Chemistry Nanostructured Materials-Synthesis, Properties, Self Assembly and Applications

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Module - 2
Lecture - 4
Synthetic Methodologies (Cont)

Welcome back to the course on nanostructure materials, synthesis properties, self assembly and applications. Today we are going to have the second lecture of model II. In I, we give a two introductory lectures and in model II, in the first lecture we started on synthetic methodologies and we would be continuing on that for 12 lectures and in the first lecture of model II, we introduced the Sol-gel methodology. In the Sol-gel methodology, we showed how you can prepare nanostructure materials starting from solve and how to make a gel and what is in aerogel, what is a xerogel. These kinds of concepts we discussed in lecture 1 of model II. We will be continuing on the Sol-gel method in this lecture also.

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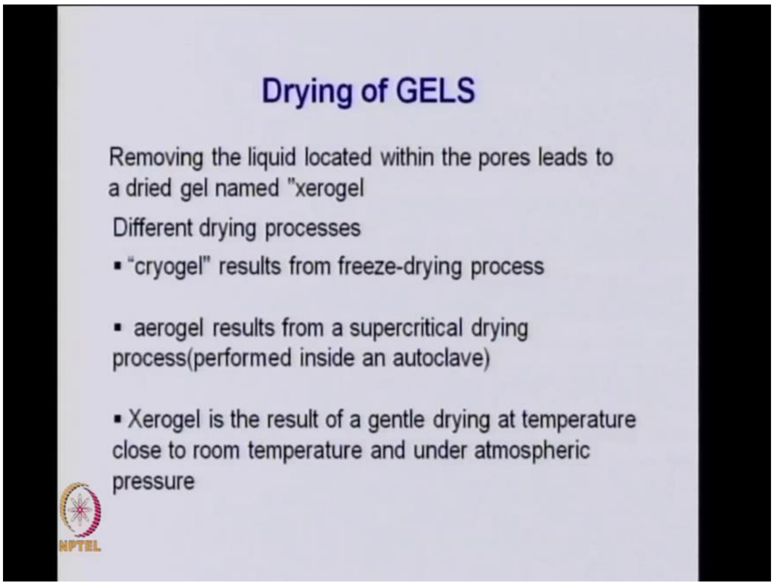

Drying of GELS

Removing the liquid located within the pores leads to a dried gel named "xerogel

Different drying processes

- "cryogel" results from freeze-drying process
- aerogel results from a supercritical drying process(performed inside an autoclave)
- Xerogel is the result of a gentle drying at temperature close to room temperature and under atmospheric pressure

So, once you get the gels, you have to dry the gels because the solvent is in sight. The pores although it is more or less like solid and it is not flowing, but you have to take out the solvent from the pores of the gels. Now, if you take out the liquid from the pores and make a dried gel, then it is called xerogel and there are different processes by which you can dry these gels.

For example, you can get cryogel which results from freeze drying process, you can get an aerogel from a supercritical drying process which is normally performed inside an autoclave. Xerogel is the result of gentle drying at temperature close to room temperature and atmospheric pressure.

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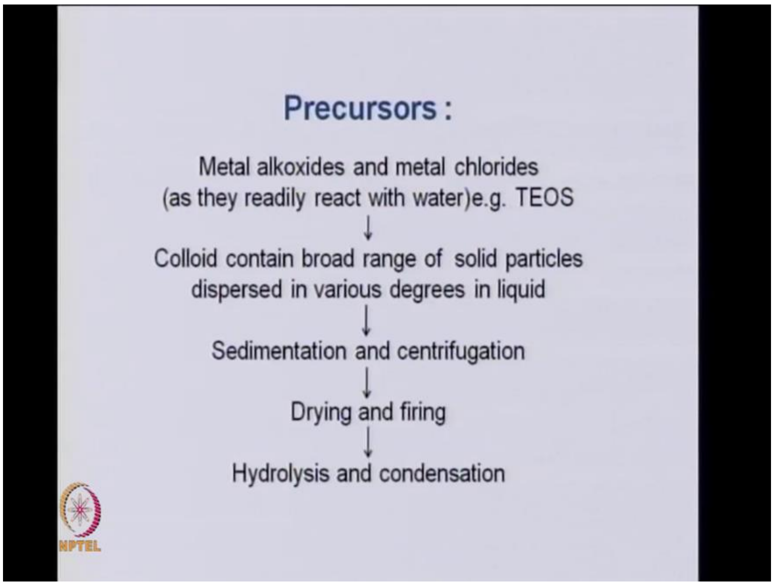

Precursors :

Metal alkoxides and metal chlorides
(as they readily react with water)e.g. TEOS
↓
Colloid contain broad range of solid particles
dispersed in various degrees in liquid
↓
Sedimentation and centrifugation
↓
Drying and firing
↓
Hydrolysis and condensation

Now, in this Sol-gel method, what are the starting materials, what are the precursors? We use metal alkoxides or typically metal chlorides since they react with water readily. For example TEOS which is a very common starting material. It is try tetraethyl orthosilicate silane. So, if silane is 4 hydrogen’s are connected to silicon and if you remove those 4 hydrogen’s with 4 alkoxy group, here a ethoxy groups, then it is tetra ethoxy silane and this is one of the most common starting materials in Sol-gel synthesis of silica based particles and this is TEOS. So, you can start with TEOS, then you can get collide with the broad range of solid particles which is dispersed in liquid, and then you sediment and centrifuge it, and then try which will lead to hydrolysis and condensation. So, that is a typical process for which you get a nanostructure material starting from metal alkoxides or metal chlorides, then reacting in water, and then draying it to get the final nanostructure materials. Two processes which are very important is hydrolysis and condensation.

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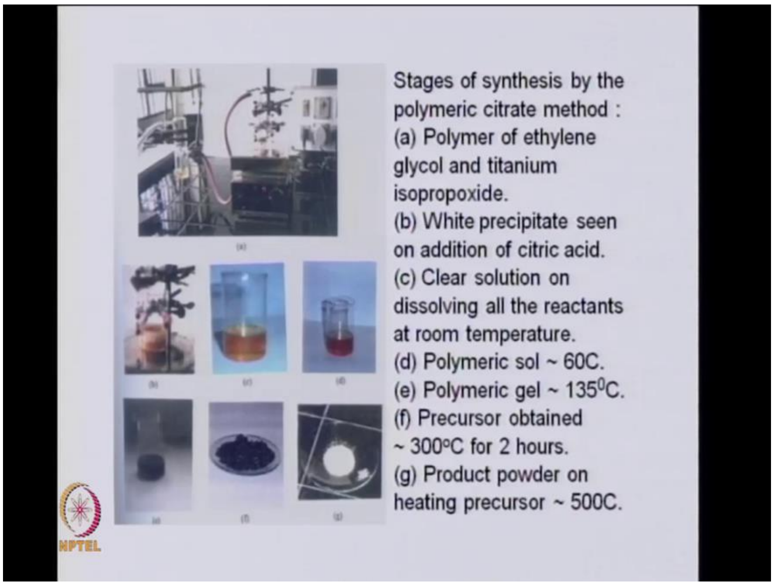

Stages of synthesis by the polymeric citrate method :

(a) Polymer of ethylene glycol and titanium isopropoxide.

(b) White precipitate seen on addition of citric acid.

(c) Clear solution on dissolving all the reactants at room temperature.

(d) Polymeric sol ~ 60C.

(e) Polymeric gel ~ 135^{0}C.

(f) Precursor obtained ~ 300^{o}C for 2 hours.

(g) Product powder on heating precursor ~ 500C.

This can be shown as various stages. For example, in the polymeric citrate method where we are starting to make a nanostructure material through a root which involves polymerization and hence, it is called a polymeric method is called the citrate method. It is polymeric citrate method because we are going to use citric acid which will help in polymerizing.

So, what you see here is, you see there is a magnetic stirrer and on that magnetic stirrer, you have a beaker. You can have a conical flask and there is a magnetic plate here and once you turn on this instrument, this magnetic stirrer, then it will stir the solutions and you can see that there is a tube in which some liquid is there. There is a rubber tube through which a gas is passed which is typically nitrogen which goes into this reaction vessel. So, what you are doing is you are stirring in absence of fear or in the presence of nitrogen and you start with say ethylene, glycol and titanium isopropoxide as your starting materials.

