Chemical Process Intensification
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Lecture 20
Preparation of Monolithic Catalyst

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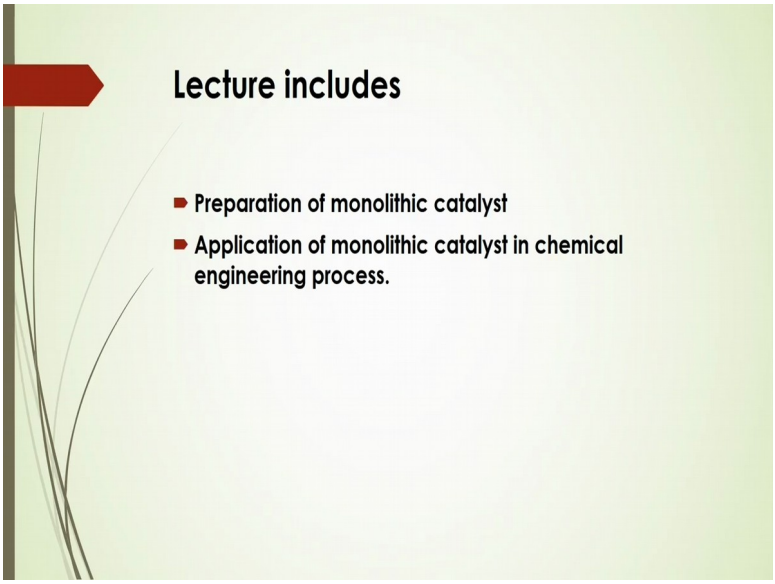

Welcome to massive online course on Chemical Process Intensification. So we have discussed in the module 7 regarding process intensification by monolith reactors. And in this lecture of this module we will discuss something about preparation of monolithic catalyst, how to prepare that monolithic catalyst and later on in next lecture we will discuss about applications of monolithic catalyst in chemical engineering process. So before going to the applications we will try to learn something about how to prepare the monolithic catalyst in this lecture.

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So as a recap, we can recall that previous lecture about monolithic structure and then how monolithic structure is actually being applied for chemical engineering process intensification. In ancient architectural structure that actually different shape of their house, buildings they have developed and this is one type of it is called monolithic structure. And here in the slides it is shown that there are different monolithic structures, so from this structure concept how this structure can be actually utilised to actually develop a reactor for the chemical engineering processes. So that concept will give you the intensification of the process in chemical engineering processes.

Now for that whenever you are going to develop any chemical engineering reactor based on this monolithic structure that is structure-based reactor, so in that case this structure actually made in this particular fashion where that catalyst is to be actually embedded here in the structure so that through the catalyst bed on this particular structure will help for the reaction in the chemical engineering processes.

So that is why the monolithic structure supports that reactor, even the catalyst support of this type of structure is being nowadays actually very important for the chemical engineering processes. Now, there are different structures that we have discussed in the previous lecture like honeycomb structure, channel-based catalytic, different shapes of the channel will be there, based on that the reactors of this particular structure is being developed for the process.

So here in this slides we have shown different shape structures of the catalytic monolithic structure reactor based on the concept of ancient architectural structure, and after that

whenever reactor is being developed and how this chemical engineering process can be applied here, it is shown in this slides there. Now generally typical example like biodiesel production and where transistor application reaction is being done on this monolithic catalytic reactor.

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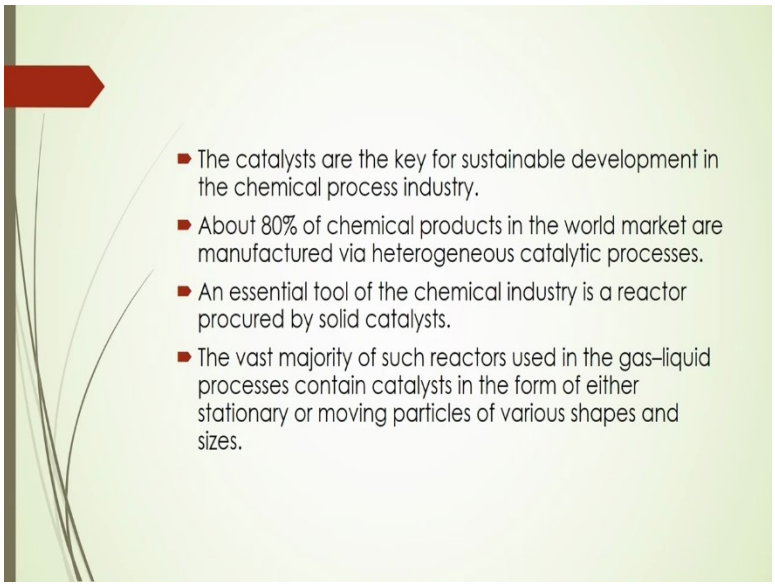

And in that case the catalyst are the key for sustainable development in the chemical process industry. We have already told that around 80 percent of the chemical products in the world market are manufactured via heterogeneous catalytic processes, in that case vast majority of such reactors used in the gas-liquid process which contains catalyst in the form of either stationary or moving particles of various shapes and sizes.

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Now this catalyst will help in the synthesis of the product in a resource protective way with less consumption of energy, and in some cases without any information of by products and also waste. The catalyst, especially if they are applied in a structured way, it will play an important role in integrated approach to environmental protection in a particular way where the intensification of the process is actually being carried out based on this catalyst structure.

They include the integration of various operations such as chemical reaction, separation and heat exchange, and also there may be momentum transfer that is several hydrodynamic aspects are also working on this particular reactor based on which the performance of the reactors will be actually assessed.

