Membrane Technology
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Lecture - 08
Inorganic Membranes Sol-Gel Process, Ceramic Membrane Preparation, Membrane Modification

Good morning students today is the lecture 8 of module 3. So, as you know that we have been discussing comparison of different types of membranes in today is lecture will discuss one of the most important membrane preparation methods for inorganic membranes that is called Sol gel process. Then we shall discuss how to prepare ceramic membranes and how to modify the membranes also.

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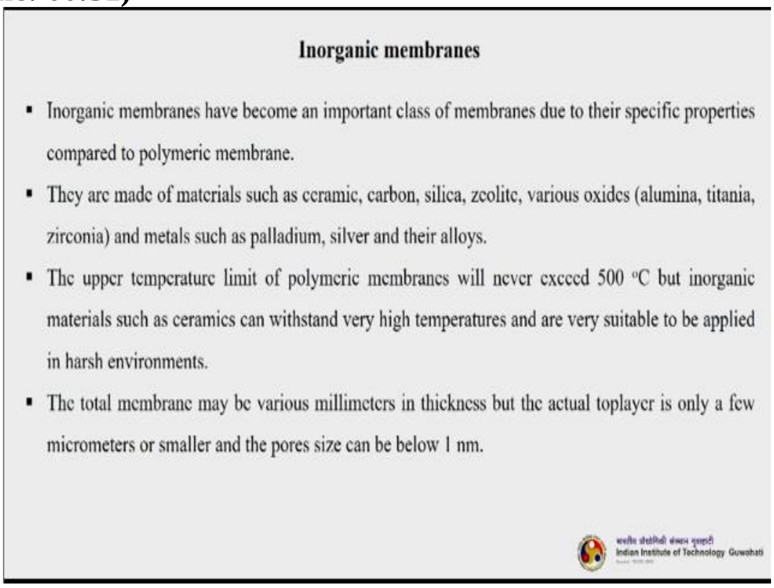

So as you know inorganic membranes have become an important class of membranes due to their specific properties compared to polymeric membrane. So they are made up of various types of materials such as ceramic, carbon, silica, zeolite, and different types of oxides like alumina, titania, zirconia and also metals such as palladium, silver and their alloys. The upper temperature limit of these polymeric membranes will hardly exceeds above 500 degrees centigrade not even 500 degrees centigrade.

Some rare polymers are highly thermally stable or else most of them are around 300, 400 in that temperature range. However the beauty of inorganic membranes are that they can withstand temperature up to almost 800, 900 even 1000 degrees centigrade very high temperature even sometimes more than that. So they can be applied where we are going for a thermal driven separation process.

The total membrane maybe various millimeter in thickness but the actual top layer which is doing the separation is only about a micrometer or even smaller than that pores sizes are below 1 nanometer usually.

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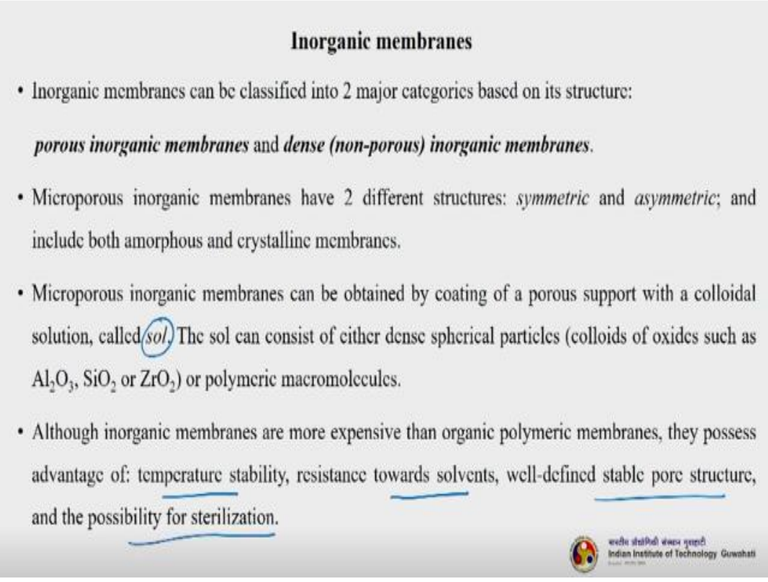

So asymmetric membranes. So the inorganic membranes can be classified into 2 major categories based on their structure. The first is porous inorganic membrane. The second is dense or non-porous inorganic membranes. Microporous inorganic membranes have 2 different structures. symmetric and asymmetric and they include both amorphous and crystalline membranes and you know in micro porous inorganic membranes can be obtained by coating a porous support with a colloidal solution it is called sol.

So sol can consist of either dense spherical particles that is colloids of oxides such as alumina, silica or zirconia or polymeric macromolccules also. So sol is basically a Colloidal dispersion of molecules. So, although inorganic membranes are more expensive than organic polymeric membranes. They possess advantage of temperature stability resistance towards solvent and well defined stable pore structure and the possibility of sterilization.

That means it is easy to autoclave actually say inorganic or ceramic membranes, but which you cannot do usually upon the polymeric membranes.

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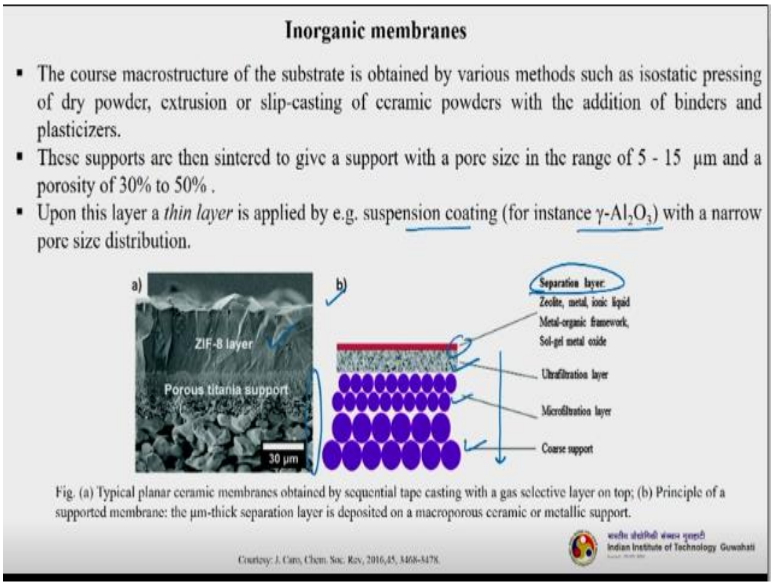

So let us see how the inorganic membranes and their structures looks like. So, the course macrostructure of the substrate is obtained by various methods such as isostatic pressing of dry powder, extrusion or slip-casting of ceramic powders with the addition of binders and plasticizers. Now, basically there is a support you can see this please look at this particular image this is b. Image b you can see this there are pore distinct layers.

First one is this red one, which is the separation layer this is the most important one which is this layer is during the separation and as I told you earlier in many times also as thin as possible. So, that the membrane thickness will not give more resistance to separation. Then it followed by another layer this is layer, another layer, another layer so, edge v gradually moves down from top to bottom, the pore sizes of these layers increases.

Now the top layer it can be porous it can be non-porous also depending upon actually what is our intendant or targeted separation. Now, the thin layer is usually applied by suspension coating for instance gamma alumina with narrow pore size distribution. So, here in this we can see us scanning electron microscope of a porous titania support. So, this is the support which is doing the mechanical support also support and the zeolite 8 layer is the top one.

So, this is how actually our inorganic membranes asymmetric membranes are being prepared. So, in this classic example, you see the top layer is the separation layer that can be porous non porous followed by ultrafilteration layer followed by microfilteration layer then there is core support.

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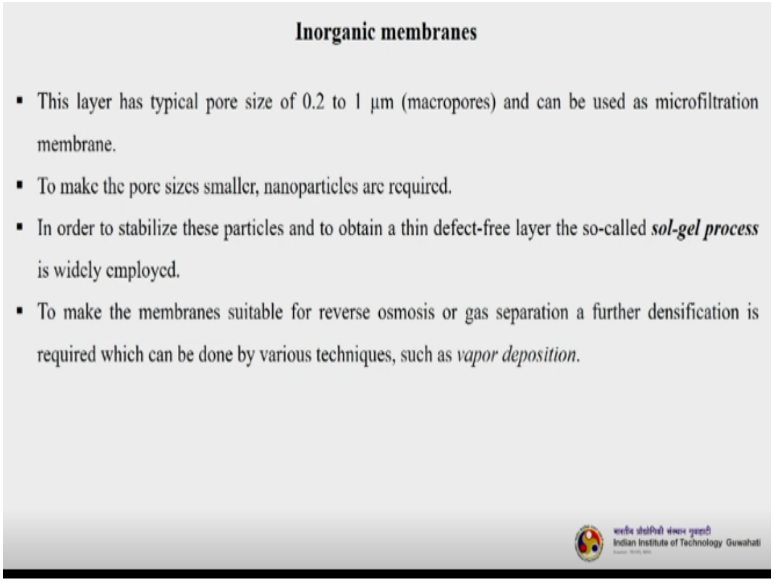

This layer is typical port size of 0.2 to 1 micron and can be used as microfiltration membrane. To make the pore sizes smaller, nanoparticles are required. So, in order to stabilize these particles and to obtain a thin defect-free layer the so called sol-gel process is actually widely employed. To make the membrane suitable for reverse osmosis or gas separation a further densification is required which can be done by various techniques such as vapor deposition.

So, once it is not that in a one step process of sol-gel, you are getting your all desired intended this one teller made membrane, sometimes it is required that a further densification on the top layer. Are applying of a very small layer on the top to achieve the targeted separation is required. So, it can be done by using a vapor deposition or there are certain other techniques or techniques also.

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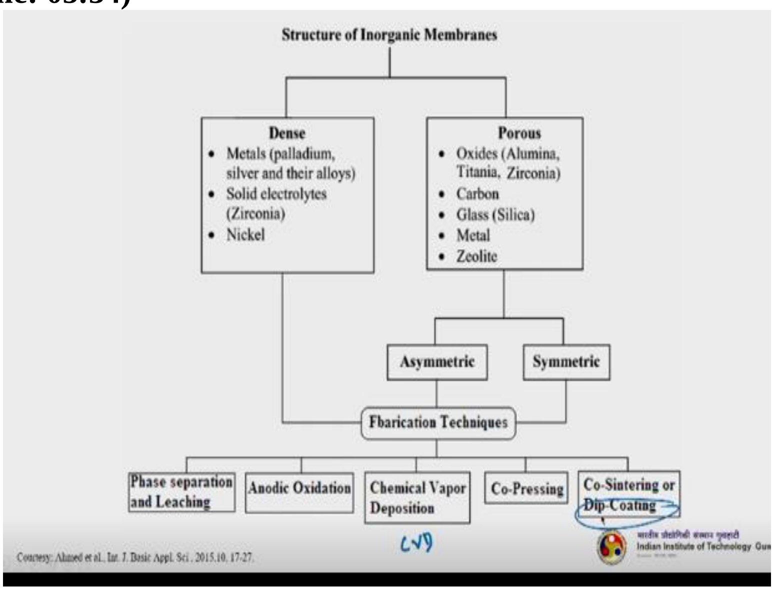

So we will see these things. So this is the structure of inorganic membranes. So, you can see dense and porous both are been given here under porous we have asymmetric and symmetric membranes then the fabrication techniques which can be used to make these membranes are either Phase separation and Leaching, Anodic Oxidation, Chemical Vapor Decomposition, which is very well known as called as CVD process.

Then Co-Pressing then Co-Sintering or Dip-Coating. A Dip-Coating is a process which is widely used in the laboratory scale to prepare inorganic membranes.