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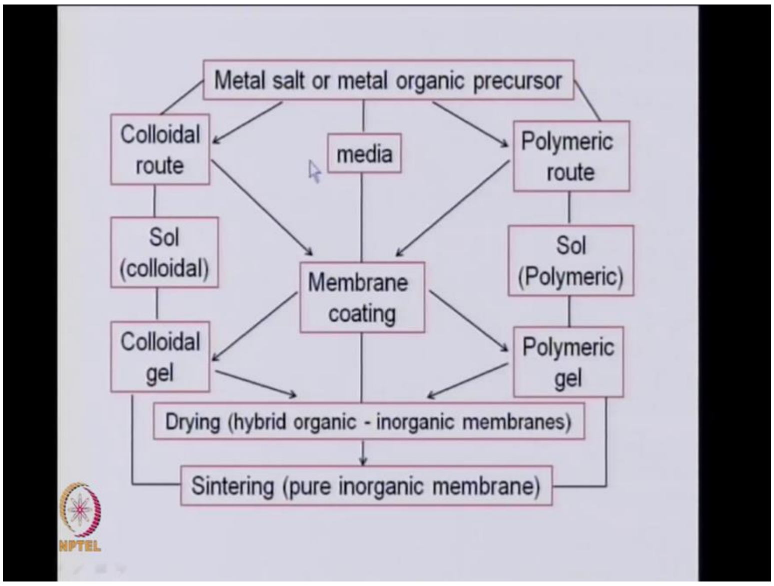

Metal salt or metal organic precursor

Colloidal route

media

Polymeric route

Sol (colloidal)

Membrane coating

Sol (Polymeric)

Colloidal gel

Polymeric gel

Drying (hybrid organic - inorganic membranes)

Sintering (pure inorganic membrane)

Then, you can see slowly after some time a white precipitate when you add citric acid and this is also being heated at some temperature like 60 degrees or so. So, this white precipitate will dissolve after some time and you will get a clear sol. So, you have added alkoxides which is titanium isopropoxide, you have added ethylene glycol and you have added citric acid. So, you will dissolve it at around 60 degrees to get a clear sol, and then you allow it to cool and settle down and slowly this will become more viscous because of condensation between citric acid and ethylene glycol. This will become darker, and then it will become black, that is that gel has formed and when you dry it little bit say around 135 degrees centigrade, you will get this black mass of polymeric gel, and then you heat it at higher temperature, and then you get the oxide nanostructure oxide of titania which you wanted.

Now, this process is typically what is called a polymeric citrate method. It is a Sol-gel method which involves polymerization using citric acid and ethylene glycol. So, you can follow either the colloidal route or the polymeric route to do this Sol-gel chemistry. So, typically if you follow the colloidal route, you get colloidal sol, and then a colloidal gel you can dry it to get a hybrid organic inorganic membrane or you can sinter it at higher temperature to get a pure inorganic compound like TIO2 or zirconia or oxide like barium, titanium oxide through this route. The other way is the polymeric route where you add ethylene glycol or citric acid, and then you get sol like we showed, and then polymeric gel which is much darker in color, and then dry it to get the organic inorganic membrane or you heat it higher when all the inorganic organic stuff will be burnt away leaving behind only that inorganic membrane. So, you can get these final products either through the colloidal route or through the polymeric route.

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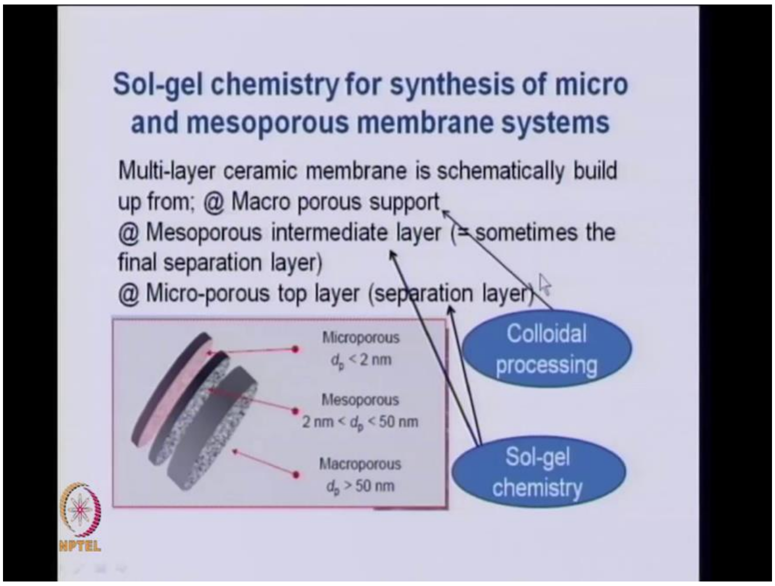

Sol-gel chemistry for synthesis of micro and mesoporous membrane systems

Multi-layer ceramic membrane is schematically build up from; @ Macro porous support
@ Mesoporous intermediate layer (= sometimes the final separation layer)
@ Micro-porous top layer (separation layer)

Colloidal processing

Sol-gel chemistry

This kind of Sol-gel chemistry is used in making membranes and one example as you can see here; this is a multilayer ceramic membrane which is made up of macro porous support. So, what you see is three layers, 1, 2, 3 in which you have a macro porous layer, mesoporous layer and micro-porous layer. How you define this micro-porous, mesoporous or macro porous is by the pore size. Each of these membranes which you are making through Sol-gel chemistry or colloidal processing, normally Sol-gel chemistry gives you mesoporous or micro porous layers.

Now, the definition of a micro-porous layer is that the pore diameter should be less than 2 nanometers, and then it is called a micro-porous solid. If the pore diameter is between 2 to 50 nanometers, then these are called mesoporous structures and if the pore diameter is much more than 50 nanometers, then these are called macro porous structures. So, together you see you can have a membrane which is made of all the three pore sizes. So, here the pores are very small because it is micro-porous and it is less than 2 nanometers. Here it is mesoporous set is between 2 nanometers and 50 nanometers, and this is the macro porous layer which has pore diameters of around 50 nanometers or more. Now, these can be used for separation of various materials and you can do filtration through these multilayer ceramic membranes, and these have a lot of inter applications in industry and elsewhere. So, you can use Sol-gel chemistry for the synthesis of micro and mesoporous membrane systems.

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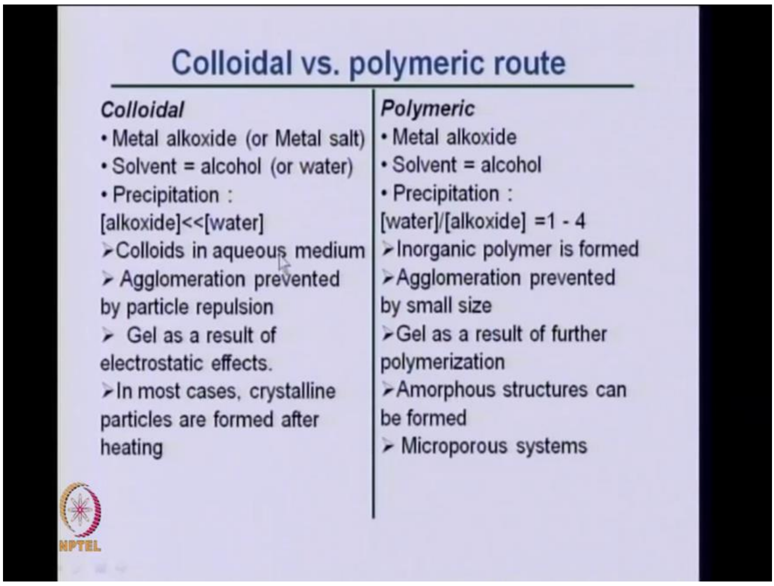

Colloidal vs. polymeric route

Colloidal	***Polymeric***
• Metal alkoxide (or Metal salt)	• Metal alkoxide
• Solvent = alcohol (or water)	• Solvent = alcohol
• Precipitation : [alkoxide]<<[water]	• Precipitation : [water]/[alkoxide] =1 - 4
➢Colloids in aqueous medium	➢Inorganic polymer is formed
➢ Agglomeration prevented by particle repulsion	➢Agglomeration prevented by small size
➢ Gel as a result of electrostatic effects.	➢Gel as a result of further polymerization
➢In most cases, crystalline particles are formed after heating	➢Amorphous structures can be formed
	➢ Microporous systems

Now, as you see that you can get these kinds of the micro-porous and mesoporous systems using Sol-gel chemistry, but you can do that using colloidal routes or the polymeric precursor route. So, in the colloidal route, you start with metal oxide and the solvent is alcohol and you do precipitation, where in this colloidal route, the alkoxides concentration is very less compared to the water whereas, in the polymeric route, you do this kind of reaction in a system where the alkoxides is much larger than the amount of water, nearly 2 to 4 times larger than the quantity of water. Here in the colloidal route, the concentration alkoxides is much less than that in water.

