gel method. These solvents their polarity their viscosity the protic behavior, they all will be important to understand the Sol Gel process.

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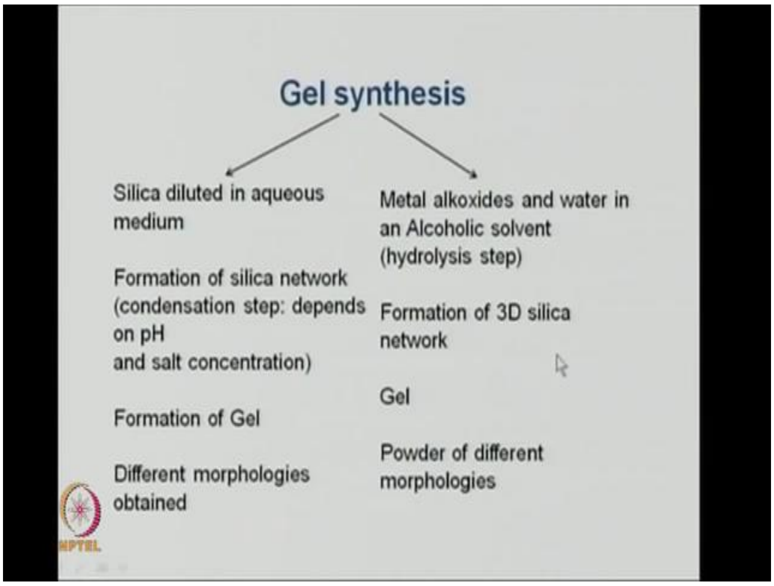

Gel synthesis

Silica diluted in aqueous medium

Formation of silica network (condensation step: depends on pH and salt concentration)

Formation of Gel

Different morphologies obtained

Metal alkoxides and water in an Alcoholic solvent (hydrolysis step)

Formation of 3D silica network

Gel

Powder of different morphologies

So, the Gel synthesis you can see how silica can be prepared in diluted aqueous medium forms a silicon network and the condensation depends on p H and metal salt concentration and it forms a Gel and with different morphologies. You can use metal alkoxides in water and you have to use an alcoholic solvent to make the miscibility range. So, that will be the hydrolysis step, you can form 3 D silicon networks and then form the Gel and again get powder of different morphologies. So, these are various processes by which you can get the Gel, so we continue our lectures on the synthesis of nanostructured materials using Sol Gel methods in the next lecture.

Today, this is where we end and I would like you to go back and recapitulate on all the concepts that we have learnt about Sol Gel synthesis. What are sols, what are gels, what is an interconnected porous structure, what is an aerogel what is a zero Gel, how to get films out of a Sol Gel process and why is it called a low temperature process, why is it a chemical route and why it is part of the bottom of approach of making nanomaterials. So, in our next lecture, we will continue with the Sol Gel methods and then continue with other methods of synthesis of nanomaterials.

Thank you very much.