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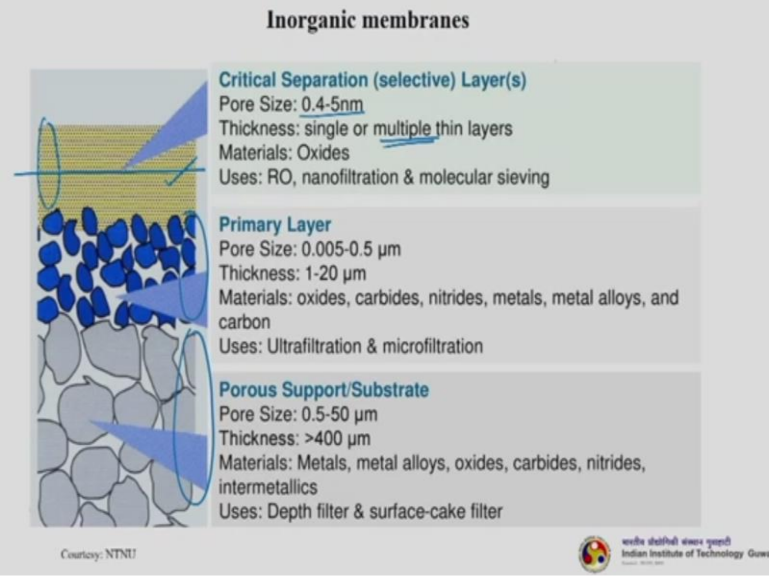

So, let us again understanding this structure and the details of inorganic membrane. So, this is a 3 layer inorganic membrane where the top layer the yellow part. So, this is doing the critical separation that is a selective layer. So, the Pore Size is usually 0.4 to 5 nanometer. So, thickness it can be single it can be of multiple. So, please remember this is also very important. So, this layer we can have a 2 layers also or we can have a single layer also. Usually the oxides are being use as the materials.

So, the uses are in Reverse Osmosis, Nanofiltration and molecular sieving. Then the primary layer this layer here the Pore Size 0.005 to 0.5 micron, thicknesses usually 1 to 20 micron. So, various oxides, carbides nitrites, metals, metal alloys, even carbon are being used, so the uses are ultrafiltration & microfiltration, then this is the core support usually mostly it is microfiltration range. So, 0.5 to 50 micron, thickness is greater than 400 micron, materials or metals, metal alloys and all these things, it is just the uses Depth filter and surface-cake filter because it is a quartz filter.

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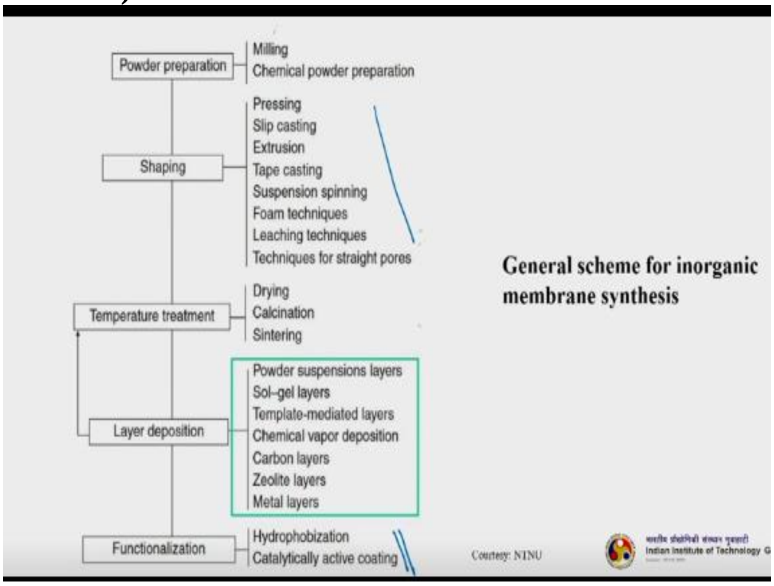

So, this is the general scheme for inorganic membrane synthesis. So, the first one is powder preparation, then there can be shaping under shaping you have different techniques you can see here there are so, many different techniques listed here pressing, slip casting, extrusion, leaching and all these techniques can be used to do the shaping. Then we go for the temperature treatment. So, under that it can be dried then it can be calcination at high temperature and sintering even more high temperature.

Then we comfort once this is done. So, you get a porous best layer so, then you go put the layer deposition to make it more as symmetry. So, here you have so many techniques layer, powder suspension layer, sol-gel layers, template-mediated layers, CVD then we can have carbon layers, zeolite layers some metal layers then finally functionalization that means, if you are looking for a hydrophobic membrane preparation.

And the membrane itself is not getting hybrid hydrophobic you can impart some functional groups or hydrophobic groups to the membrane surface even the pores also. So, or otherwise if you want to make a catalytic membrane, so, you can impregnated some catalyst on the surface of the membrane as well as in the pores of the membrane. So, these are finishing memory techniques functionalization processes, which are required to modify that membrane.

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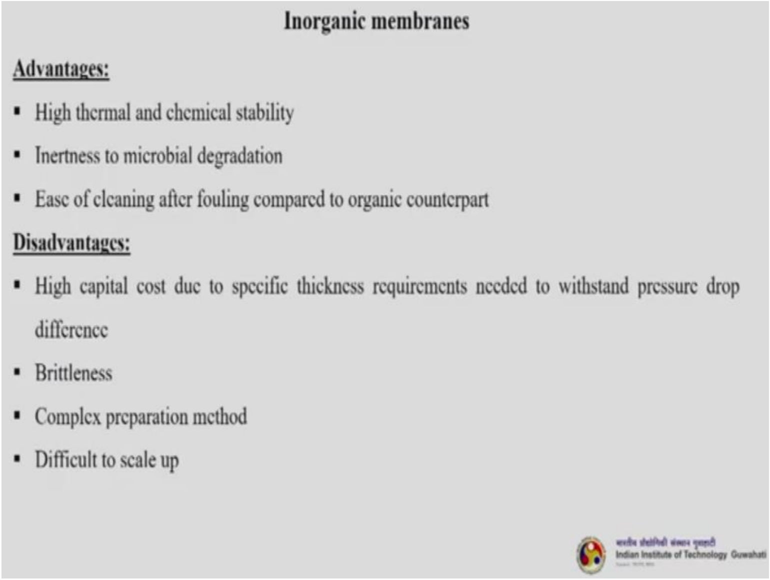

So, the advantages and disadvantages of Inorganic membranes. So, advantage this we have discussed earlier that it is high thermal and chemical stability. Inertness to microbial degradation the cleaning is very easily done, because fouling compared to the organic counterpart in our polymeric membranes, which are more attached to the surface by virtue of the charges. Here it can be clean easily.

The disadvantages high capital costs due to specific thickness requirements needed to withstand high pressure drop dependence cost is always a better when you talk about it inorganic membranes brittleness is another problem, complex preparation method and difficult to scale up. So, these are the subject of the disadvantages which are associated with inorganic membranes now, nevertheless inorganic membranes due to their high thermal and chemical stability and easy of cleaning or gaining actually a lot of pattinson in industrial applications over the various industrial applications.

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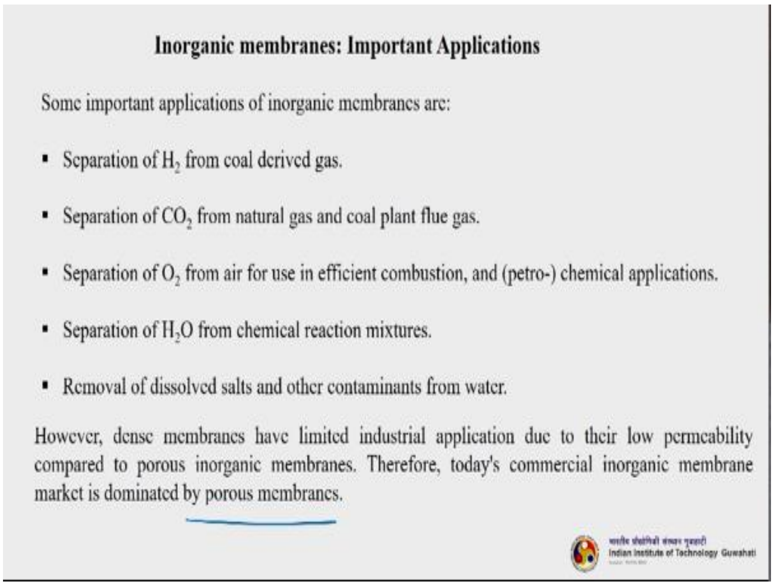

So, some of the important applications of inorganic membranes which I have listed here are separation of hydrogen from coal derived gas, then separation of carbon dioxide from natural gas and coal plant flue gas, separation of oxygen from air for use in efficient combustion or petrochemical applications. Then separation of water from chemical reaction mixtures, removal of dissolved solids salts and other contaminants from water.

Now, however, dense membranes have limited industrial applications due to their low permeability compared to the porous in inorganic membranes. Therefore, today's commercial inorganic membranes are all mostly they are dominated by the porous membranes.

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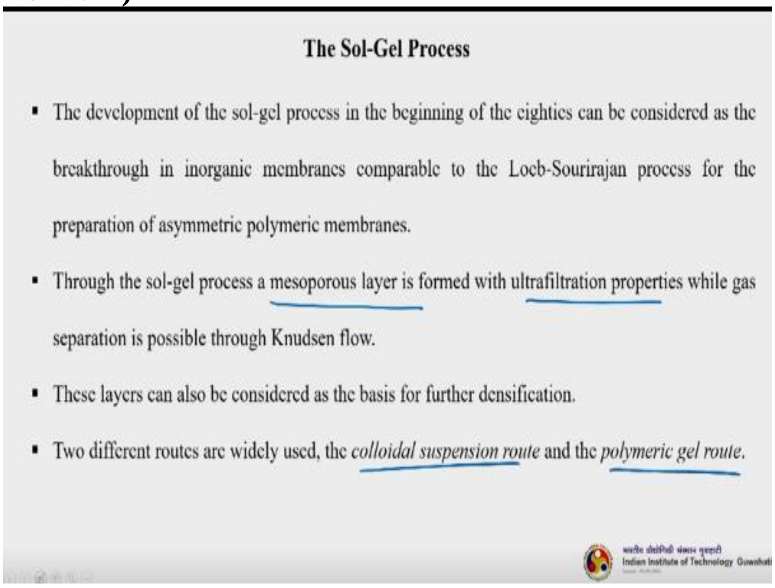

Now, let us discuss the classic sol gel process. Now, the development of sol-gel process in the beginning of 1980s is one of the most important breakthrough in membrane science and technology. So, this was started this started with the Locb-Sourirajan process, for the preparation of the asymmetric polymeric membrane. Now, today we are having huge commercial applications of ceramic membranes.

And there are so many companies who are making ceramic membranes is worldwide manufacturers in India also have so many membranes and manufacturers who are preparing ceramic membranes on a commercial scale. So, you can understand that their scope is become very wide and they are being adapted in spite of their initial cost is high. So, the sol-gel process is a mesoporous layer is through sol-gel process, a mesoporous layer is formed with a ultrafiltration properties, while gas separation is possible also using Knudsen flow.

These layer can also be considered as the basis for further densification that means, once we get some membrane using our sol-gel process, further we can densify it using Vapor Deposition. To achieve certain target oriented separation and 2 different routes are widely used one is called colloidal suspension route another is called the polymeric gel route.