Then, in this colloidal route, you get collides in an aqueous medium which are separated due to repulsion between the particles, and that is how agglomeration is prevented in the polymer route. You get an inorganic polymer like from the condensation of ethylene, glycol and citric acid. You get a polymer and the agglomeration is prevented by a small size of these agglomerates in the colloidal route, you get a gel as a result of electrostatic effects. As you see that the particles are prevented by the particle repulsion and there are some charges on the surfaces, and you get a gel as a result of electrostatic effects in the polymeric route. You get the gel as a result of polymerization. In most cases, in the colloidal route, you get crystalline particles. That means the particles in which the atoms are regularly arranged over a long range. So, they are called crystalline whereas, in the polymeric precursor route, the gel which form as a result of polymerization leads to amorphous structures and most of the time in the polymeric route, you get micro-porous systems. So, there are some little differences between the colloidal route and the polymeric route for making nanostructure materials through these Sol-gel based methods.

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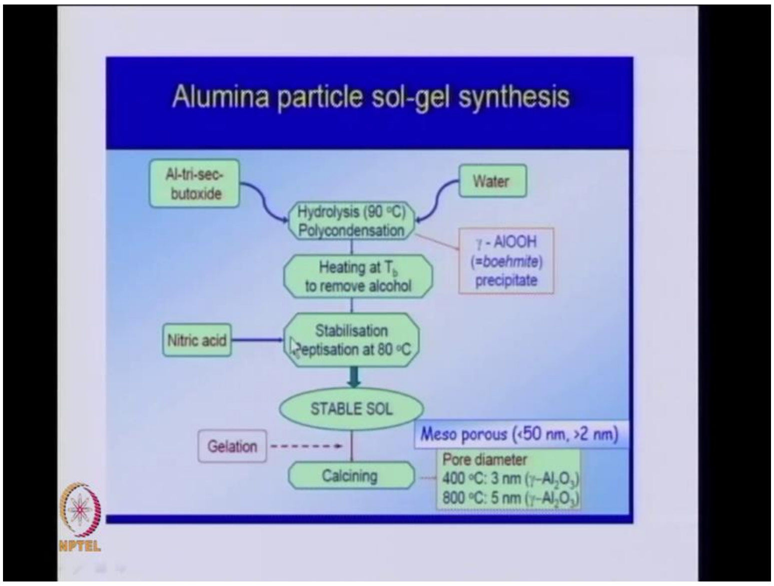

Alumina particle sol-gel synthesis

Al-tri-sec-butoxide

Water

Hydrolysis (90 °C)
Polycondensation

γ - AlOOH
(=*boehmite*)
precipitate

Heating at T_b
to remove alcohol

Nitric acid

Stabilisation
Peptisation at 80 °C

STABLE SOL

Gelation

Calcining

Meso porous (<50 nm, >2 nm)

Pore diameter
400 °C: 3 nm (γ-Al_2O_3)
800 °C: 5 nm (γ-Al_2O_3)

This is a typical example of synthesis of alumina of nano particles using the Sol-gel method. So, what you have here is alkoxides here that your choice is an aluminum alkoxides. It is a tri aluminum, second butoxide and you hydrolysis it with water. So, there is hydrolysis and keep the temperature around 90 degrees Celsius. So, there is hydrolysis, and then poly condensation and you get what is gamma alpha oxyhydroxide, which is commonly called boehmite and this is a precipitate, and then you heat it to remove the alcohol. You add some nitric acid to maintain stabilization, and then you heat it at 80 degrees for the peptizing action to take place which will give you a stable sol, and then after the gelation, you cancel them and you get mesoporous particles of between 2 to 50 nanometers.

Typically if the temperature of this cancelation is kept around 400 degrees Celsius, you get pore diameters of around 3 nanometers and if you heat it at higher temperature like

800 centigrade, then you get particles which are mesoporous and have average pore diameter of around 5 nanometers and these are gamma alumina. So, you start with the aluminum alkoxides, and you end of with gamma alumina nanostructure particles and with porosity in the range of 3 to 5 nanometers. So, you get mesoporous alumina using this Sol-gel synthesis.

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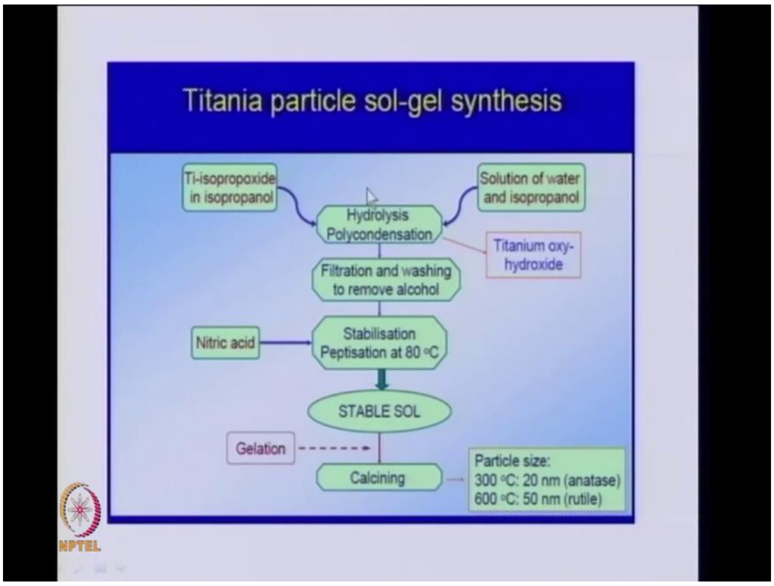

Titania particle sol-gel synthesis

Ti-isopropoxide in isopropanol

Solution of water and isopropanol

Hydrolysis Polycondensation

Titanium oxy-hydroxide

Filtration and washing to remove alcohol

Nitric acid

Stabilisation Peptisation at 80 °C

STABLE SOL

Gelation

Calcining

Particle size:
300 °C: 20 nm (anatase)
600 °C: 50 nm (rutile)

This is a similar example except now instead alumina, you are going to make titania. Titania is TIO2 and TIO2 you have to if you have to prepare using the Sol-gel synthesis, you start with titanium isopropyl oxide and you take this titanium isopropoxide in isopropanol and alcohol. So, you dissolve this titanium isopropoxide in a isopropanol, and at another solution containing isopropanol and water, and then hydrolysis and polycondensation occur which then gives you some precipitate which is filter and wash to remove the alcohol.

Similarly, to the synthesis of alumina, you add nitric acid for stabilization, and then peptisation at 8 degree centigrade to get a stable sol, and then it undergoes gelation and further cancelation at different temperatures gives particles of different sizes. So, here the particle size varies from 20 nanometers to 50 nanometers if you are depending on the temperature at which you can see. If you are calcining at 300 degree centigrade, you get particles whose average diameter is 20 nanometers and if you look at its crystal structure using powder x-ray diffraction, then you will find that this TIO2 has a structure which is called the anatase form of TIO2.

TIO2 has three different forms. One is anatase, another is rutile and the third one is brookite. So, in this methodology if you heat calcine at 300 hundred degrees centigrade, you get anatase form of TIO2, but if you heat at 600 degrees, not only the particle size increases, it goes to 50 nanometers. You also change the structure of TIO2. You now get the rutile form of TIO2. So, both anatase and rutile structures have the same composition of TIO2, but they have different structures and depending on your temperature of calcinations, you can get either anatase or rutile.

So, this is a typical synthesis, one of the most important nanostructure materials which is TIO2 which is used for many applications using the Sol-gel method using titanium, alkoxides and hydrolysis and polycondensation, and then calcination to get the final inorganic oxide which is titanium dioxide at TIO2 in two different forms at two different temperatures. Of course, the particle size changes. At low temperature, you always get smaller sized particles and at high temperatures, you get higher size particles. So, this is again Sol-gel example. So, we looked at alumina synthesis, and then titania synthesis, and then this is an example of silica which is again a very important nanostructure materials for many applications.