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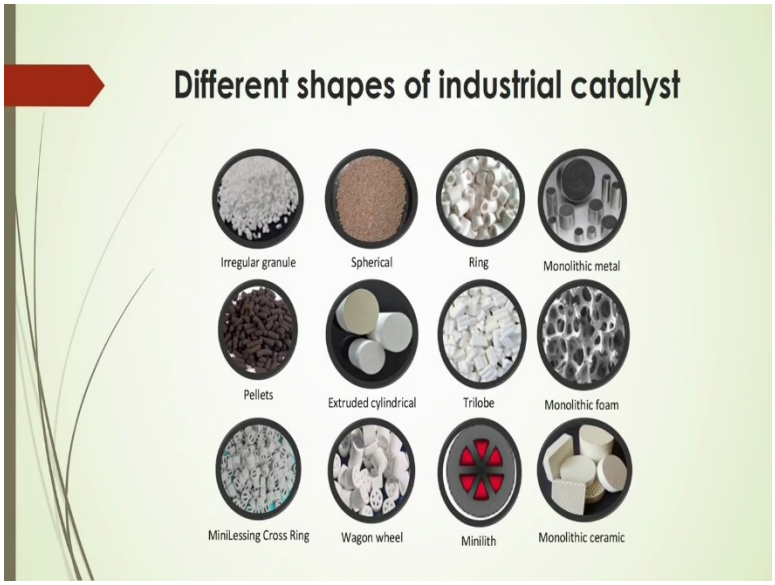

And of course before going to that, discussion of the catalyst structured bed, different monolithic reactor. In that case, what are the different shapes of the industrial catalyst are actually being developed that to be actually noted down like here different structure of the catalyst here, irregular, granular, earlier it is as you know that dispesred phase of catalyst is being used in slurry reactor. Here spherical particles are being used in the slurry system where the gas liquid solid system reactions are being carried out.

And also ring type where packed bed are actually used for the chemical reactions in a packed bed condition with the ring type catalyst. And then pellets type then cylindrical shape, trilobe shape, minilessing cross ring-shaped, even wagon wheel shape catalyst particles, even minilith catalyst particles as shown in the slides here.

And after that assessing of chemical process based on these catalyst bed, it is seen that there will be certain shortcomings of reactors of packed bed, slurry reactor even other different packed conditions where the reactor are being actually is acting as chemical engineering process equipment there. So based on that, catalyst bed reactor is seen that the performance of the reactions are not up to the mark that is 100 percent conversion or there will be some other shortcomings there, even maybe some hydrodynamic aspects where it is seen that the pressure drop will be very high, sometimes pressure drop is less also, where it is not also suitable for particular reactions.

And also some other chemical engineering processes where the mixing of the phases and also the catalyst particles should be uniform to get the utilisation of the whole surface of the catalyst bed.

So in that case you know that sometimes the development of slurry reactor, where the fluidisation reactor, where that mixing of the catalyst particles with the phase mixing so that the reaction should be more high. Still there are some other shortcomings of those reactors in packed bed slurry reactors, so later on to get more intensification of that reaction process, actually these monolithic type of reactors are being developed and also it is being now in the commercial stage almost there.

And there are several others, even research and development is going on this monolithic structure reactor where you can intensify the process efficiency based on this monolithic structure. So that is why the catalyst are being synthesised, after that it is given a shape of like this monolithic structure so that is why the different shape of the industrial catalyst like monolithic metal catalyst is one of the shape.

And also monolithic foam is also another type of shape of catalyst shape, and monolithic ceramic structure also is there. So there are three types here; monolithic metal, monolithic foam and monolithic ceramic, this type of structure is now being actually procured based on the catalyst particles, catalyst metal, suitable catalysts substances or solvents also sometimes is being used so that you can get it as foam type monolithic structure there.

So that is why we can see that there are several different types of industrial catalysts are being here used from the beginning that is from that in 1977 onwards it is actually being developed in different shapes of catalyst. In this case, the present-day that monolithic structure is one of the important shape of the catalyst where based on the catalytic operation

catalyst aided any reaction in which that reaction is being carried out is called catalytic monolithic reactor.

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Now, as per basic construction material, there are mostly two types of material based monoliths there it is actually being procured; there are ceramic and metallic type. So ceramic mainly cordierite, it is a silicate mineral that is found in metamorphic and igneous rocks and this ceramics may be sometimes foam type ceramic also is being there. And also metallic mainly stainless steel, metal alloys, et cetera, metals are being used for this procurement of this type of metallic monolithic structure.

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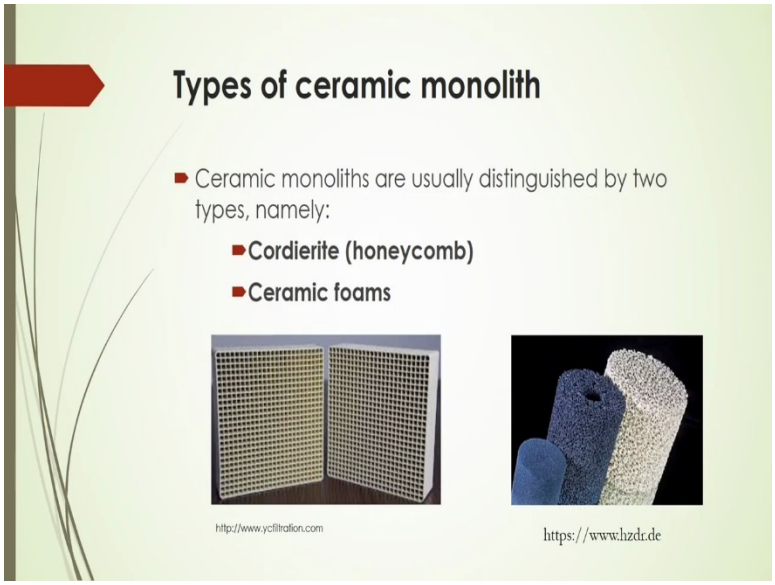

And ceramic monoliths are usually distinguished by two types namely; cordierite it is called sometimes honeycomb ceramic monolithic structure, and ceramic foam is another. Here in this slide, the shape of that cordierite or honeycomb type structure is shown here in this case, and also this is called that foam type ceramic structure there.