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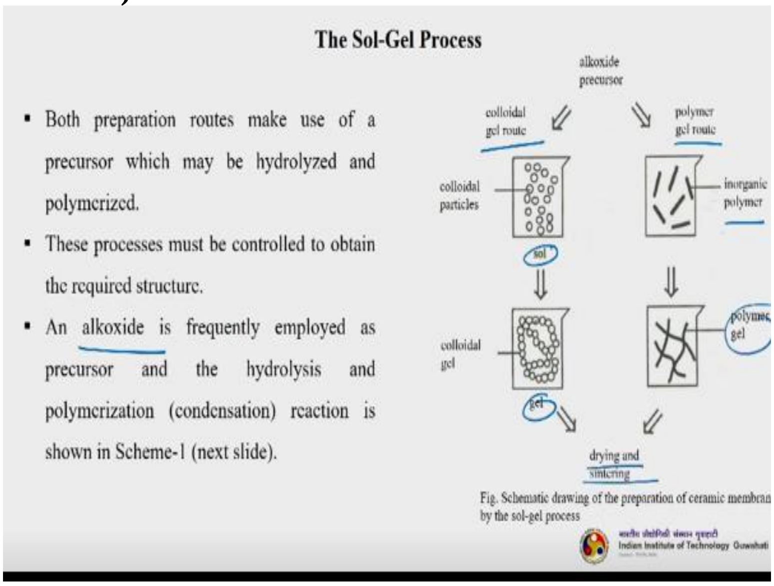

So, let us now understand when a schematic representation how this looks like actually, so, usually both the processes both the routes physically, so, make use of a precursor. So, the precursor is usually alkoxide. So, what has been done with the precursor is that initially they it will be hydrolyzed then it will be polymerized so 2 step processes physically. So, either you go for a colloidal gel route or you can go for a polymeric gel route.

So, you are hydrolyzing both so, these processes needs to be controlled. So, many process parameters are there actually the pH has to be controlled the temperature so, many other things are also there. So, that we are not going to discuss in detail. So, in an brief will try to understand how the sol gel process actually happens. So, usually the alkoxide as I told alkoxide is used that is the precursor then it is hydrolyzed and then it polymerized.

So, you can see how this routes actually happening. So, here preparing is sol here we are preparing a inorganic polymer. So, then followed by sol we get a gel here, this is a polymer then here we also get a polymer gel then it goes for drying and sintering.

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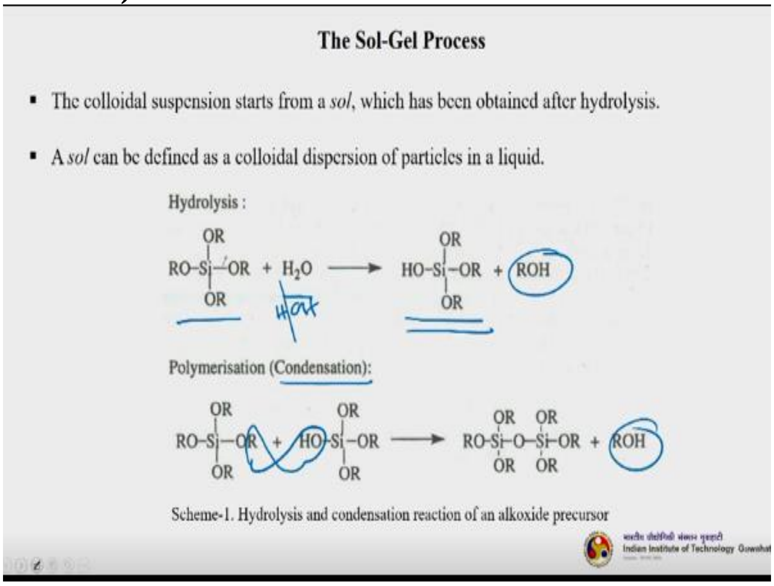

See that let us see the reaction actual then it is easy to understand. So, the colloidal suspension starts from a sol, which has been obtained after hydrolysis. A sol can be defined as a colloidal dispersion of particles in a liquid. Now this is an alkoxide and it is hydrolyzed. So the OH from here you can write like this. So, what we can understand from this particular reaction is this so OH is reacting with one of the R and forming ROH.

And then this is one of the monomer that is found for the further polymerisation reaction in the hydrolysis reaction. Now this monomer will react to with other monomers at the same type and eventually we will start the polymerisation reaction we can call it a condensation reaction you will see that again here we are getting one ROH like this. So we get ROH here. So, this is 2 step reaction hydrolysis and Condensation and open alkoxide precursors.

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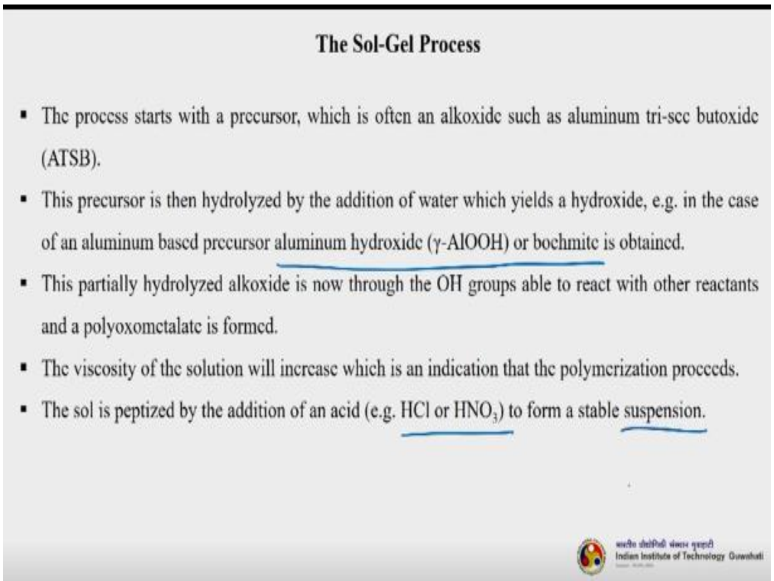

So, the process starts with a precursor, which is often a aluminum tri-sec butoxide, it is called actually ATSB. Now this precursor is hydrolyzed by addition of water which yields a hydroxide for example of an aluminum based precursor aluminum hydroxide or bochmite is obtained. So, that is actually the monomer that we get and after that the polmersation reaction starts. So, this partially hydrolyzed alkoxide is now through the OH groups able to react with other reactants and a polyoxometalatc is formed.

Now, the viscosity of the solution will increase which is an indication that the polymerization is started. Now, the sol peptized by the addition of an acid to form a stable suspension.

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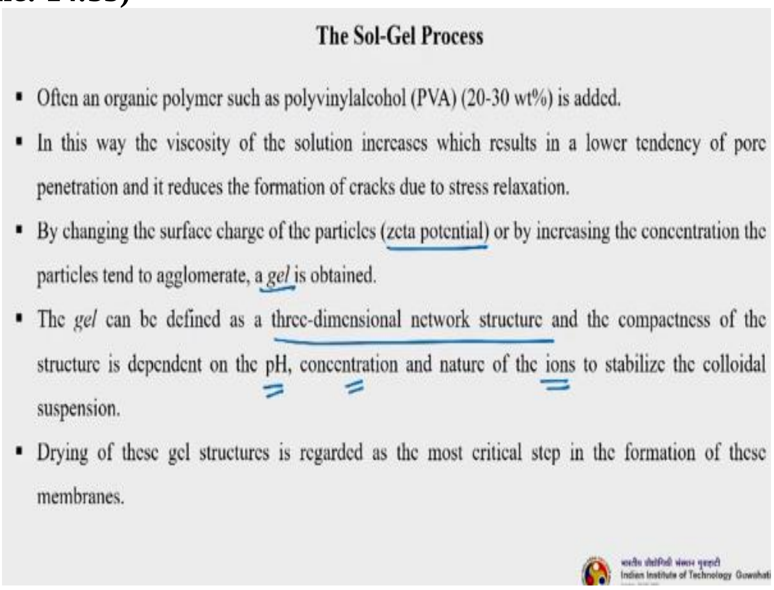

Often an organic polymers such as polyvinyl alcohol usually 20 to 30% is added. Now, in this way the viscosity of the solution increases which results in a lower tendency of pore penetration and it further reduces the formation of cracks also due to stress relaxation. Now, by changing the surface charge of the particles that is the zeta potential or by increasing the concentration of the particles tend to agglomerate, a gel is obtained.

So, you are getting gel by 2 ways either polymeric or through the colloidal route. So, gel can be defined as a 3 dimensional network structure and the compactness of the structure is dependent on the pH, concentration and nature of the ions to stabilize the colloidal suspension. I was telling you in the previous to previous slide that there are so many other parameters which also affect this sol gel process.

So, pH is one of the most important parameter apart from that the concentration of the molecules and the nature of the ions that stabilize the colloidal suspension. Then, drying of the gel structure is regarded as the most critical step in the formation of these membranes. Because, if the drying is not proper, then the membrane will be will get disrupted membrane.

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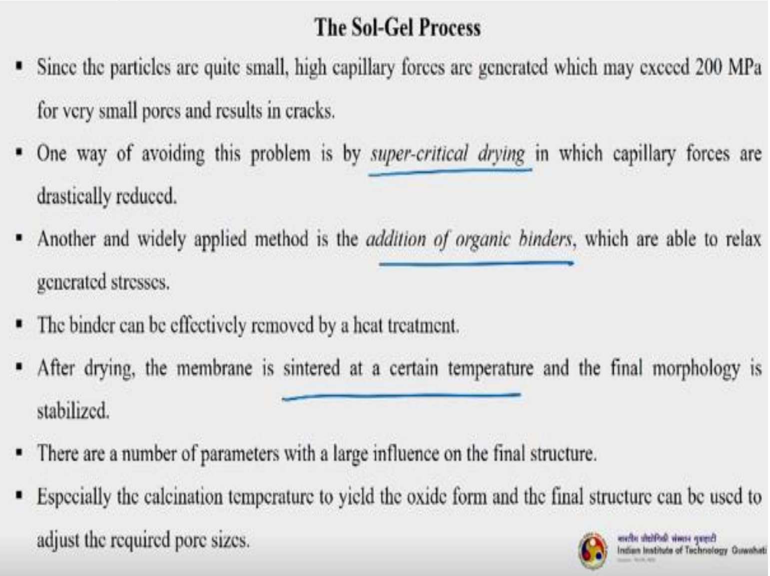

Since the particles are quite small, high capillary forces are generated, which may exceed 200 Mega Pascal for very small pores and results in cracks. So, this is what we do not want our intention is always to avoid that cracking during drying. So one way of doing this is super-critical drying. But you know, those of you understand what is super critical, you may know that any super critical process whether it is the external, whether it the drying.

Whether it is the extraction, it is an extremely costly process, because of the initial capital costs involved in that, though, it is one of the most excellent or you can say the excellent technology. However, the cost makes it very difficult to be adapter in a small scale. So, in large scale industries, people are using supercritical drying because the initial investment is very high. And so, they can report small scale industries it is very difficult to adapt.

So another and widely applied method is additional organic binder. So, this is one of the easy way to do that a cheap actually a proper drying steps. So what is being done is that you add some organic binders organic some organic components. Now, they will relax the polymer in such a way that the polymer can withstand the high stress which is getting generated during the drying.

Now, what will happen to these binders now, these binders you can effectively take it out by a suitable heat treatment process? So, after drying the membrane is sintered at certain temperature and the final morphology is stabilized. So sintering as you know have discussed sintering. Sintering is a process in which the material is being heated to elevated temperature set this sintering during this sintering whatever binders are being added to the polymeric matron will all go away basically evaporated you can say.

So, there are a number of parameters with a large influence on the final structure especially the calcination temperature to yield the oxide form and the final structure can be used to adjust the required pore sizes.