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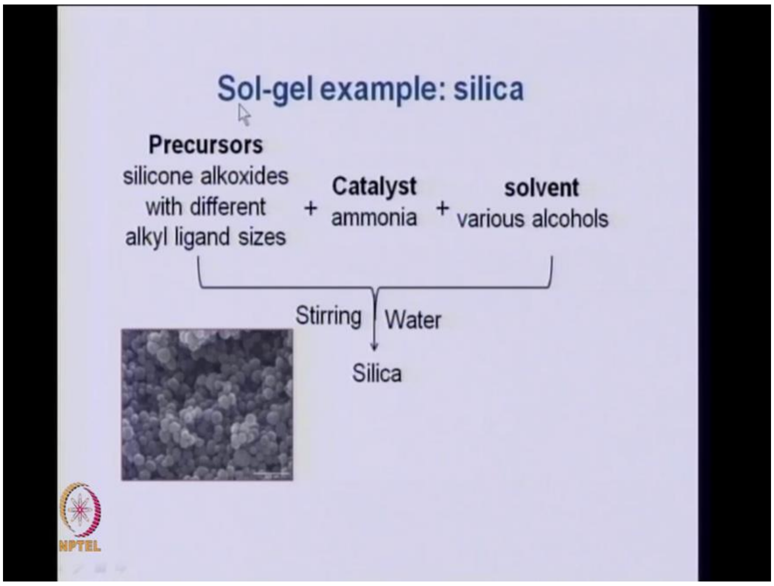

Sol-gel example: silica

Precursors
silicone alkoxides
with different
alkyl ligand sizes

+ **Catalyst**
ammonia

+ **solvent**
various alcohols

Stirring | Water

Silica

So, again starting from silicon alkoxide with different alkoxy group, you can vary them. You can take toxic group, propoxy group, butoxy groups and you can vary them, and once you reacts these alkoxides of silicon with ammonia in some alcohol, then you hydrolyze it, you add water. Under constant stirring, you can get silica and you can get very nice fierce of silica which are of the order of few nanometers 10-20 nanometers. So, we discussed three examples of some of the most important nano structured materials used in large tons or kilograms or used thousands of tons or kilograms of these materials of Titania alumina or silica are used in industry.

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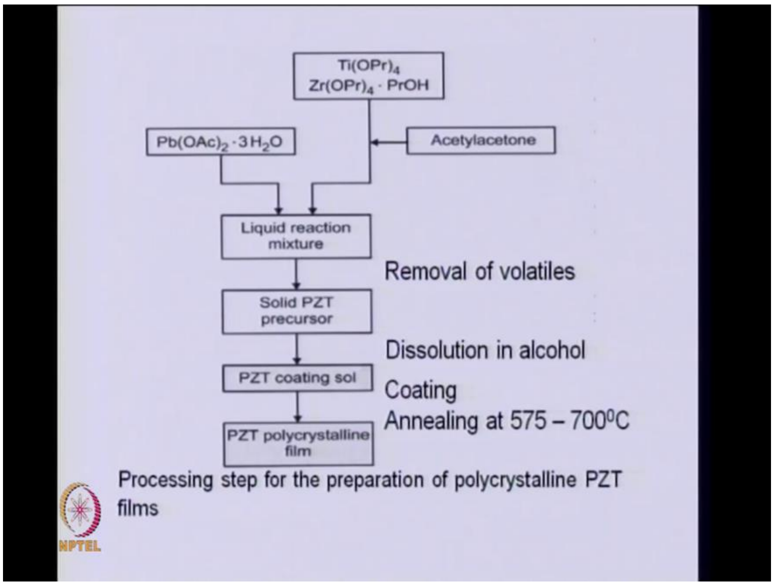

Processing step for the preparation of polycrystalline PZT films

This is a synthesis of another very important material. It is called PZT where P stands for lead, Z for zirconium and T for titanium. So, this is an oxide of lead, zirconium and titanium and it is a very important dialectic oxide. It is used in capacitors and many other devices for example transducers etcetera. So, this is a material which involves lead, zirconium and titanium. So, how you obtain this material using the Sol-gel process is you start with titanium and zirconium alkoxides. So, you have this tetra propylene alkoxides of titanium and zirconium, and you take alcohol, dissolve them in alcohol. So, this is propylene alcohol propranol, and then you add acetyl acetone allegiant and simultaneously, you add lead acetate hydrate.

So, you dissolve it in water and add the solution of lead acetate. So, basically it will have lead ions in solution. So, you have titanium ions and zirconium ions through these alkoxides in solution in isopropanol, and you have lead ions in solution and you mix this. This liquid reaction mixture will be having all the three metal ions, lead, titanium and zirconium in the right proportions that you want, and then you remove all the volatile that is the acetyl acetone and water and alcohol and you are left with a solid lead, zirconium, titanium oxide precursor, and then you can dissolve in alcohol and you can quote on a substrate. If few want to get the powder, you heat it or any lead between 575 to 700 centigrade's, and then you can get a polycrystalline film or nano crystalline film.

So, this is a process using Sol-gel chemistry to get a polycrystalline PZT film. If you need a powder, then you just dry it and you do not have to quote it, but after this precursor, you can dissolve this solid precursor. You can heat at high temperatures to get the oxide powder. I have to coat it, you have to dissolve in alcohol, and then make coating sol, and then after coating you have to anneal the film for further applications.

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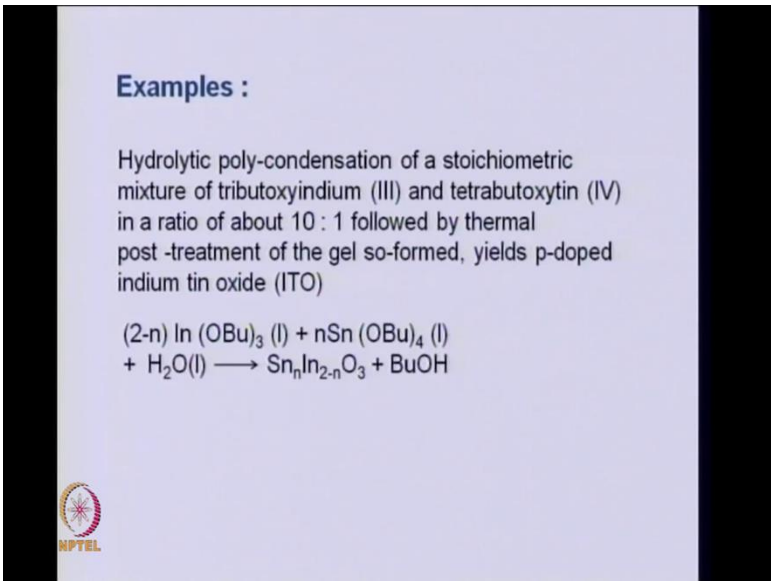

Examples :

Hydrolytic poly-condensation of a stoichiometric mixture of tributoxyindium (III) and tetrabutoxytin (IV) in a ratio of about 10 : 1 followed by thermal post -treatment of the gel so-formed, yields p-doped indium tin oxide (ITO)

$$(2-n)\ In(OBu)_3\ (l) + nSn(OBu)_4\ (l) + H_2O(l) \longrightarrow Sn_nIn_{2-n}O_3 + BuOH$$

So, this is another example now of making a very important material which is p-doped indium tin oxide and indium tin oxide is a very important semi-conducting material and is used in many applications. So, as a substrate ITO is used as a substrate and this is prepared using condensation of stoichiometric mixture of an alkoxides of indium. Here, it is shown as tributoxyindium and you add to that tetrabutoxytin. So, you have an indium and tin in a ratio of 10 raise to 2, and then you heat it, so that you get the gel and this will lead to p-doped indium tin oxide. So, that is the reaction shown here, where you have the tributoxyindium reacting with tetrabutoxytin to your indium tin oxide which is very important material.