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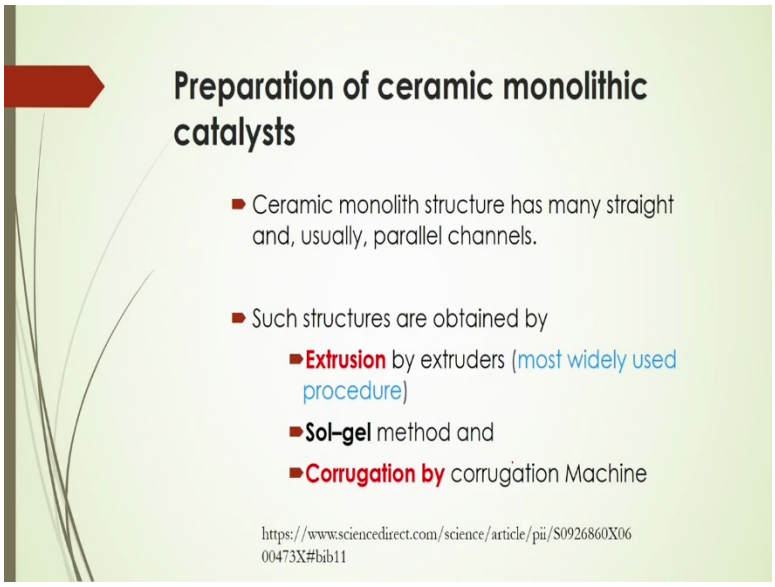

Now question is that how to prepare this type of ceramic monolithic catalyst surface. In this case the ceramic monolithic structure has many straight and usually parallel channels, channel type monolithic structures are being developed so that you can expect that there will be uniform flow through the channel. And also you know that slag flow or you can say flat flow type flow there so that you can get that uniform mixing over the solid particles so that you can get the more efficiency of the reaction, so such structures are obtained by Extrusion method, Sol-gel method and Corrugation method.

And extrusion method mostly actually used for procurement of making of the structure of this monolithic ceramic catalyst. In this case you know that mainly different types of oxide materials are being used in extrusion procedure as I will show in the next slide, how to actually prepare this that monolithic catalyst structure by this extrusion. Then Sol-gel method is generally used for giving the active support material procurement for this catalyst surface. And corrugation method is used for procurement of the metallic monolithic catalyst there.

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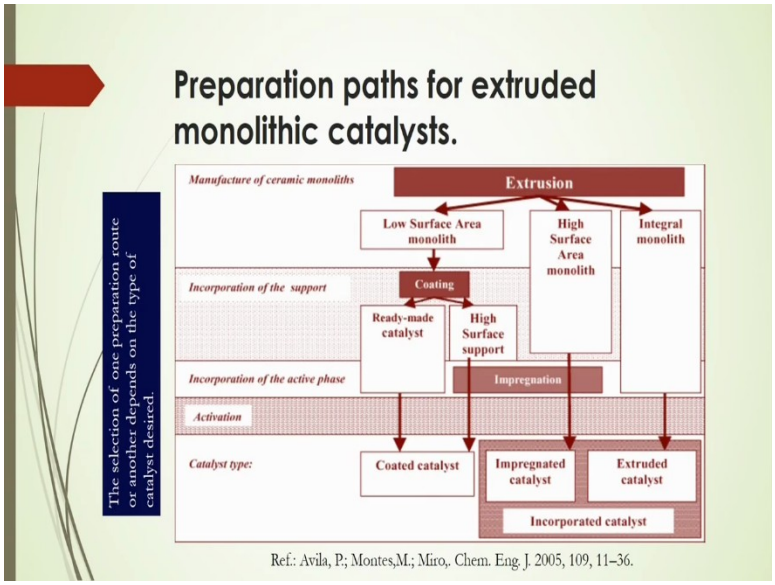

And also in this case is if we discuss about the preparation paths for the extruded monolithic catalyst, we are having this structure it is given by Avila in 2005 under publication Chemical engineering Journal. So if you go through that paper you will get the more illustrative discussion of this preparation paths for extruded monolithic catalyst. Here it is given that for the manufacturer of ceramic monolithic by extrusion, you get this low surface area monolithic and high surface area monolithic as well as some integral monolithic structure based on this extrusion method. And after that you know that you have to do this extrusion extruded materials of this low surface or high surface area monolithic even in integral monolith, you have to coat it by a suitable catalyst material.

So this is called incorporation of the support, so you have to make the support with the suitable catalyst. The support may be you know that ready-made catalyst based support, even high surface support also can be made based on the coated catalyst particles there. So incorporation of that active phase by this coated catalyst surface on this catalyst particles on this support material of this monolithic structure, there it should be the impregnation method.

Now based on this impregnation you can use the suitable coated catalyst, and also different types of impregnated catalyst and also extruded catalyst should be used. And this impregnated catalyst and extruded catalyst should be referred to as incorporated catalyst there. So there are 3 different types of catalyst can be used for the impregnation for the active surface of this catalyst on the support material.

So that is why the support material should be coated by different types of catalyst particles. So then you can get that particular structure on which that catalyst layer will be there and through which that flow will be there, the reaction will be there for that particular chemical engineering process. Now in this case the selection of one preparation route or another that depends upon the type of catalyst that should be desired for that particular process or particular reaction.

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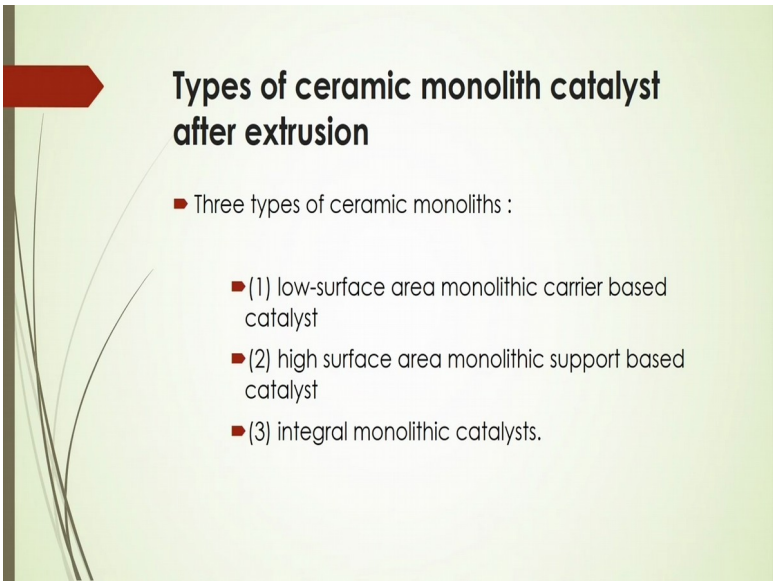

Now the type of ceramic monolithic catalyst after extrusion, you see that there are 3 types of ceramic monoliths are there; low surface area monolithic, carrier-based catalyst and high surface area monolithic support based catalyst and integral monolithic catalyst are there.