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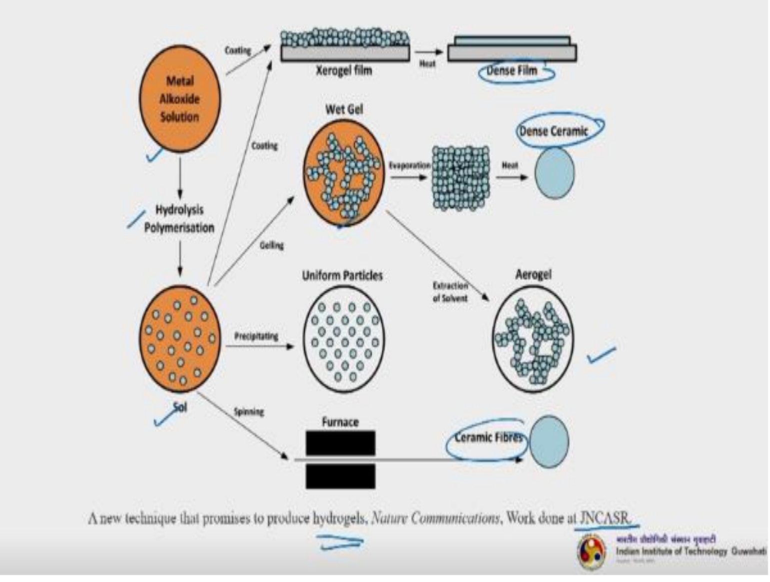

So, this is one of the recent publication by the group in JNCASR in Bengaluru. So, it was published in nature communication. So this technique was proposed to produce hydrogels.

Now, why I am showing this you that because ceramics also can be prepared using this is very wonderful process. So you have metal alkoxide solution here, you Hydrolysis them polymerization process then you get a sol from the sol you can prepare a dense film.

The usual coating processes you go for a gelling or gel process. So, you get wet gel then you evaporate then you go for a heat treatment and you get a dense ceramic membrane. From the sol again precipitating it, you get uniform particles. You spin it and use some thermal treatment you get ceramic fibers. From the wet gel after extraction of the solvent you get Aerogel. So, this is one of the very good technology or process that was proposed by this particular group.

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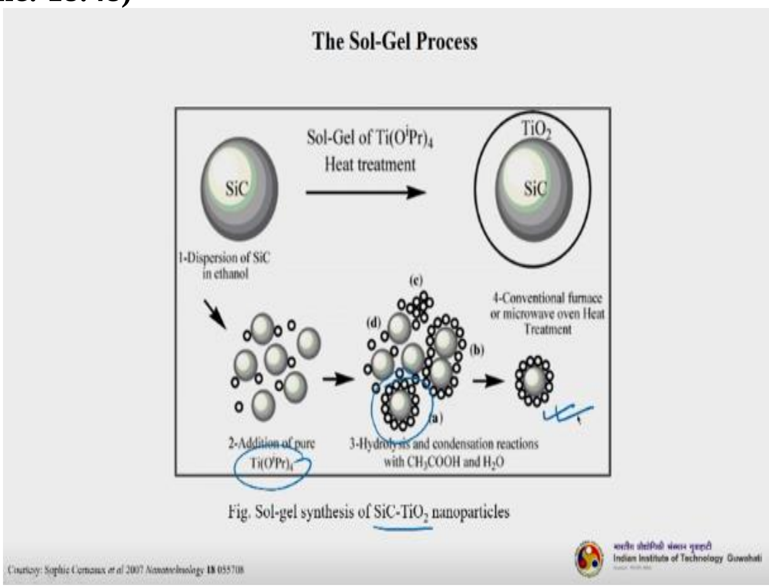

This is one of the classic example of the Sol-gel process and to prepare the silicon carbide and titanium dioxide nanoparticles. So you can see the silicon carbide is actually dispersed in eternal. Then after heat treatment addition of pure titanium is added to this silicon carbide, then you can see how they are forming structures here. So hydrolysis and condensation reactions with acidic acid and water. So, we get a stable form of nanoparticles here.

So, then you can go for a conventional combination of microwave oven treatment and you get a silicon titanium oxide coated silicon carbide.

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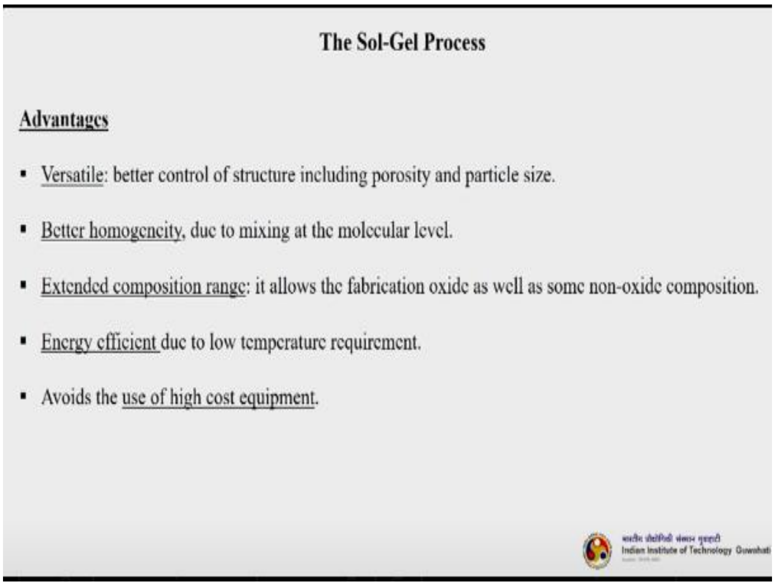

So, the advantages of sol gel process is that it is versatile. So, better control of structure including porosity in particular size can be possible with the using the sol-gel process. Better homogeneity also due to mixing at the molecular level. Extended composition range so, it allows the fabrication oxide as well as some non-oxide composition energy efficient due to low temperature requirement and avoid the use of high cost equipment. So, in the last class also it can be done easily.

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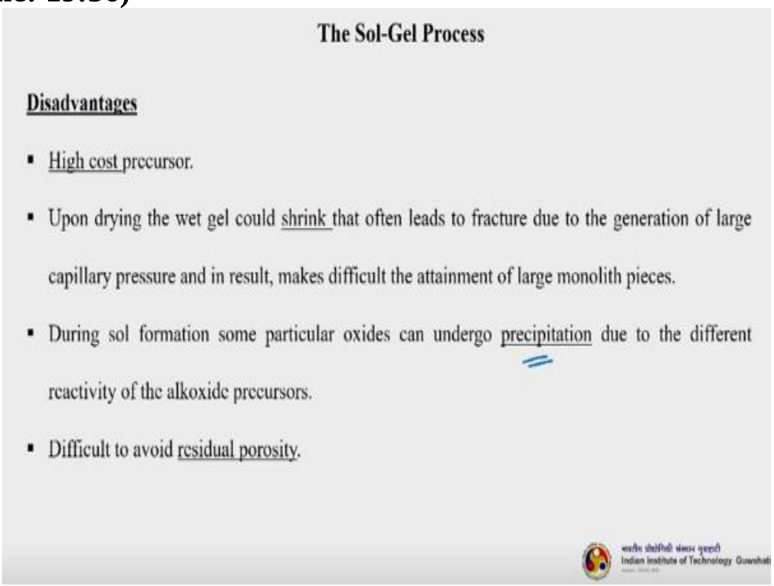

However, there are certain disadvantages also. So, disadvantages the high cost of the precursor the precursors, usually which are used alkoxide they are costly. So upon drying the gel would shrink. So, as we already discussed that drying is one of the most critical steps to found this type of membranes. So, when shrink it often leads to capture a development of the cracks inside the membrane due to the capillary pressure.

And during sol formation some particular oxides can undergo precipitation. So, this is another disadvantage during the sol-gel process. So, but it do not happens for every alkoxide few precursors undergo this type of process, but they can be dealt with carefully so, that this will not happen and difficult to avoid residual porosity also.

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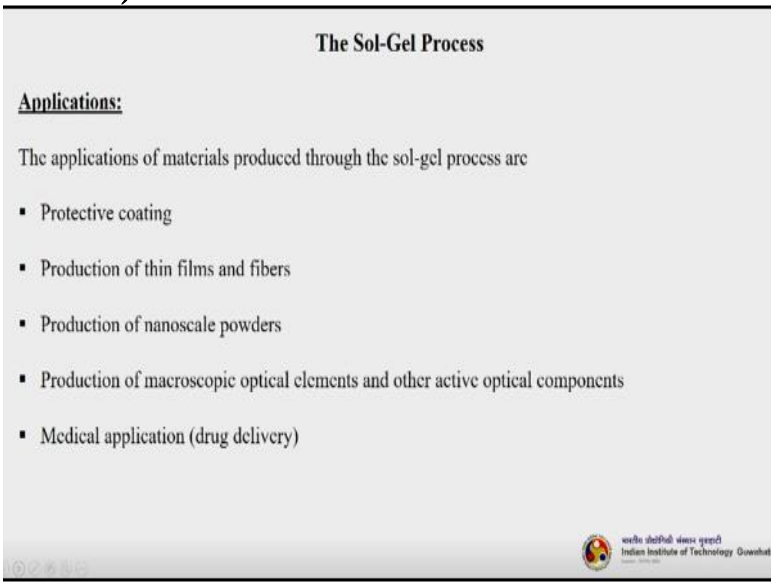

So, applications are protective coating, production of thin film and fibers, production of nanoscale powders, production of macroscopic optical elements and other active optical components and medical application that is especially in drug delivery.

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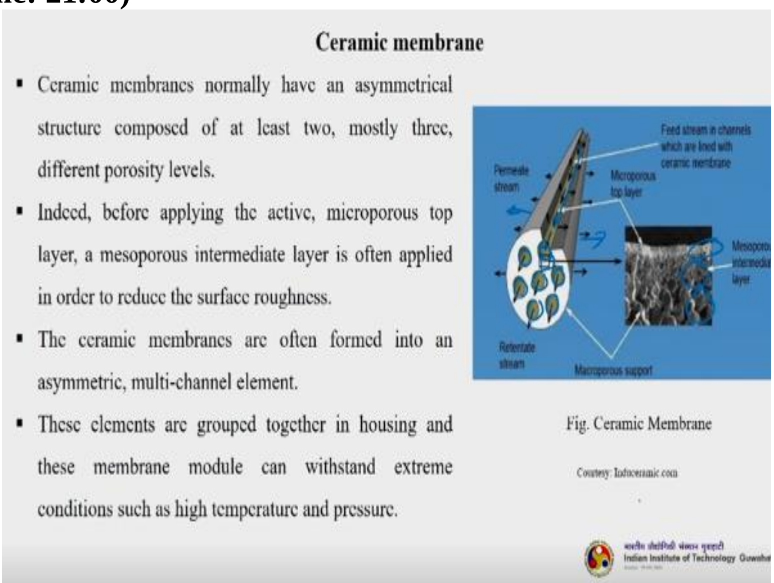

Now students let us understand the preparation of ceramic membrane. Ceramic membranes normally have an asymmetrical structure composed of at least 2 or mostly 3 different porosity levels or distinct levels. So, indeed we are applying the active micro porous top layer, a mesoporous intermediate layer is often applied in order to reduce the surface roughness. But the ceramic numbers are often formed into an asymmetric, multi-channel element.

These elements are grouped together in housing and this membrane model can withstand extreme conditions such as high temperature and pressure. Now, in this particular figure, you can see a ceramic membrane you can see similar type of structure here. So you are seeing so many holes here actually these are here membranes and these are the lumens through which your feed will flow speed is flow.