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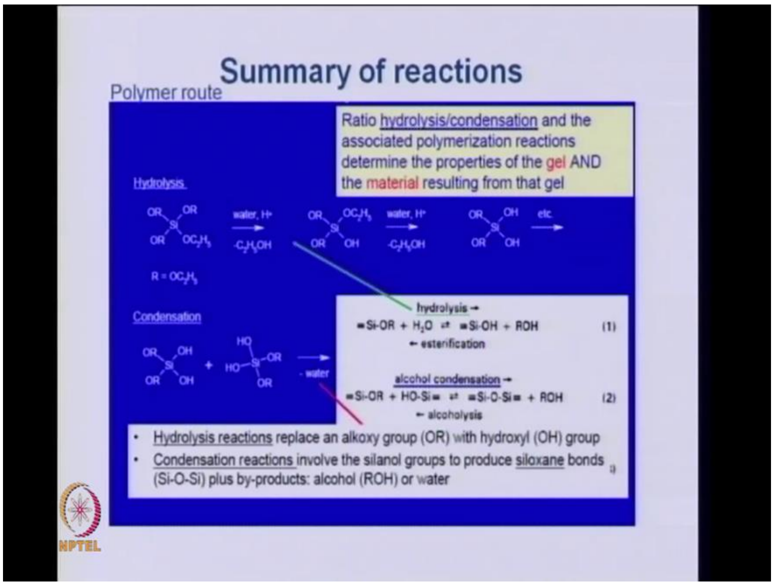

Summary of reactions

Polymer route

Ratio hydrolysis/condensation and the associated polymerization reactions determine the properties of the gel AND the material resulting from that gel

Hydrolysis

$R = OC_2H_5$

Condensation

hydrolysis →

$\equiv Si\text{-}OR + H_2O \rightleftarrows \equiv Si\text{-}OH + ROH$ (1)

← esterification

alcohol condensation →

$\equiv Si\text{-}OR + HO\text{-}Si\equiv \rightleftarrows \equiv Si\text{-}O\text{-}Si\equiv + ROH$ (2)

← alcoholysis

- Hydrolysis reactions replace an alkoxy group (OR) with hydroxyl (OH) group
- Condensation reactions involve the silanol groups to produce siloxane bonds (Si-O-Si) plus by-products: alcohol (ROH) or water

This polymer is a route of making nanostructure materials through the Sol-gel. Polymerization route is again shown here where two important steps are again shown where you have the hydrolysis step. So, this is alkoxy silane, a trialkoxysilane and on hydrolysis, it loses alcohol which you have to remove, and then you get this hydroxyl group in here right under you again further hydrolyze till you get all these hydroxyl groups which can then undergo polymerization, condensation polymerization and yield to you finally these Si-O-Si links structures. So, in short you have hydrolysis, and then you have alcohol condensation. So, this is the reverse of this esterification and the reverse of this alcohol condensation is alcoholysis. So, in hydrolysis actions, you replace an alkoxy group with the hydroxyl group and in the condensation reactions, you involve the silanol groups. The Si-OH groups react condense to form Si-O-Si bonds which are called siloxane bonds and you get by products like alcohol and water. So, this is to summarize these two important actions which always take place in Sol-gel chemistry.

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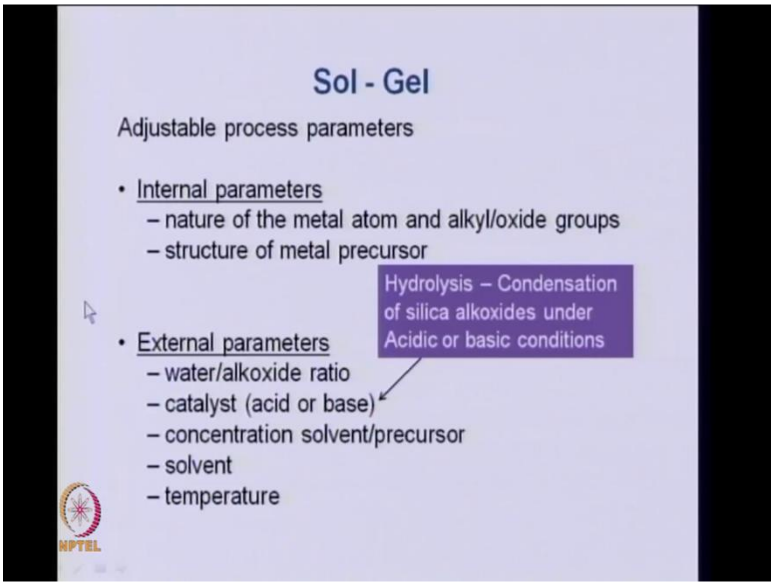

Sol - Gel

Adjustable process parameters

- Internal parameters
  - nature of the metal atom and alkyl/oxide groups
  - structure of metal precursor
- External parameters
  - water/alkoxide ratio
  - catalyst (acid or base)
  - concentration solvent/precursor
  - solvent
  - temperature

Hydrolysis – Condensation of silica alkoxides under Acidic or basic conditions

How do you adjust the processing parameters in a typical Sol-gel method? So, how do you control a Sol-gel process? There are various controls. You have some internal parameters and you have some external parameters. So, the internal diameters which affect Sol-gel reaction is basically the nature of the metal atom and the alkyl or oxide groups present on it. The second thing which depends internally is the structure of the metal precursor. The factors which you can change from outside is like water are the amount of alkoxide that you take the amount of catalyst that you add, whether you do acid catalysis or basis catalysis. That means, when it is acid hydrolysis, the action which catalyze is hydrolysis or condensation of reactions.

So, these are affected by the conditions present, the acidic conditions or basic conditions when determined the extent of hydrolysis and condensation and to rates at which these hydrolysis and condensation takes place. So, this can be controlled using amount acid or base that you add further. You can vary the concentration of the solvent, you can vary the concentration of the precursor, also the nature of solvent you can change and finally, the temperature. So, all these parameters will affect the rate of this Sol-gel process and that will depend on your final product.

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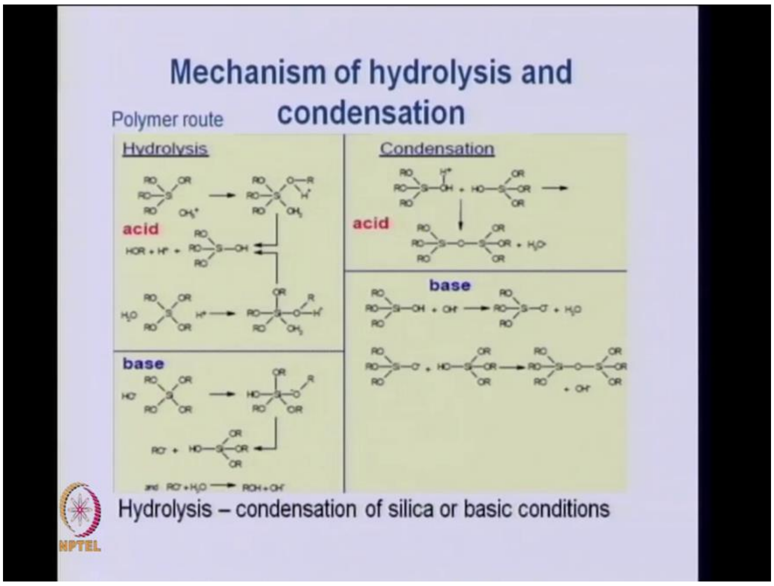

Mechanism of hydrolysis and condensation

Polymer route

Hydrolysis – condensation of silica or basic conditions

So, again to tell you the mechanism of hydrolysis and condensation in the polymeric route, you have the hydrolysis process. If it is acid hydrolyzed, then the presence of water, this proton will first protonate this oxygen and you get this, and then it removes this alcohol OH group and you get this silane group introduced. So, this is a typical acid hydrolysis which is guided by the initial attack by the proton on this oxygen. Now, if you do further on this product, you have one alcoholic group. You can continue this further and replace the other alkoxides group with alcoholic groups. You can also have a process like this, where you have water molecule which is reacting with these alkoxides, and then giving you this product, and then this ROH leaves to give this.

Now, if it is base catalyzed, then you have the OH minus group which will react and with attached on the silicon and making this oxygen negative, and then you get this Si-O tri alkoxy group. With alcohol group here because one of this alkoxy group which is leaving group, it will leave and so, in total one are all Si-OH bond is formed, a silanol bond is formed and one more group is eliminated. So, this group of course reacts with water and forms an alcohol group. Now, this is the reaction mechanism for hydrolysis in the presence of acid or in the presence of base. Similarly, you can have condensation in the presence of acid. So, you have two of these silanol groups, and then they form Si-O-Si linkage in the presence of this proton on which is protonoting here on this oxygen, and giving you a condensed product in which Si-O-Si bond is formed.