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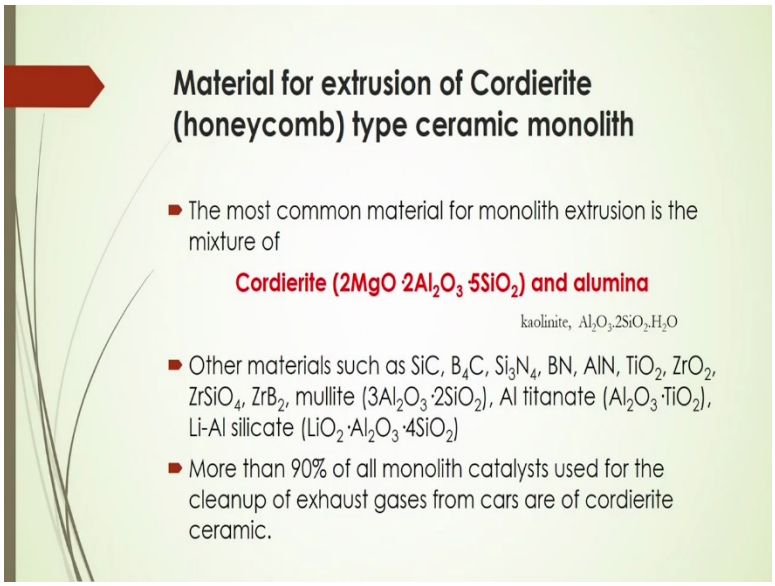

And then materials for extrusion of course should be selective and to make that ceramic monolith by that extrusion process for the particular shape of like cordierite or honeycomb structure, in that case you have to use some material for that monolithic extrusion. And most common material for the monolith extrusion is the mixture of cordierite, it is actually the ore of magnesium oxide, aluminium oxide and silicon dioxide mixture. And then you have to add with that cordierite with Alumina, which is basically obtained from the ore of kaolinite that is aluminium oxide and silica crystals there. So in that case and material which is actually being used initially for that extrusion process for the preparation of ceramic monolithic is called the cordierite material.

Other materials also you can use such as silicon carbide, bismuth carbide, some other materials, boron nitrate, or even aluminium nitride, titanium dioxide, zirconium oxide, other oxide also you can use, and also Mullite, aluminium titanate, lithium aluminate silicate, this type of materials also can be used for the extrusion of materials to make the ceramic monolithic structure.

Now, more than 90 percent of all monolith catalyst that is being used for the clean-up of exhaust gases from the cars are of this cordierite ceramic monolithic structure. So this type of material is being used generally for this extrusion for preparation of ceramic monolith.

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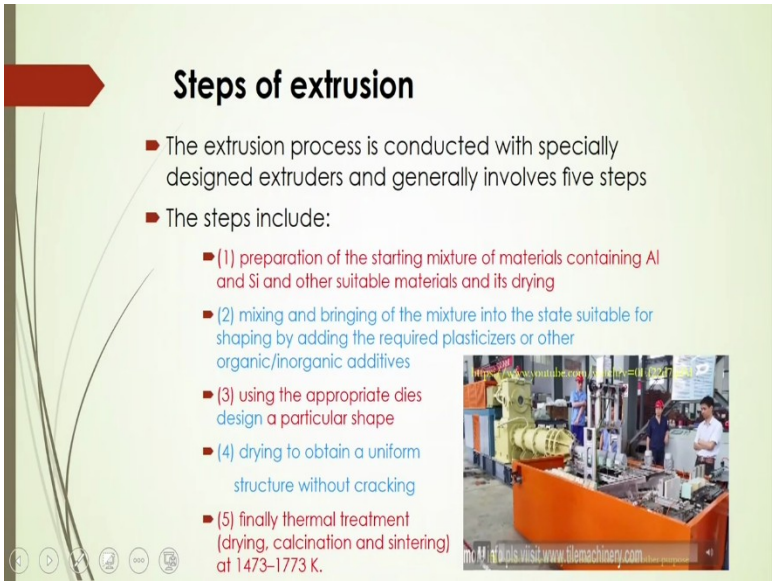

Now, what are the steps of the extrusion, one by one procedure will be there. In that case the extrusion process is conducted with specially designed extruders and generally involves five steps. The steps are like this; preparation of the starting mixture of materials that contains

aluminium and silicon, other suitable materials and is then drying. After that what you have to do, you have to mix that materials well and bringing of this mixture into the state where suitable for shaping by adding the required additives, it is called plasticisers or other organic or inorganic additives. And after that using this appropriate dye shapes that you have to design that structure of this monolithic in a particular shape.

After that you have to drive to obtain a uniform structure without cracking in this case you know that for getting uniform structure of this monolithic structure. So you have to dry, now that drying should be of particular temperature that should be thermally stable, and in that case you have to be careful that whether it is being cracked or not, then you have to change the suitable material where that you are not getting any cracking after drying. Generally for this cordierite material it is not being actually cracked at 1473 to 1773 Kelvin.

So finally this thermal treatment that is drying, calcination and sintering should be done at 1473 to 1773 Kelvin there. So these are the different steps, these 5 steps are actually being followed for this extrusion process.

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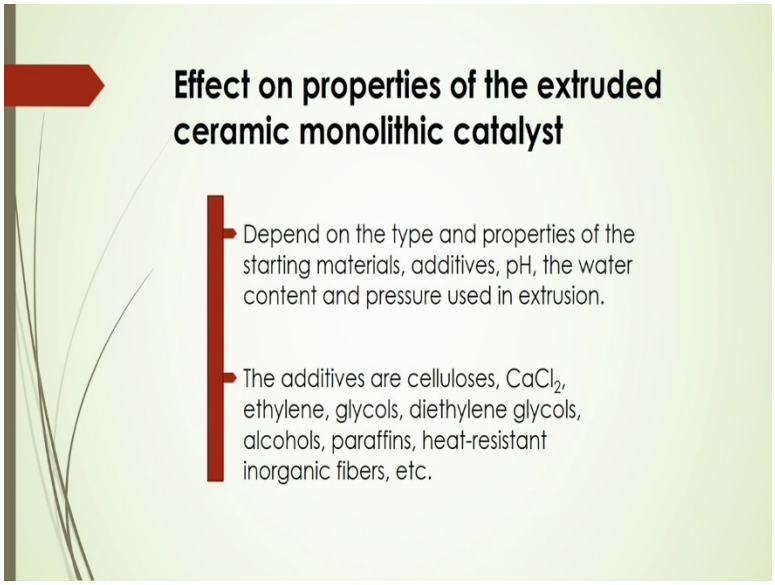

Now, what are the different effects on the properties of the extruded ceramic monolithic catalyst are being by the extrusion process. It generally depends on the type and properties of the starting material, what type of materials you are initially using for the extrusion process, and also what type of additives you are using, what are the mediums, conditions, whether it is acidic or alkylene, that you have to know that is why you have to maintain certain pH of that particular medium to make that shape in the extrusion process.