You can see the speed is flowing here and the permeate is out from the overall memory sticks. If you consider the pen, something like this you can imagine there are holes here. Through the speed will flow and the permeate will come from the outside of this membrane from all across the membrane all the surface area. So, you can see a scanning electron micrograph of a particular section here, one of the lumen here to a section of a lumen small section.

We can see distinctly as you can see, this is one layer, this is another layer, this is another layer. So, this tells us that house around 7 million membrane are actually preparing how they look like.

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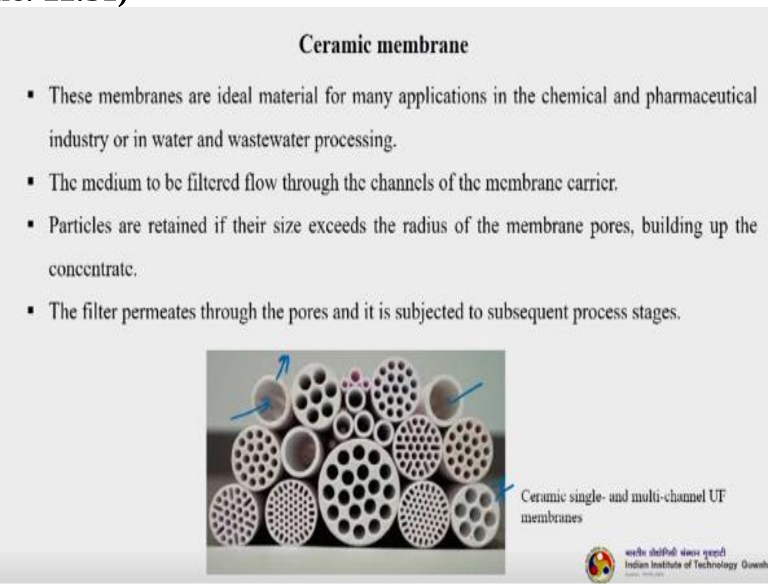

So, these membranes are ideal material for many applications in chemical and pharmaceutical industry are in water and wastewater processing. The medium to be filtered flow through the channels of the membrane carrier. So, these are this is what see this is a single lumen, you can see this is a single lumen ceramic membrane, you can see here, this is 1 2 3 4 5 6 7. This is 7 lumen ceramic membranes. Membrane so here these are multiple also.

So, the medium to be filtered through a flow through the channels of the membrane. So, you feed actually flows through this and the permeate will be out from the surface of the membrane. So, a particles are retained if their size exceeds the radius of the membrane pores and that is building up the concentrate and the filter permeates through the pores and it is subjected to sol-gel subsequent process stages.

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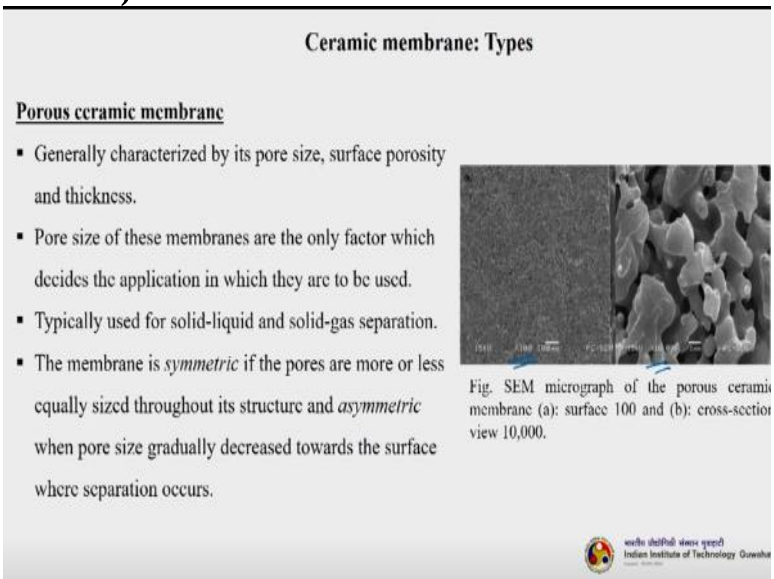

So, the different types of ceramic membranes. The first one is the porous ceramic membrane. So, generally characterized by its pore size, surface porosity and thickness. So pore sizes of these membranes are the only factor which decides the application in which they are to be used. Typically used for solid-liquid and solid-gas separation. The membrane is symmetric if the pores are more or less equally sized throughout its structure and there will be asymmetric when pore size gradually decreased towards the surface where the separation occurs.

So, you can see a scanning electron microscope of the porous ceramic membrane. So, this is a 100 magnification and this is a 10,000 magnification and you can see how beautifully we can see the membrane materials there and the pore also.

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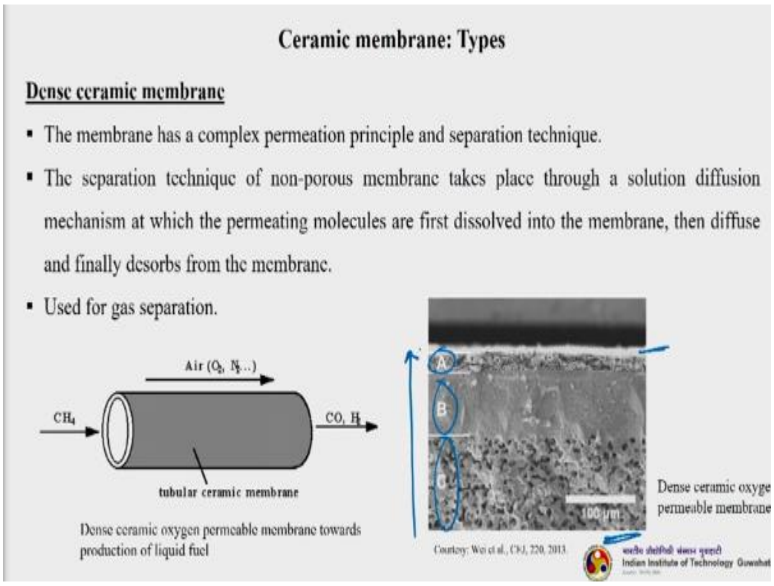

Then the next is the dense ceramic membranes. Now, the membrane has a complex permeation principle and separation technique. The separation technique of non-porous membrane takes place through a solution diffusion mechanism at which the permeating molecules are first dissolved into the membrane and then diffuse and finally desorbs from that membrane. So, these are extensively used for the gas separation.

Application developers unless there are other applications also you can see here, this particular scanning electron microscopy image tells you that there are 3 distinct layers A, B and C. And as you know that as you move from bottom, this is the bottom, then this is the top so, as you move from bottom to top, your pore size decreases.

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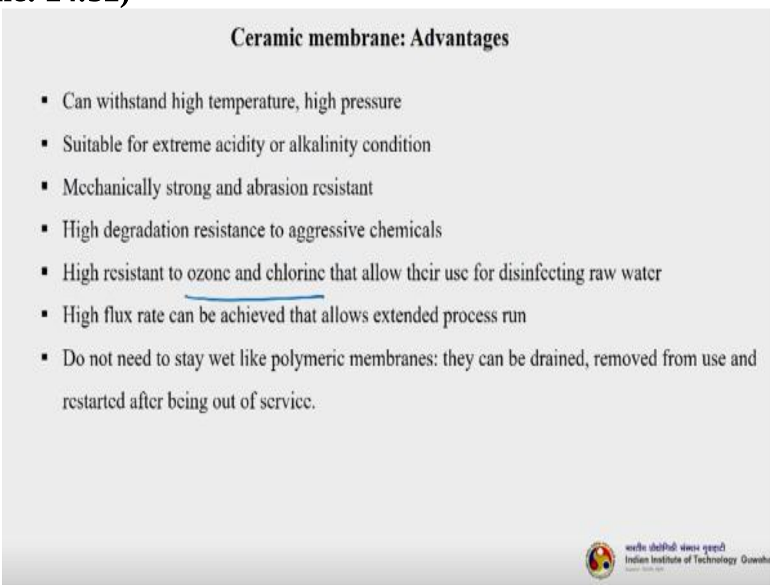

So, the advantages of ceramic membranes they can withstand high temperature, high pressure. Suitable for extreme acidity and alkalinity condition. Mechanically strong and abrasion resistance. High degradation resistance to aggressive chemicals. High resistance to ozone and chloric this is also very important when you use these numbers for water and wastewater treatment and high flux rate can be achieved that allows extended process runs.

And do not need to stay wet like polymeric membrane. So, we do not see you know, once you use a polymeric membrane and you need to keep it in wait condition otherwise we wants the pores will become dry then it will not do give the proper targeted separation when you are going to use it for the next row. So, but the such things do not happen for your organic membranes. If you are using a busy beggar becomes dry also nothing will happen to them.

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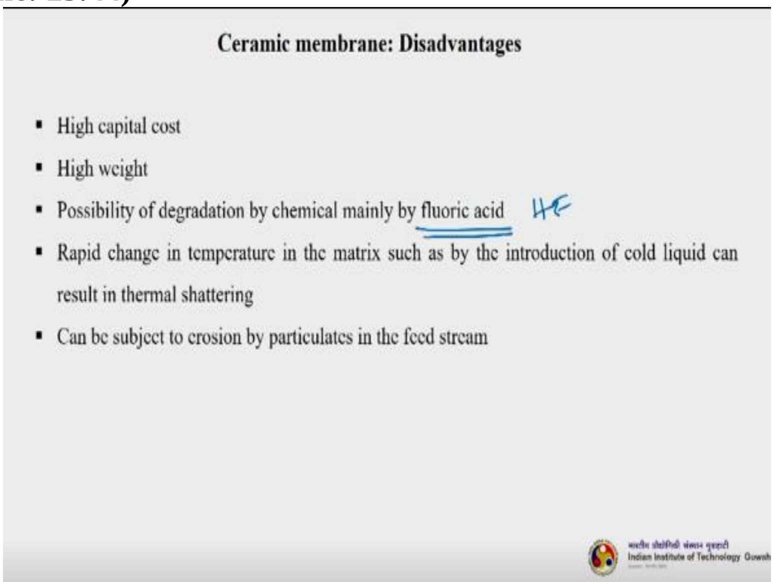

Again disadvantages is the happier we have been discussing this actually high capital costs weight is a big problem. So weight is a problem that is my caring and transportation is also problem. So possibility of degradation by that the HF hydrofluoric acid. So, if you are somewhere here using it where hydrochloric acid is there, then they will slowly try to degrade. So rapid change in temperature the matrix such as the introduction of cold liquid can result in thermal shattering and so, this is a disadvantage.

So, what is the meaning of this suppose, I am using the ceramic membrane for a thermal process in which let us set the temperature is 200, 200 or 300 series . So, I have used one which is over then suddenly to clean it I push cold water inside that, so, that means the membrane which is at a limited temperature suddenly get a cold thermal shock and the reverse also may happen from cold application to very high to liquid and this one cleaning application.

So, they cannot tolerate the thermal socks so, and they are very brittle. And another one problem is that there can be subjected to erosion by particulates in the feed stream.