If you do a base condensation, then you have a hydroxyl group here to react and one water molecule leaves, and you have this O minus group and this O minus group then reacts with another molecule of this alkoxy saline, and you have this Si-O-Si bond with a loss of OH minus group. So, you can have hydrolysis under acidic or basic conditions. Similarly, you can have condensation in acidic or basic media, ok.

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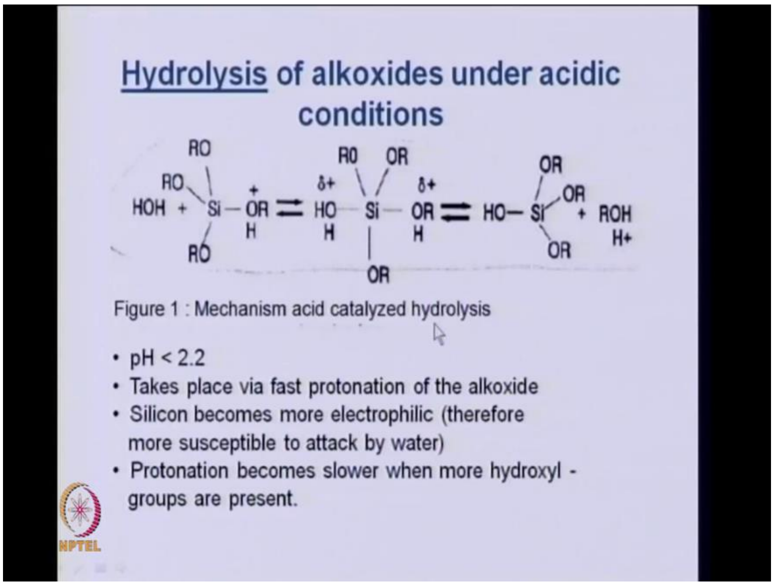

Hydrolysis of alkoxides under acidic conditions

Figure 1 : Mechanism acid catalyzed hydrolysis

- pH < 2.2
- Takes place via fast protonation of the alkoxide
- Silicon becomes more electrophilic (therefore more susceptible to attack by water)
- Protonation becomes slower when more hydroxyl - groups are present.

So, this is probably another clearer picture of the mechanism of acid catalyzed hydrolysis. So, you can see this we described in the previous slide too. So, you have first protonation, and then this water molecule reacts because now there is this electron density or oxygen here react on this silicon, and then you get a delta positive charge on this water molecule, and is delta positives out remains here. So, one alcohol group will leave creating one new Si-OH linkage. This acid catalyzed reaction normally takes place at pH of less than 2.2, and it has fast protonation step and the silicon becomes electrophilic after the protonation. Therefore, it is more susceptible to attack by water and the protonation become slower when more hydroxyl groups are present.

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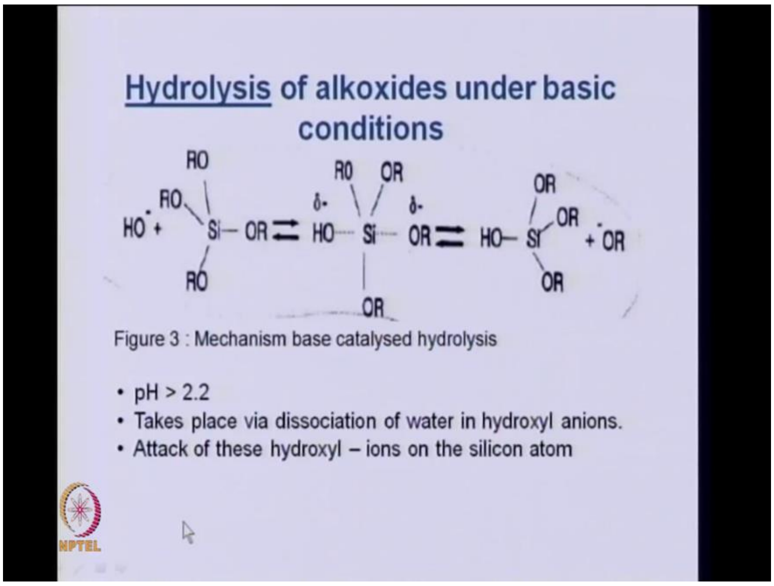

Hydrolysis of alkoxides under basic conditions

Figure 3 : Mechanism base catalysed hydrolysis

- pH > 2.2
- Takes place via dissociation of water in hydroxyl anions.
- Attack of these hydroxyl – ions on the silicon atom

Now, in basic conditions, the OH minus group attacks this saline, tetra alkoxides saline and you get this kind of OH delta minus charge here, and this also gets OR delta minus charge. Then, this OR minus leaves and you are left with a new silicon hydroxyl linkage and this base catalyzed reaction normally takes place at pH greater than 2.2, and it takes place via dissociation of water in hydroxyl anions and the attack of these hydroxyl ions on silicon. So, that is how the base catalyzed hydrolysis takes place.

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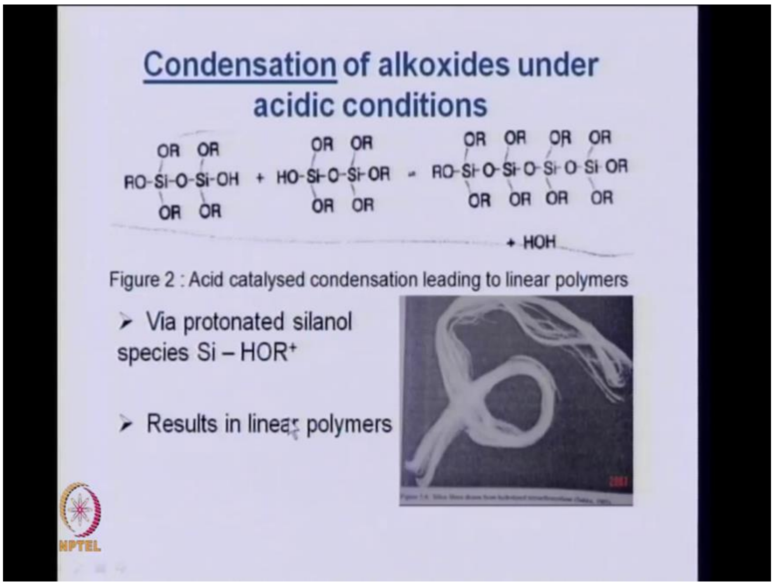

Condensation of alkoxides under acidic conditions

Figure 2 : Acid catalysed condensation leading to linear polymers

- Via protonated silanol species Si – HOR⁺
- Results in linear polymers

When you have condensation of alkoxides, this is the second step after hydrolysis. You have condensation and when you have condensation of alkoxides under acidic conditions, then you are going to create this Si-O-Si linkage and this real gives you a linear kind of polymer. So, acid catalyzed condensation always leads to linear polymers and you can see these chains of linear polymers based on condensation of alkoxides. This is scanning electron microscope picture of these kinds of linear polymers. So, this reaction occurs through the protonated silanol species Si-HOR plus and results in linear polymers. This is under acidic conditions.

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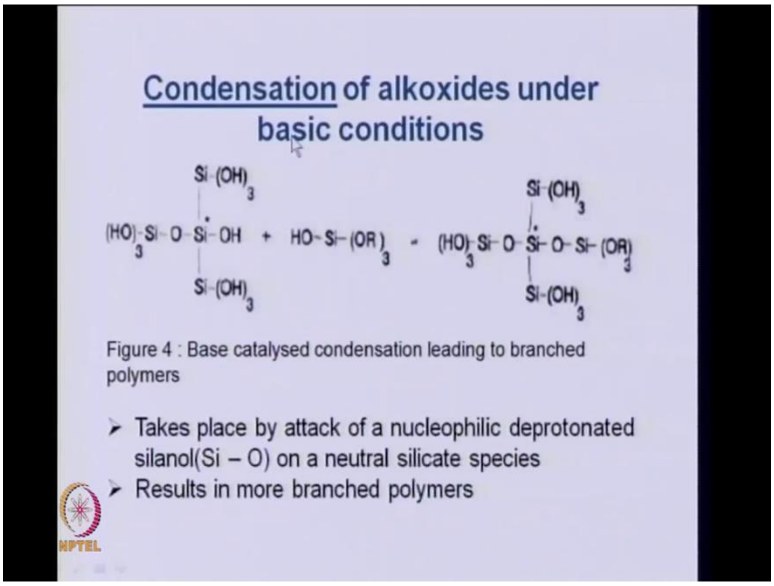

Condensation of alkoxides under basic conditions

Figure 4 : Base catalysed condensation leading to branched polymers

- Takes place by attack of a nucleophilic deprotonated silanol(Si – O) on a neutral silicate species
- Results in more branched polymers

What happens in basic conditions is that this condensation normally leads to branched compounds. So, this kind of branch compounds you can see because this will bind here to form silicon oxygen silicon bond and this silicon oxygen silicon bond will give raise to this branching. So, base catalyzed condensation always leads to branched polymers whereas, acid condensation, acid catalyzed condensation leads to linear polymers. The base condensation will take place through the attack of nucleophilic deprotonated silanol which takes place on a neutral silicate species which is shown here and results in more branched polymers.