And also you have to wisely use the water content that is also very important. To get that mechanical strength there should not be that enough of water content in that structure. And also pressure that is also another important factor which may effect on the properties that is called mechanical properties of the extruded ceramic monolithic catalyst. So the additives are generally being used as cellulose, calcium chloride, ethylene glycols, diethylene glycols, alcohols, paraffin, heat resistant inorganic fibres, et cetera, so these are the additives generally being used for extrusion process to make the ceramic monolithic catalyst.

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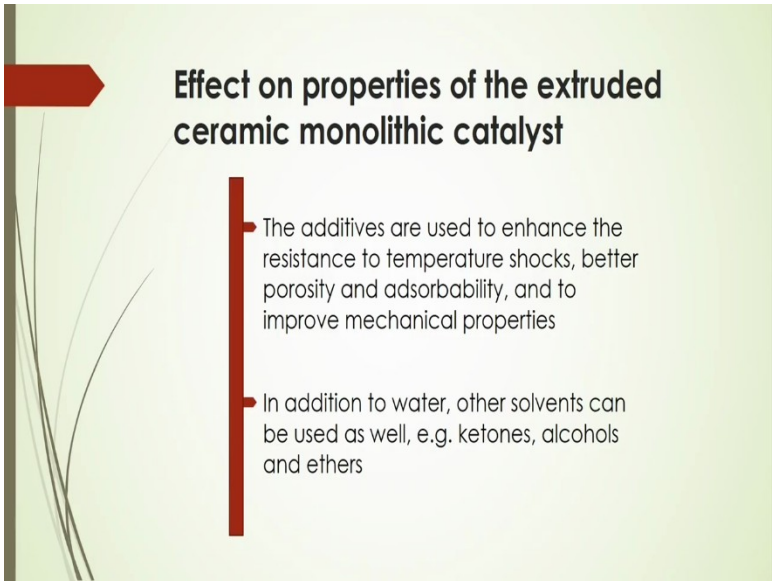

And the additives are used to enhance the resistance to temperature shocks, better porosity and absorbability and to improve the mechanical properties. So you have to remember that you have to use some to table additives where you could enhance the resistance to temperature, shocks, better porosity and also absorbability. And also I told that in addition to water, other solvents can be used as well so that you can get more stable structure of that monolithic catalyst, in that case ketones, alcohols and ethers can be used along with using water.

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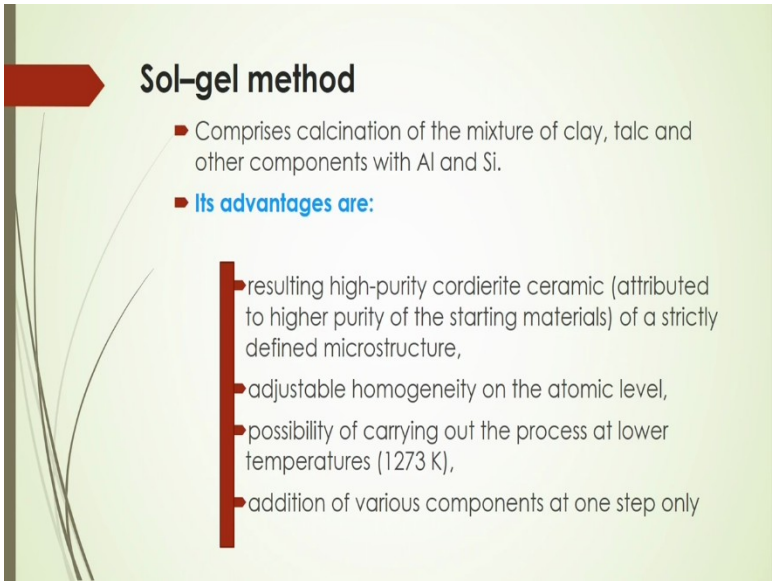

Another important matter is called Sol-gel method, it is generally a calcination of the mixture of clay, talc and other components with aluminium and silica. And its advantages are resulting high purity cordierite ceramic that is attributed to higher purity of the starting material and also in this case you have to use that certain proportion of clay or talc or other components material with aluminium and silica because to get that the microstructure should be well thermally stable so that is why cordierite ceramic material that should be high purity with certain proportion also.

And adjustable homogeneity at the atomic level also should be considered there, so it is there in the Sol-gel method so in this method it can be easily adjust the homogeneity of the atomic level. And also in this matter it is possible to carry out the process at lower temperatures at 1273 Kelvin also. And in this case addition of various components at one step is actually feasible that is why this method is very advantageous compared to the other methods.

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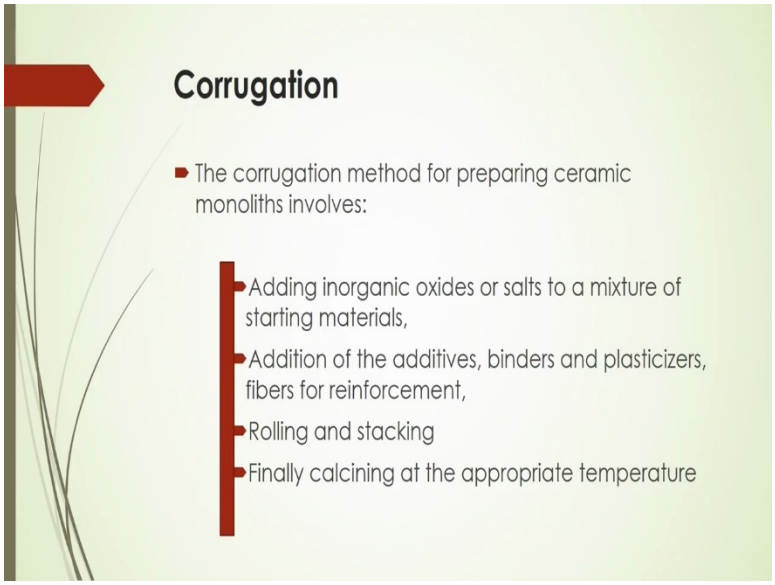

Whereas, in case of corrugation method for the preparation of ceramic monolith involves the addition of inorganic oxides or salts to the mixture of starting materials. And in this case addition of the additives like different materials that earlier we have discussed that these types of materials for additives like cellulose, calcium chloride, ethylene, glycols, diethylene glycols, alcohols, paraffins, etc. are actually to be used, and also binders, plasticisers, fibres for reinforcement of monolithic structures.