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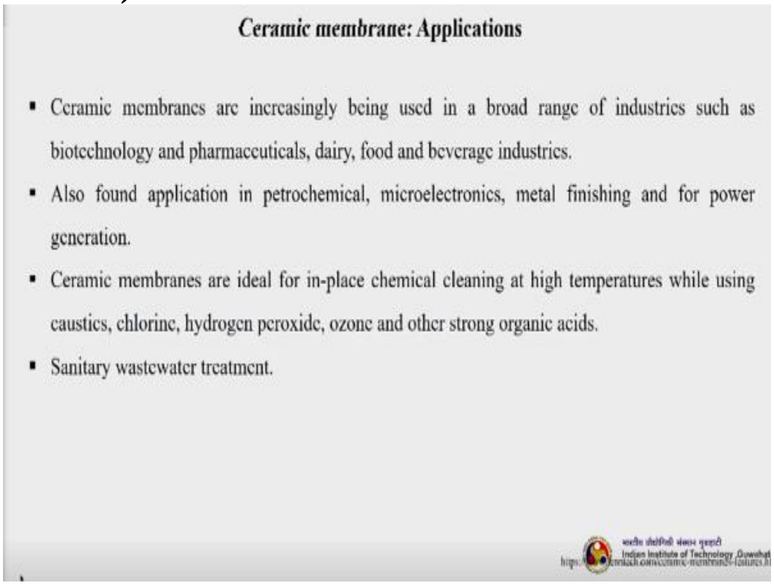

So, the applications are being used in broad range of industries such as biotechnology, pharmaceuticals, dairy, food and beverage industries. Also found application petrochemical, microelectronics, metal finishing powder and power generation. Ceramic membranes are ideal for in-place chemical cleaning at high temperatures while using caustics chlorine, hydrogen peroxide, ozone or other strong organic acids. Sanitary waste water treatment so, they are being used.

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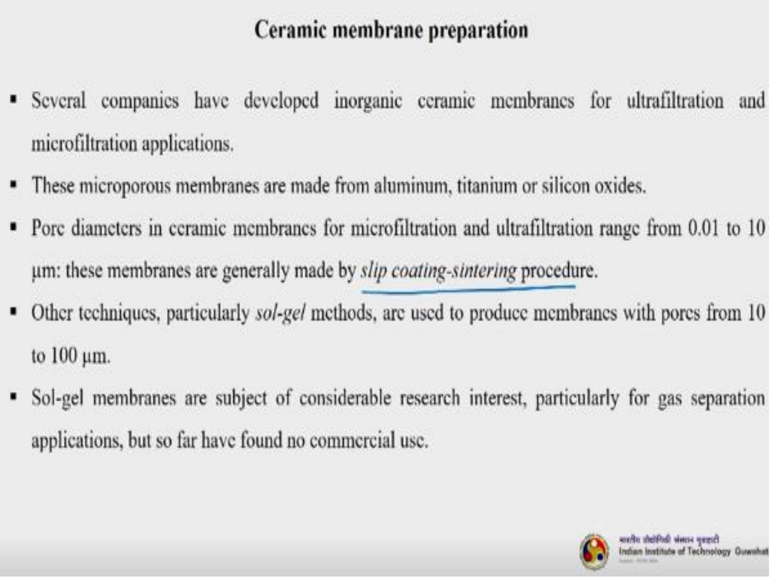

Several companies have developed inorganic ceramic membranes for ultrafiltration and microfiltration applications. Now, these microporous membranes are made from aluminum titanium or silicon oxide. Now, please note that there are many other components also from which we can prepare our inorganic or ceramic membranes. It is not that every ceramic membrane said prepare from aluminum, titanium, silicon, oxide or zirconia not that or other materials also.

So pore diameter in ceramic membranes for microfiltration and ultrafiltration range from 0.01 to 10 micron. These membranes are generally made by the slip coating-sintering procedure will discuss this. So, other techniques particularly the sol-gel methods are used to produce membranes with the pores from with the pore size from 10 to 100 micron. Sol-gel membranes are subject of considerable research interest, particularly for gas separation applications, but so far have found no commercial use.

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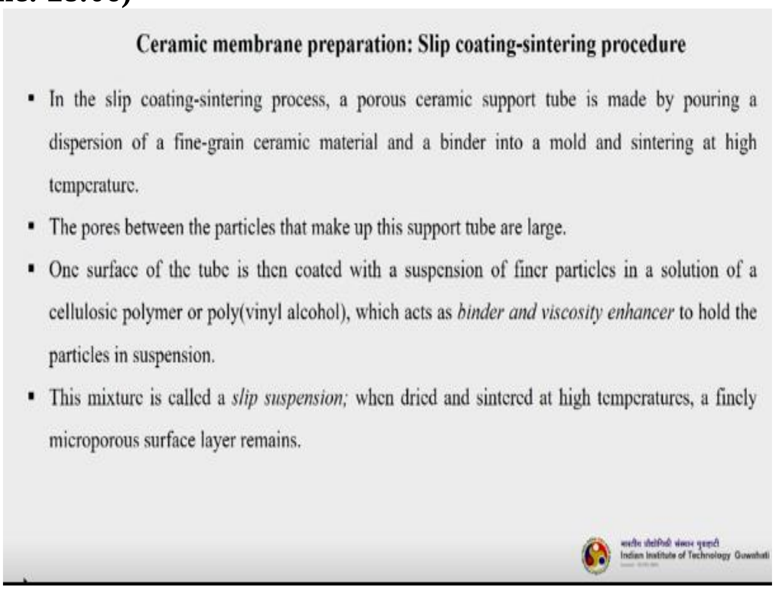

Let us understand what is the slip coating-sintering procedure to prepare ceramic membranes? Now, in the slip coating sintering process a porous ceramic support tube is made by pouring a dispersion of fine-grain ceramic material and a binder to a mold and sintering at high temperature. The pores between the particles that make up this support tube are large. One surface of the tube is then coated with the suspension of finer particles in a solution of cellulosic polymer or poly (vinyl alcohol).

Which excess wind and viscosity enhancer to hold the particles in suspension? This mixture is called a slip suspension when dried and sintered at high temperature, finally, a micro porous surface layer remains.

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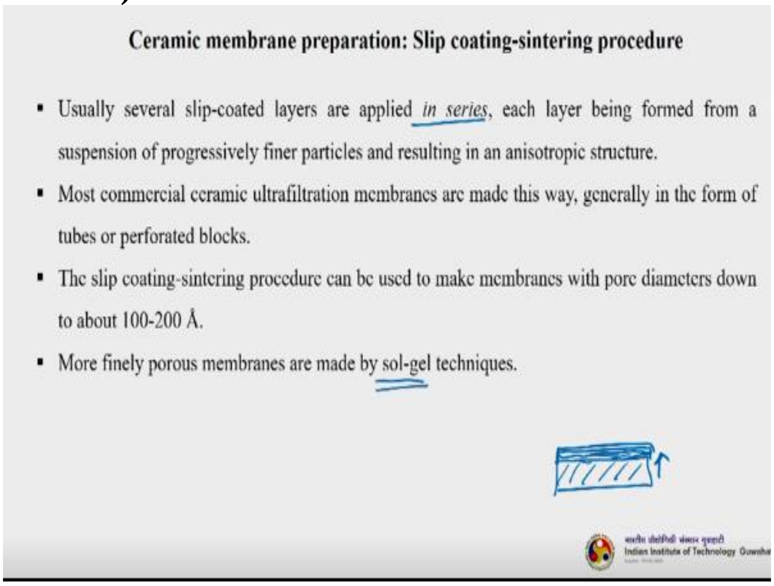

Usually several slip-coated layers are applied in series. So, one by one. So, once we have membrane like this, with some structure, then we go for another slip-coated membrane with some structure like this. Then we can have another theme layer. So gradually as we increase from bottom to top, the thickness of the layers of supports actually decreases. So, most commercial ceramic ultra-filtration membranes are made by this way generally in the form of tubes or perforated blocks.

The slip coating-sintering procedure can be used to make membranes with pore diameter down about 100 to 200 angstrom. More finely porous membranes are made by sol-gel technique. So, you cannot prepare very fine membranes using the slip coating-sintering procedure.

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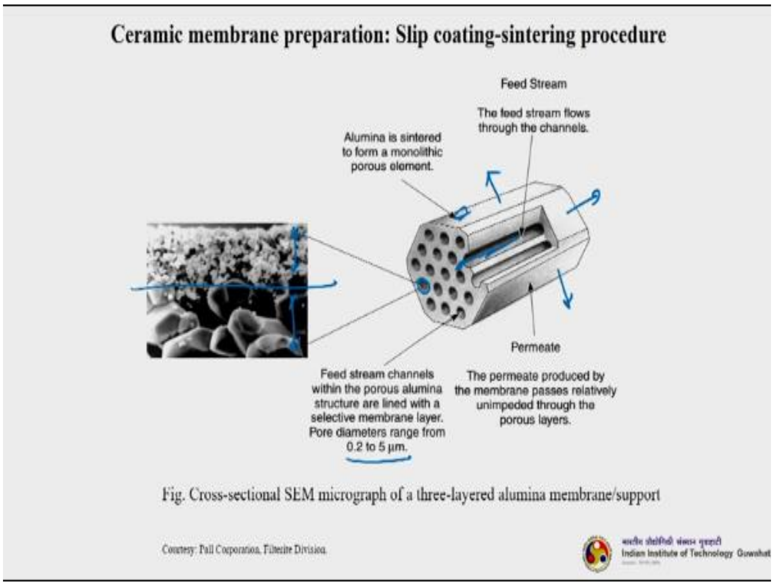

You can see this figure up the ceramic membrane which is prepared using this slip coating-sintering procedure here the alumina which is sintered to form monolithic porous element and here the feed is flowing, this is the lumen you can call it the lumen through which other channels many people call it channel through which feed stream flowing permeate is coming out from here in this direction.

We are also so feed stream channels within the porous alumina structure are lined with a selective memory layer. So here you can see this is the one skilling electron micrography shown here. So, you can see there are 2 distinct layers here. So, one is alumina structure there. So, about that there is another membrane layer which is deposited physically the pore diameter is 0.2 to 5 microns. So, this is one layer, this is another layer.

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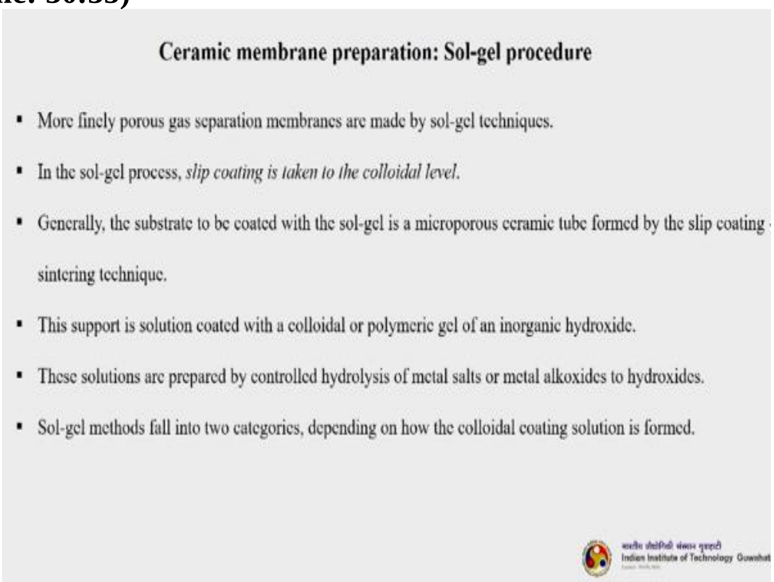

So, let us understand how the ceramic membrane can be used to prepare by sol-gel process we have already discussed in today's class also. So, just quickly again go through the sol-gel process, for preparing ceramic membranes. So, for finely porous gas separation membranes by sol-gel technique is actually used. So, slip coating is taken into the colloidal in the sol-gel process initially, a slip coating is taken to the colloidal level than the usual sol-gel process starts.

Generally, the substrate to be coated with the sol-gel is a micro porous ceramic tube formed by the slip coating-sintering technique that means, so here the sol-gel process is one of the finishing process. So, what is happening when you are going for a sol-gel procedure, you already have a tubeless ceramic membrane which are prepared by the slip coating methodology. Now, further we are going to densified the supporting solution is coated with a colloidal gel or polymeric gel of an inorganic hydroxide.