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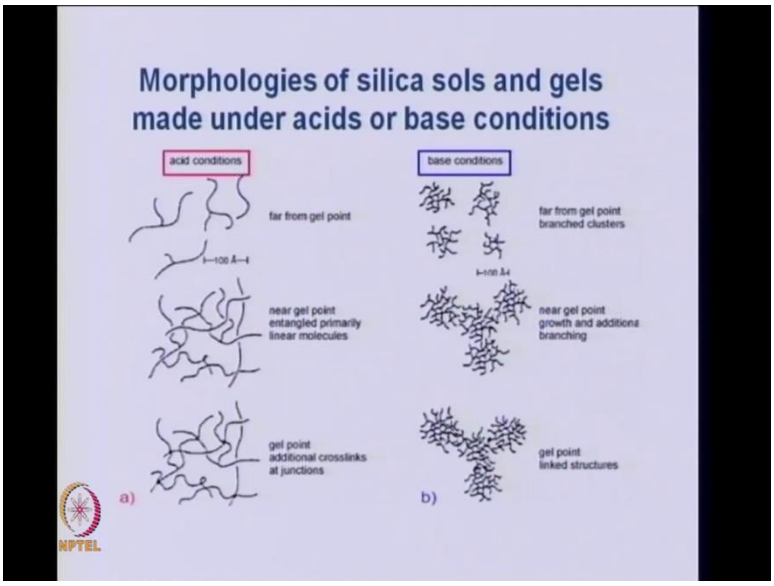

Morphologies of silica sols and gels
made under acids or base conditions

So, then the kind of morphologies, morphology means the shape of the particles or the polymers that you get under acid are base conditions are different depending on where you are close to the gel point or far from the gel point etcetera and also, whether you are using acidic conditions or basic conditions.

So, if under acid, the conditions you are doing this reaction and you are far from the gel point, then you get this kind of linear polymers with very less branching which are very lose. However, if we use acidic conditions and you are near the gel point, then you get entangled linear molecule. So, lot of linear molecules which are kind of criss-crossing themselves, this is when you are close to the gel point and yet using acidic conditions. So, here also you see long chains like you see in this case, but there are more chains and more crossing each other. When you are at the gel point, we will have additional cross links at the junctions where they meet. You will have additional linkages if you are at the gel point.

Now, if you look under basic conditions and you are very far from the gel point, then you see this kind of branched cluster kind of things. However, when you are close to the gel point, then you will see lot of growth and additions and lot of branching of course whereas, if you add the gel point, you get nearly connected structure. However, with lot of branching, but the whole thing gets interconnected when you are in the gel point. This is the basic conditions. So, if you compare the acidic and the basic condensation, you see that under acidic conditions, guess get more pores or more sparsely arranged chains whereas, in basic conditions, you get more close net chains or clusters which have smaller lengths. However, when they get interconnected especially at the gel point, these small clusters are all network together. So, these are different type of morphologies or structures which you can observe at acidic and basic conditions.

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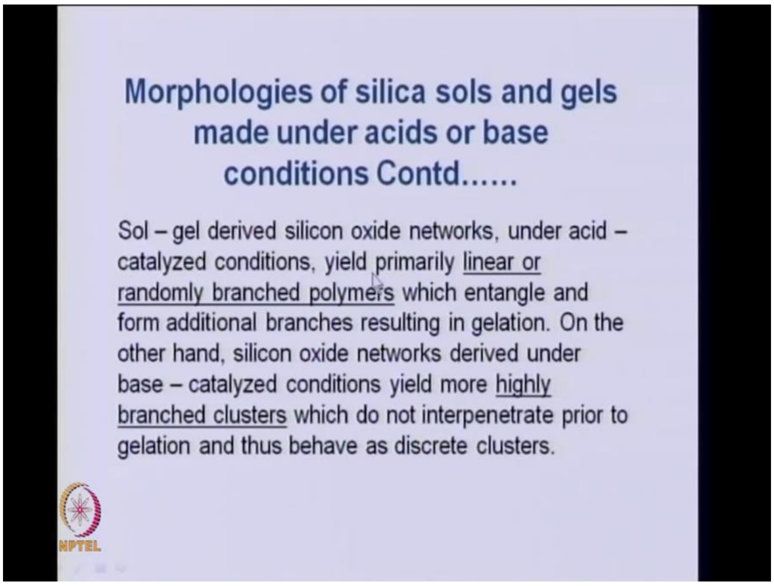

Morphologies of silica sols and gels made under acids or base conditions Contd……

Sol – gel derived silicon oxide networks, under acid – catalyzed conditions, yield primarily linear or randomly branched polymers which entangle and form additional branches resulting in gelation. On the other hand, silicon oxide networks derived under base – catalyzed conditions yield more highly branched clusters which do not interpenetrate prior to gelation and thus behave as discrete clusters.

So, the Sol-gel derived silicon oxide networks, under acid and basic conditions, yield linear or randomly branched polymers and as you increase or come close to the gel point, they will entangle and form additional branches. On the other hand, if you use this, using acid catalyzed reactions when you use base catalyzed conditions, they use they yield highly branched clusters which do not interpenetrate prior to gelation and thus behave as discrete clusters.

So, this is when gelation is taken place before the gelation. They exist as independent clusters which are highly branched now.

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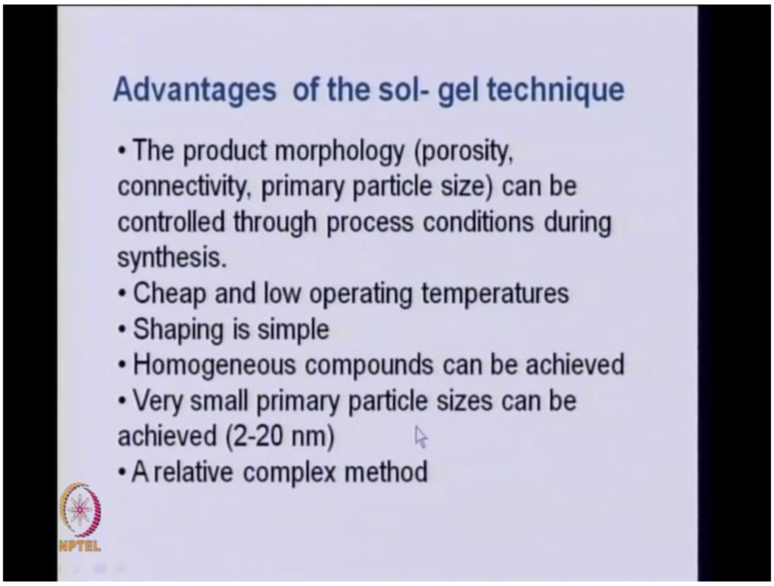

Advantages of the sol- gel technique

- The product morphology (porosity, connectivity, primary particle size) can be controlled through process conditions during synthesis.
- Cheap and low operating temperatures
- Shaping is simple
- Homogeneous compounds can be achieved
- Very small primary particle sizes can be achieved (2-20 nm)
- A relative complex method

What are the advantages of the Sol-gel technique? So, gel technique you can make many different types of nano structured materials. As you saw that we looked at examples of gamma, alumina, anatase and rutile form of TIO2 or the dielectric ceramic like PZT, lead, zirconium and titanate. So, several different materials can be obtained in the nano structured form using the Sol-gel technique. The advantages of using this technique are as follows.