And also after that in this process you have to roll it down and then stacking should be done, finally calcination should be done at a particular temperature which should be selected in such a way that the material should not be cracked at that particular higher temperature.

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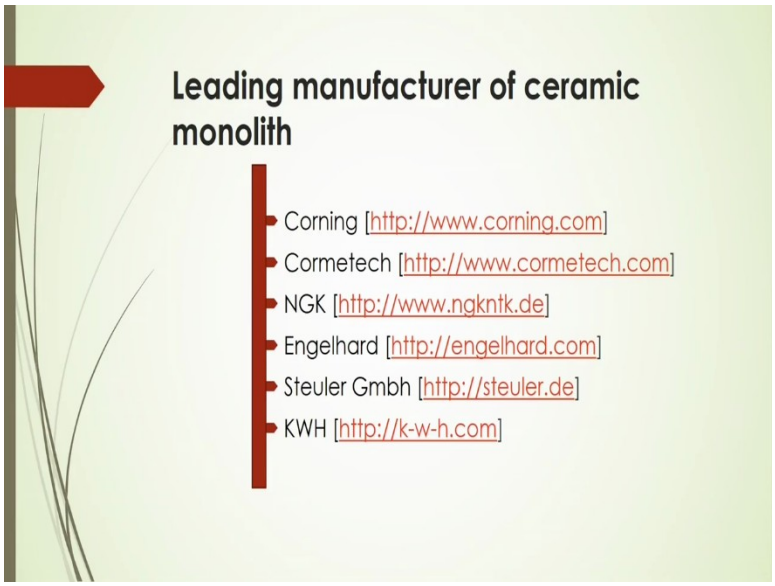

Now, let us have some you know leading manufacturers of ceramic type of monolith like Corning Company. These websites are given; Cormetech, NGK, Engelhard also very important in this respect, they are also producing different types of ceramic monoliths, even Steuler Gmbh, and also KWH, these are the actual potential companies, they can supply this type of ceramic monoliths and they are also manufacturing this type of ceramic monolithic structure.

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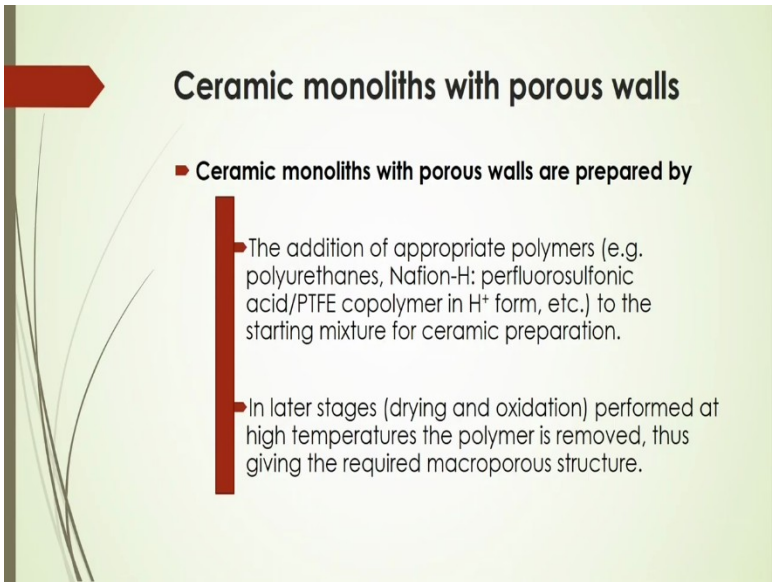

Now, how to actually prepare ceramic monolithic with porous walls? In this case the addition of appropriate polymers like polyurethane, Nafion-H, perfluorosulphonic acid, also PTFE that is polytetrafluoroethylene copolymer in hydrogen ion form, et cetera to the starting mixture for ceramic preparation. In later stages what you have to do that, you have to do drying and oxidation and then you have to perform this drying and oxidation at high temperatures. In this case the polymer will be removed at high temperature and thus giving the required macro structure that ceramic monoliths.

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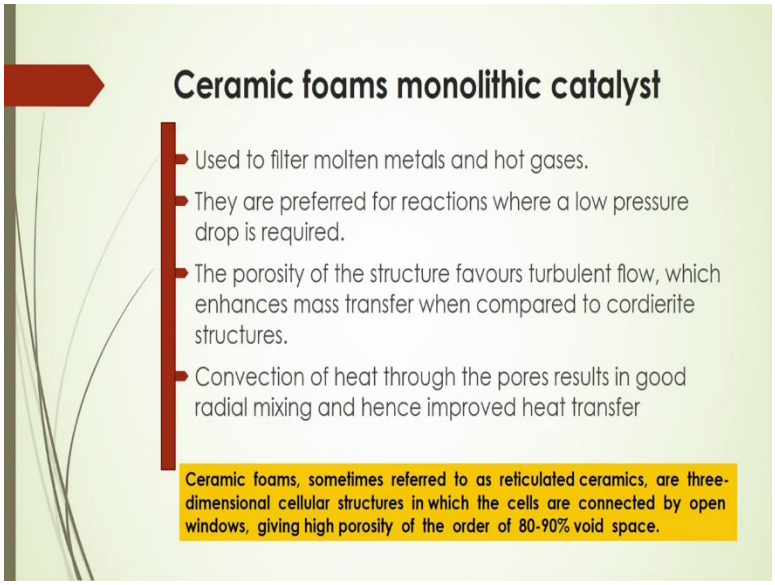

In this case the ceramic foams monolithic catalyst also another type of monolithic catalyst, in that case how to prepare, in that case you know that it is generally being used to filter molten metals and hot gases and they are prepared for the reactions where a low-pressure drop is required. And in this case the porosity of the structure that favours turbulent flow, which enhances mass transfer with compared to cordierite structures.