These solutions are prepared by controlled hydrolysis of metal salts or metal alkoxide or hydroxides. Sol-gel methods fall into 2 categories, depending upon how the colloidal coating solution is formed

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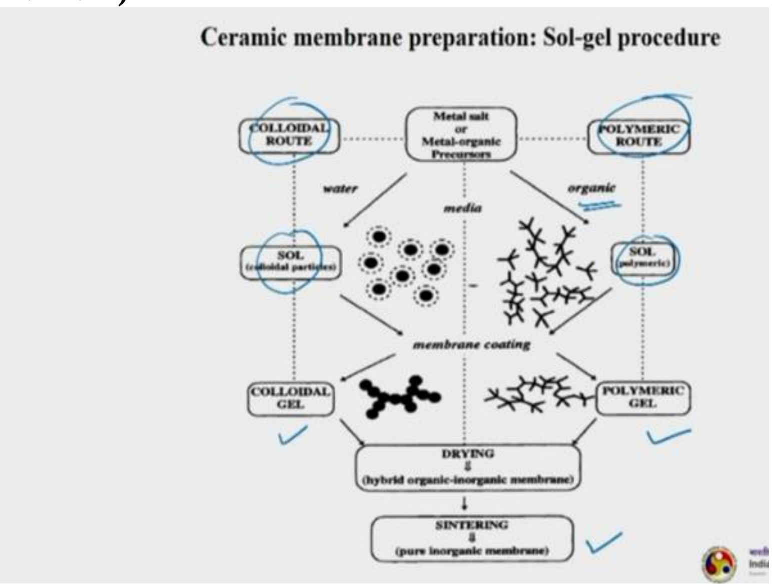

The usual route we discussed the colloidal route and the polymeric gel route so metal salt or metallic organic precursors is being used. So you used water then you get this sol or colloidal particles using some organic gel you get the polymeric salt. Then you get a colloidal gel here we get polymeric gel then after that you go for your finishing processes such as drying. So, you can go for a supercritical drying then add some other processes. Then finally as sintering method in this sintering what about the binders are being added here will mostly they will evaporate.

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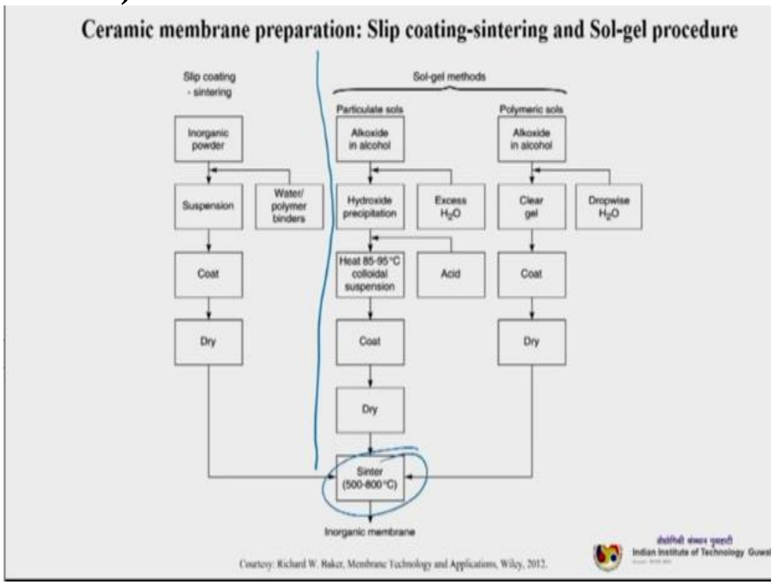

So, this is a slip coating sintering and sol-gel procedure to prepare ceramic membrane this is the flow seat basically. So, you can see this you are preparing this is a 2 distinct process actually you can see till this drying process the slip coating membranes are prepared then both slip coated tubular ceramic membrane. As well as sol-gel tubular ceramic membrane are finally sinter at 500 to 800 degrees centigrade to prepare the final organic inorganic or ceramic membranes

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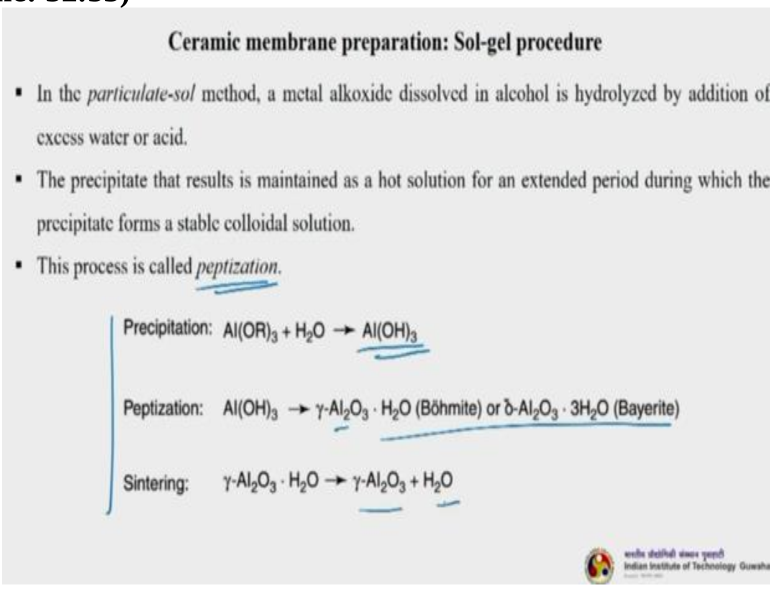

So, in particulate-sol method, a metal alkoxide dissolved in alcohol is hydrolyzed by additional of excess water or acid. So, the precipitate that results is maintained as a hot solution for an extended period during which the precipitate forms stable a colloidal solution.

So, that process is called actually peptization. So, 3 step process here. So, precipitation on oxide a plus water you will get this Bhomite type of molecule then in the peptization you get this Bohmite and Bayerite.

Then the sintering is happening this you can see the gamma alumina water so, you get a gamma alumina plus water here

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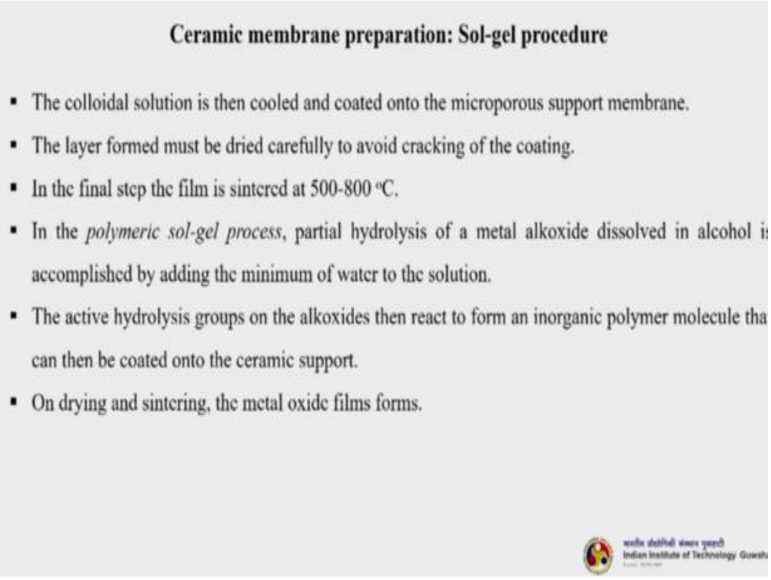

So, the colloidal a solution is then cooled and coated onto the micro porous support membrane. The layer formed must be dried carefully to avoid cracking of the coating. In the final step the film is sintered is usually 500 to 800 degrees centigrade. Depending upon of course, what is the material in the polymeric gel process parcel hydrolysis of a metal alkoxide dissolved in alcohol is accomplished by adding the minimum of water to the solution?

The active hydrolysis groups on the alkoxides then react to form an inorganic polymer molecule that can then be coated onto the ceramic support. On drying and sintering, the metal oxide films forms.

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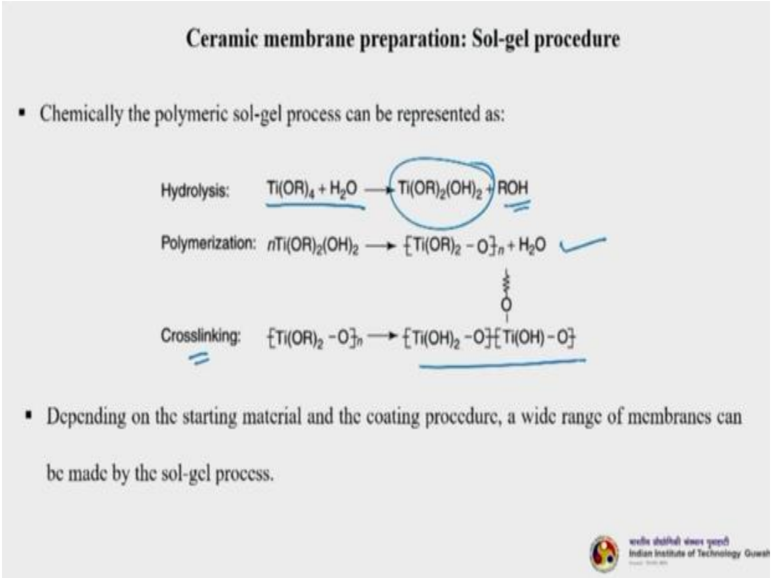

So this is the chemical polymeric soldier process. again the same type of reaction, this is one precursor, they are getting hydrolyzed you see ROH group is formed, then polymerization is happening of this monomer we get a polymer so, to make it more stable, so cross linking reactions are carried out. So you get a crosslink polymer. So, depending on the starting material and the coating procedure, a wide range of membrane can be made by the sol-gel process. This is one of the beauty of this particular process actually.

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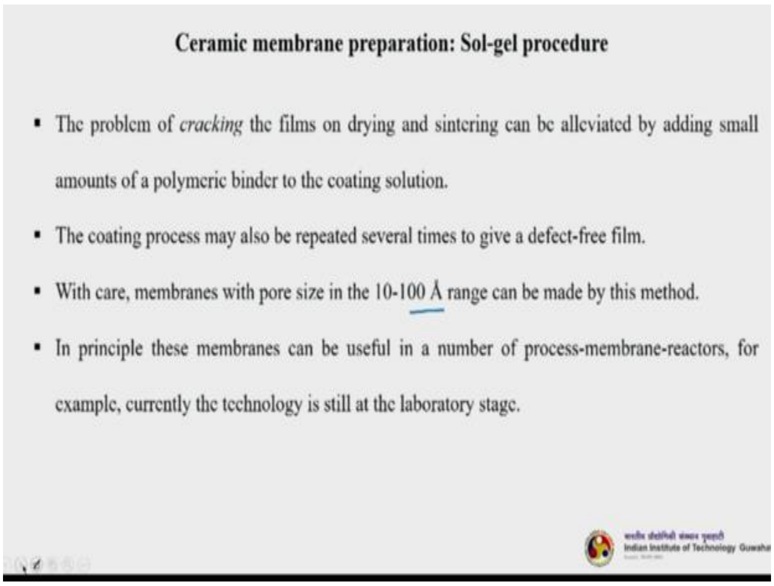

So, let the problem of cracking the films on drying and sintering can be alleviated by adding small amounts of a polymeric binder this we have already discussed, but just again since we are using ceramic membrane, the same procedure is adopted in ceramic membranes also. So, the coating process may also be repeated several times to give a defect free film, but the coating must be as thin as possible. So, that you can go coatings or you can coating series basically.