You have control of the product morphology. So, you have control on the porosity, the connectivity, the primary particle size during the processing of the material using the Sol-gel technique. You can change the amount of water, the amount of alcohol, the amount of citric acid if you are using a polymer method. So, all that comes in the processing, there are several ways of controlling the product morphology. Sol-gel method is cheap and the temperatures at which you are operating are not very high. Then, you can easily shape the material once it is formed as a powder, or you can make a film. Those powders can be compressed and make into monoliths. You can get very pure monophasic compounds. That means, the stoichiometry of the ions can be maintained by proper control.

So, homogeneous compounds or pure phases can be obtained. You can get very small particle sizes. If you want you can get 2, 3, 5, 23 nanometer particles. So, you can vary the particle size by varying the conditions of the Sol-gel process. Then, it is a regularly complex method. Of course, you have to know some chemistry and you must know how to handle these chemicals. You must know when to avoid air like to pass nitrogen as we showed. When you are doing a citrate gel method synthesis, you stir the solution properly. You have to make a clear transparent sol which will settle to gel. So, some good handling and chemistry is required to use the Sol-gel technique to the full potential.

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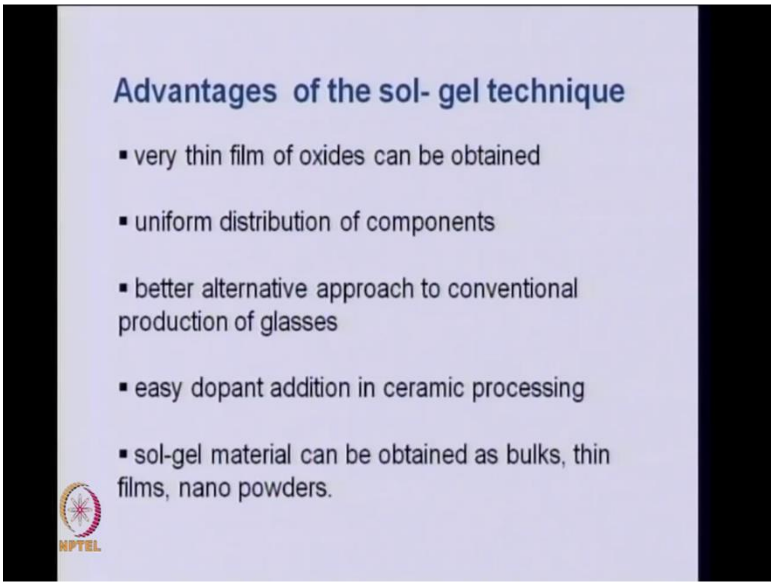

Advantages of the sol- gel technique

- very thin film of oxides can be obtained
- uniform distribution of components
- better alternative approach to conventional production of glasses
- easy dopant addition in ceramic processing
- sol-gel material can be obtained as bulks, thin films, nano powders.

Continuing on the advantages of the Sol-gel technique, you can not only get powders, you can get very thin film of these oxides on various substrates. You can quote them. Since, you get a transparent sol at that stage, you can quote that sol on various substrates like glass or quads or silicon, and then you can dry them to make thin films of oxides. Those thin films of course once with the sol have to be heated to get more mechanically stable films or ceramic films on the substrates.

The other advantage is the uniform distribution of the components. So, if you have lead, zirconium and titanium, three different metal ions in an oxide, so using the sol you can get very homogeneous solution because it is now not solid, and then with this homogeneous sol is not a solution. Homogeneous sol can give raise to very good quality of coatings or powders as you wish. So, it is better alternative approach to conventional production of glasses. So, many times you make glasses using very high temperatures. Glasses are also called amorphous solid. So, many times they are obtained using very high temperatures, and then they are cool very rapidly to obtain glasses.

However, with the Sol-gel technique, it is very easy to get glasses or amorphous solids at much lower temperatures. You can control the addition of each dopant during the ceramic processing. So, you can really make compounds with several different ions using the Sol-gel process. The Sol-gel material can be obtained in various forms and bulk materials as thin films and as nano powders. So, all these are various advantages of the Sol-gel technique.

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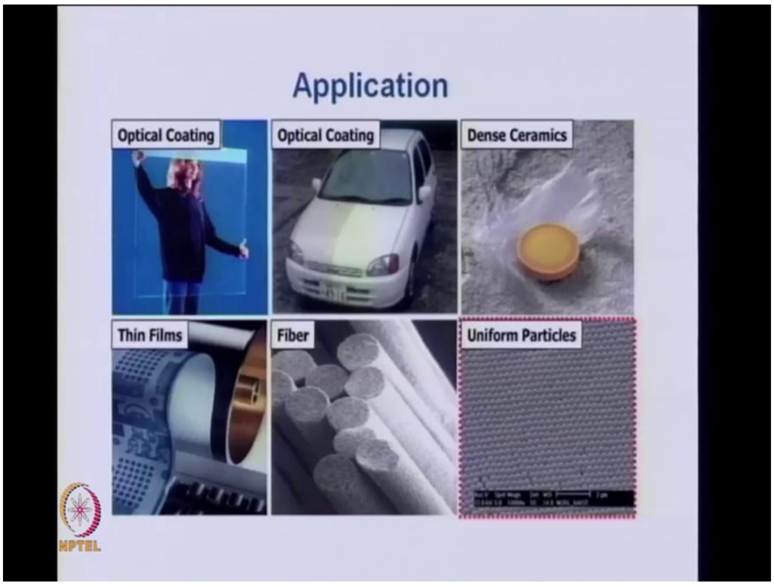

Application

Now, these Sol-gel produced powders or coatings have several applications, and as you see this is an optical coating. So, this is a glass on which there is a coating using a sol which is converted into a gel. So, when it is sol, it is this glass plate is dipped in a solution in that sol in which is kept in a vessel, and then it is taken out of that vessel and backed a coating ahead. It is a transparent coating and hence, you can see through, but it may have other properties depending on what was there in the sol. So, you can have different properties of this glass by the coating of the material using the Sol-gel process. So, if you coat with silica, you can get some properties. If you coat with titania, you get some properties also. What is the size of the nano particles? In the Sol-gel derived titania or zirconia film which is on top of the glass well determine its properties for example, the optical properties of this glass can be controlled by the kind of material you coat on that using the Sol-gel process.

So, if you coat a particular type of material may be it will cut down UV radiation. So, only visible range of radiation which is not harmful and past through this glass or you can have glasses which will be transparent to some wavelength. Other than what is visible and for some specific applications maybe you need, only I have wavelength of light to pass through. Then, it will require coating of a different kind than one which passes through only visible. So, these are applications for optical coatings, and then you can have similar optical coatings on the car windows, you can have dense ceramics.

So, this is a dense ceramic which is made up of a nano crystalline, polycrystalline powder which was obtained by the Sol-gel method, and then it was compacted and sintered to get this kind of a disk form which may have properties depending on what is the compound by which you are made this disk. Now, you can make think films on top of sub substrate like shown here using Sol-gel chemistry, you can have powders. So, these ceramics you can put it in a mold and get powder rods like this, which have certain applications. Then, you can just have a layer of uniform particles on a surface made through the Sol-gel process.

So, with all this what I wanted to discuss with you was the first method in a bottom up approach which is the Sol-gel method which we have discussed so far, and we will be discussing other methods, chemical routes or a low temperature routes as they call which together form the bottom up approach to nano structured materials.

So, today we are finishing the second lecture of model II, and we have basically discussed in these two lectures, the chemistry and the processing and applications of a methodology which is the Sol-gel process to make nano structured materials which may be in powder form, in thin film form or as fibers our disks. So many shapes and sizes you can make nano structured materials using the Sol-gel process. So, you must remember that Sol-gel processes is a low temperature process which has wide applications, and some of the general oxide which is used in industry in very large amounts as I said thousands of tons, maybe million of tons. Some of them we discussed, alumina gamma, alumina titanium dioxide or anatase form and rutile form and lead zirconia titanate. These are some very few examples. There are thousands of the other examples of making materials using the Sol-gel process.

So, in the next two lectures, we will discuss another low temperature method, another bottom-up approach to make nano structured materials and that is a met method using micro emulsions. So, we will discuss what micro emulsions are and how they are useful in making nano materials with controlled size, shape and hence, by which we can control the properties of those nano structured materials. So, goodbye for now and we will meet for the next lecture which will be the third lecture of model II.

Thank you very much and see you again.