And conventional heat through the pores that results in good radial mixing and hence improves the heat transfer that is why the ceramic foam is also procured as an alternative of ceramic monolithic catalyst and because it has some advantage of low pressure drop in particular preferred reactions where the pressure drop will be low.

And also the porosity of the structure that may sometimes favour the turbulent flow for enhancing that mass transfer and in this case it will be advantageous over the cordierite structure. And in this case, one of the important aspects that you have to remember that here you will see that convection of the heat through the porous materials will be resulted and it may give good radial mixing and hence improve the heat transfer, and it is very important for that particular reaction where it is generally being in endothermic or exothermic reactions there, how heat would will be distributed over there.

And also you will see that in this case you can use some molten metals and hot gases for particular specific engineering process for reaction purpose. And ceramic foams sometimes referred to as reticulated ceramic which are three-dimensional cellular structure in which the

cells are connected by open windows that may give the high porosity of the order of 80 to 90 percent void fractions there.

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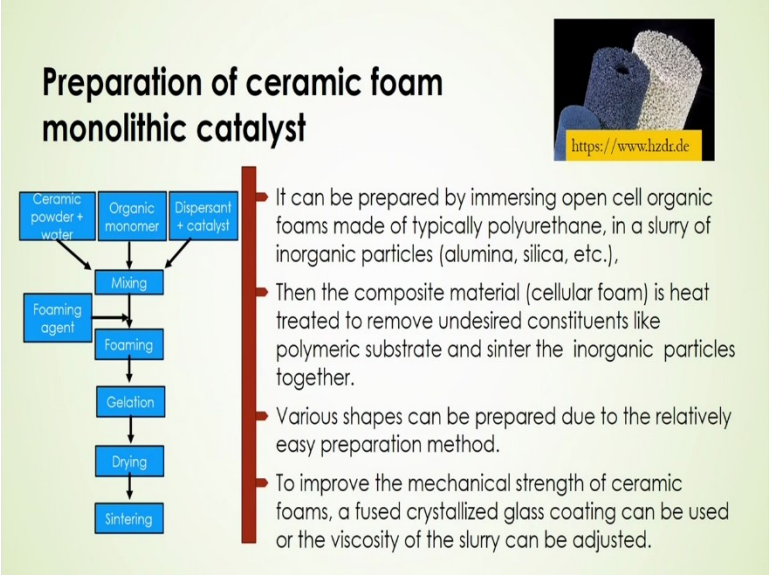

And how to then prepare this type of Foam monolithic catalyst there? There are several steps are there, here in this case like you know you have to make a mixture of ceramic powder with water that is slurry system you have to make with organic monomer, even dispersants catalyst particles. After that you have to mix it well and then you have to add some foaming agent, after that you will see at a certain temperature this foaming will be formed and then you have to make it in the form of gelation and then after gelation you have to dry it and then finally you have to sinter it to get that foam type monolithic structure.

So in this case, various shapes can be prepared due to the relatively easy preparation method by this procedure. In this case you can get the composite material of the cellular foam that is heat treated to remove that undesired constituents like polymeric substrates and sinter the inorganic particles together. Now in this case, this type of material can be prepared by immersing open organic foams made of typically polyurethane in a slurry of inorganic particles like alumina, silica, et cetera. To improve the mechanical strength of these ceramic foams what you have to do, a fused crystallised class coating can be used or the viscosity of the slurry can be adjusted.

So that is very important, you have to remember that you have to adjust the viscosity of the slurry. Initially, you are actually making the mixture of ceramic powder with water to make the slurry along with that organic monomer and dispersants and also catalyst. In that case you

will see that there will be slurry system that viscosity of that slurry should be adjusted by giving the proportionate of that ceramic powder because if you add more ceramic powder, there may be viscosity will be higher. So effective viscosity will be changing because the slurry system has the apparent viscosity change with respect to time also.

So that is sometimes it is referred as the CO_2 plastic fluid so that is to get the higher strength of the ceramic foams you have to use some fused crystalline glass coating and in that case otherwise you can use that appropriate maintenance of viscosity of slurry.

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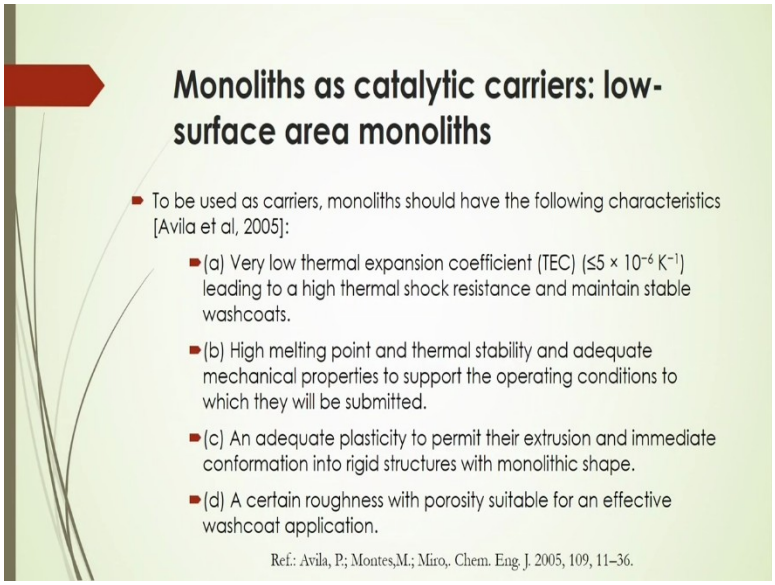

Now, monolith as catalytic carriers that is low surface area monoliths have to actually use that is to be used as carrier monoliths should have the following characteristics. In that case you have to remember like as per Avila et al they pointed out some characteristics of that monolith catalyst which is to be carried out as a carrier, which is to be actually used as a carrier, so in that case very low thermal expansion coefficient should be there, it should be less than or equal to $5 \times 10^{-6}\ K^{-1}$.

And which may lead to a higher thermal shock resistance and maintains the stable wash coat there. High melting point and thermal stability and adequate mechanical properties are to support the operating conditions to which they will be submitted.

And also an adequate plasticity to permit their extrusion and immediate conformation into rigid structure with monolithic shape. In that case certain roughness of the porosity that should be suitable for an effective wash coat application there. So these are the different characteristics of monoliths which can be used as carriers there.