So, with care membranes with the pore size of 10 to 100 angstrom ranges can be made by this method. In principle these membranes can be useful in a number of process-membrane-reactors, for example, currently the technology is still at the laboratory stage.

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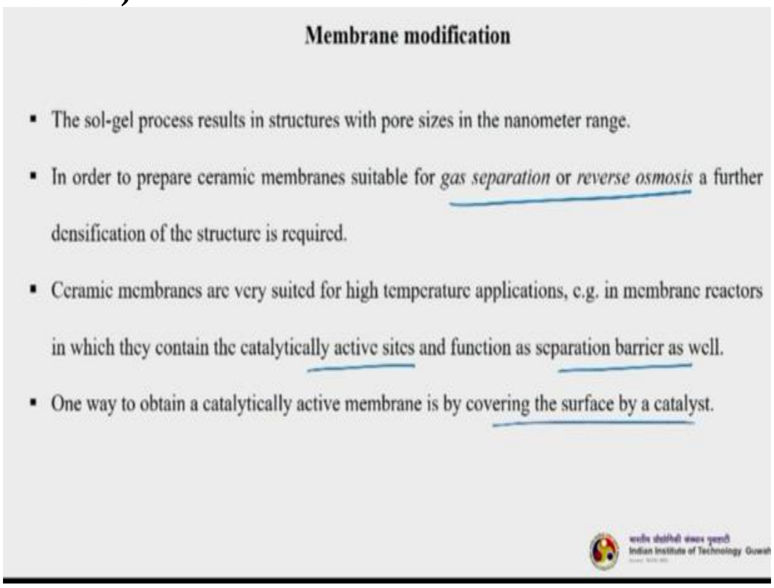

So, next is the membrane modification. So, you know, we need to prepare a membrane for a target oriented separation and in certain cases, we need to import certain functional groups or maybe certain catalysts to make a catalytic membrane to achieve a particular separation or of to carry out certain reactions using the membrane, catalytic membranes, so in that time we need to modify the membrane.

Now, the sol-gel process usually results in structures with pore sizes in the nanometer range. So, in order to prepare ceramic membrane suitable for gas separation application or reverse osmosis application a further densification is required because we need very it may be nonpartisan rates are extremely fine thin narrow ports. So, ceramic membranes are very suited for high temperature applications as per example, in membrane reactors in which the content the catalytically active sites and functional separation very barrier as well.

So, they are doing the job catalyst as well as they are doing this separation also. So, one way to obtain a catalytic active membrane is by covering the surface by a catalyst.

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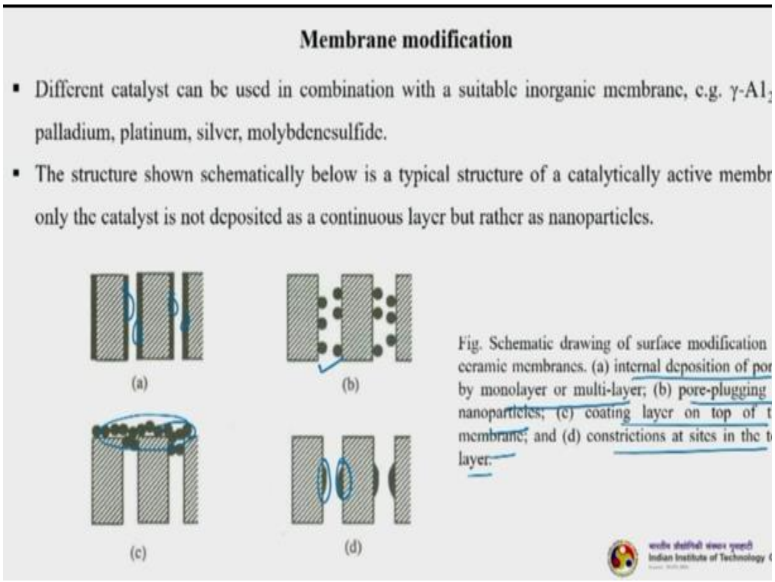

So, this can be done by this particular method you can see how this structure is showing. So, the schematic drying up a surface modification of a ceramic membrane. So, the first one A is the internal the deposition of the pores by monolayer of multi-layer. So, here you see that deposition is happening here. It can be a single layer deposition it can be multilayer. The second is pore-plugging of nanoparticles.

So b, so here extended complete this one layer deposition here the molecule, this one the particles are allowed to be deposited on the surface of inside the pores. Just like this, you can see how it is being happening third one is coating layer on the top of the membrane. So, here coating on the membrane surface and some of the particles may get inside the pores also, and fourth is actually, the latest development here the construction sites in the top layer.

Now, certain particular groups or particles are important or let us say they are deposited inside the pores such as like this, they are forming construction. So, they may be catalyst, they may move some other functional groups. So, the structure schematically below is a typical structure of calculate active catalytically active membrane heard the catalyst is not at all is not only deposited as a continuous layer but there can be deposition of the nanoparticle.

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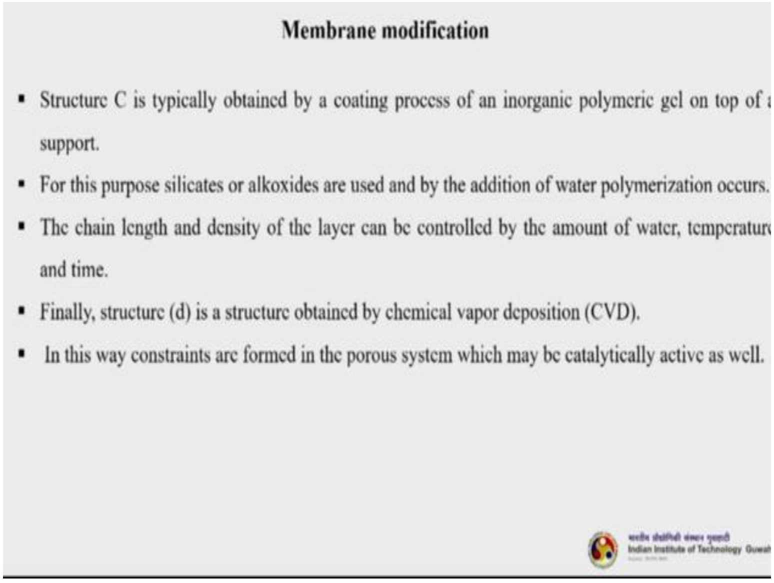

So, structure C is typically obtained by a coating process of an inorganic polymeric gel on the top of a support this one here and for this purpose silicates or alkoxides are used and by the additional of water polymerization occurs. The chain length and density of the layer can be controlled by the amount of water, temperature and time. Finally, structure D which is I was talking about this construction.

So, this is done by chemical vapor decomposition process very distinct sites inside the membrane ports we can deposit this nanoparticles which are also catalytically active. So, in this way constraints are formed in the porous system which may be catalytically active as well.

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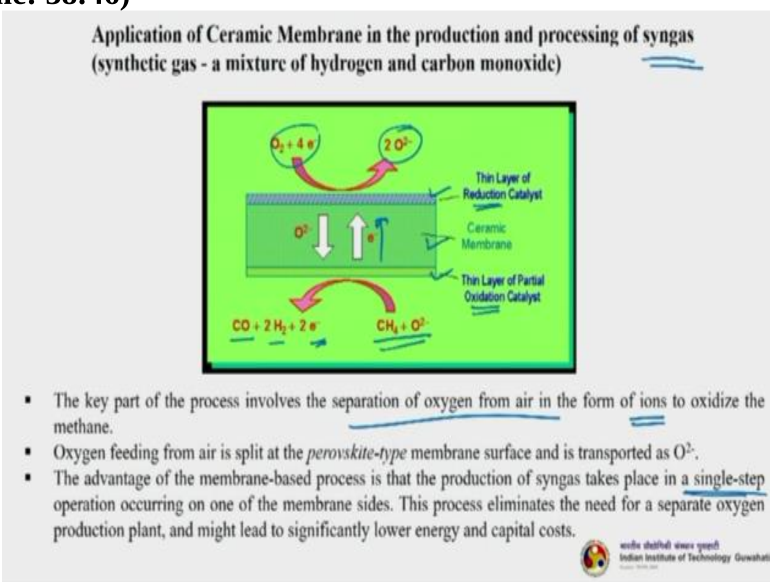

So, finally, let us see one classic example of the application of ceramic membrane in the production and processing of syngas, so you know syngas synthetic gas is a mixture of hydrogen and carbon monoxide. So what is happening you see this is the ceramic membrane here we have 2 layers to this different distinct layers of the catalyst. The first one top layer is the thin layer of reduction catalyst here the here it is a depositors of oxidation catalyst.

2 different types of catalyst are being fused to the membrane, top surface as well as the bottom surface and then what is happening so it is the separation of oxygen from air in the form of ions is being done to oxidize the methane, so how it is happening so, this is a perovskite type of membrane surface and it is when oxygen is coming. When it is getting in touch with the reduction catalyst then it is for me 2 or 2 minus.

So these R 2 minus it is getting diffused to the other side of the membrane and then it is reacting with the methane and thereby heart it is forming carbon monoxide plus 2 hydrogen a plus 2 electrons. Now these 2 electrons are again getting transponent and there again reacting with the oxygen and reducing it 2 or 2 minus continuously this process goes on it is a beautiful technique actually.

So, the advantage of this membrane but why do we need a membrane basically is that the production of syngas takes place in a single step operation, occurring on one of the membrane side, this process eliminates the need for a separate oxygen production plant. So, you understand what is the meaning of this. So, the membrane is chosen in such a way that whenever the O 2 minus is only diffusing the site and reacting with methane, forming carbon monoxide and hydrogen.

Now, neither carbon monoxide nor the hydrogen is diffusing back to the other side; otherwise the process will not be feasible. So, this is the role of the membrane, this particular ceramic membrane.

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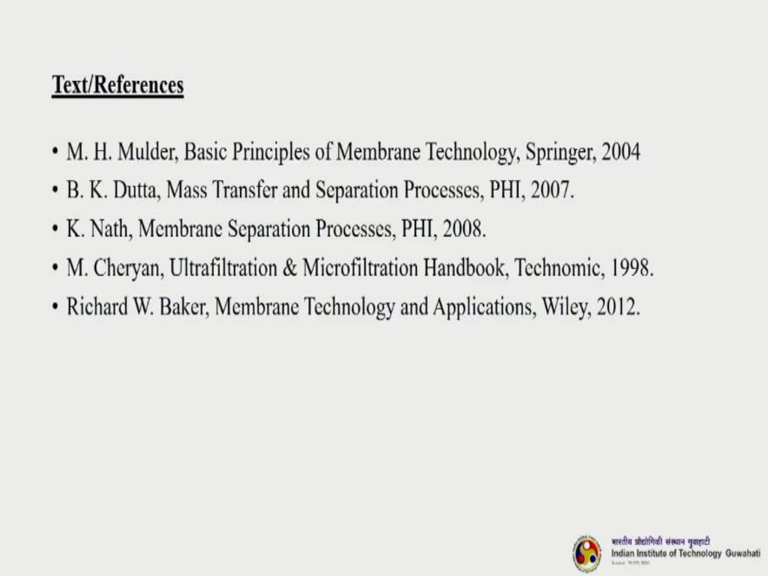

So, you can use these are the texts Mulder and co Syngas book. So, you can refer other books also for today's lecture. So, thank you very much and in the next lecture we will discuss about the preparation of porous and non-porous membranes nominal and absolute rating will try to understand and start the once you prepare the porous membrane, and we will try to understand what are the different types of characterization and membranes are, and maybe next class we will discuss the characters.

And characterization of the micro filtration membrane by Same terms and technique. So in case you have any query to feel free to write to me kmohanty@iitg.ac.in. Thank you very much.