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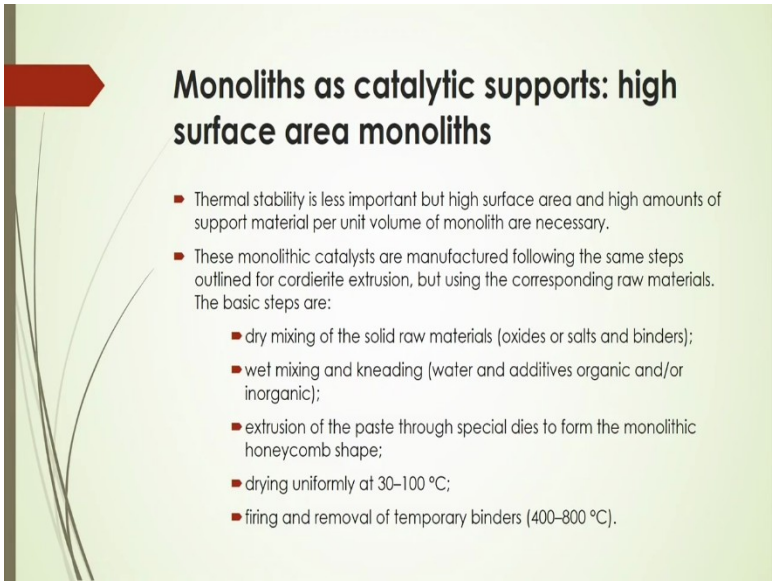

And also you will see that for high surface area you will get also some other characteristics. In that case thermal stability should be less, and in that case the thermal stability is less important, but high surface area and high amount of support material per unit volume and monoliths are in that case it will be necessary. These monolithic catalyst are manufactured following the same steps that is outlined in case of extrusion of cordierite material, but in this case using the corresponding raw material the basic steps should be followed like here dry mixing of the solid raw materials, and like here solid materials may be oxide or salts and binders.

And then what you have to do that you have to do weight mixing and kneading where water and additives like organic and inorganic substances to be used. And then extrusion of the paste through special dies to form the monolithic honeycombs shapes, and then drying uniformly at 30 to 100 degree centigrade, and then you have to sinter it or fire it and then removal of temporary binders at 400 to 800 degree Celsius. So these are the steps that you have to follow to get this high surface area monoliths.

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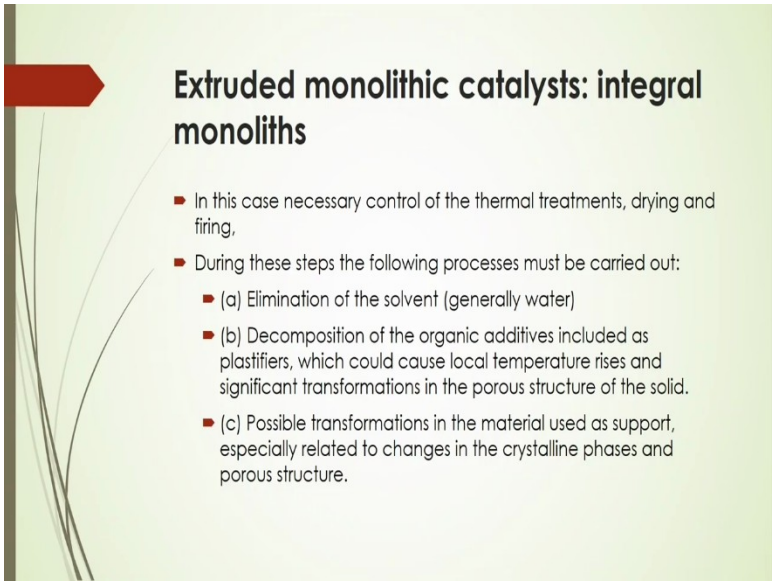

And in case of integral monoliths, in this case some necessary control of the thermal treatments should be done as well as drying and firing. And during these steps the following process must be carried out like elimination of the solvent generally water should be done. The composition of the organic additives that may be included as plastifiers which may cause the local temperature rises and also significant transformations in the porous structure of the solid. And these possible transformations in the material that is used as a support, especially related to changes in the crystalline phases and also porous structure.

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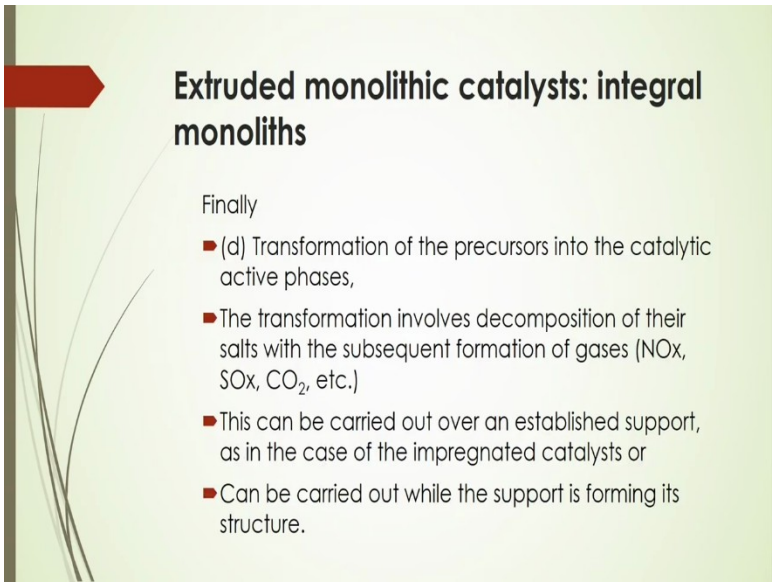

Now, finally what you have to do that you have to transform these precursor into the catalytic active phases. And the transformation that may involve the decomposition of their salts with

the subsequent formation of gases like NO_x, SO_x or even CO_x also. And this can be carried out over an established support as in the case of impregnated catalyst or you can do it while the support is forming its structure.

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After that you have to see, we got the different procedures of preparing monolithic structure whether it is ceramic, foaming high surface or low surface area-based monolith structure. After that you have to incorporate active phases into the monoliths, so in this case extruded catalyst the incorporation of the active phases in a monolithic support for the high surface area and low surface area that should be coated with a support should be carried out in that case, so incorporation is very important for activating the surface of the monolith surface.

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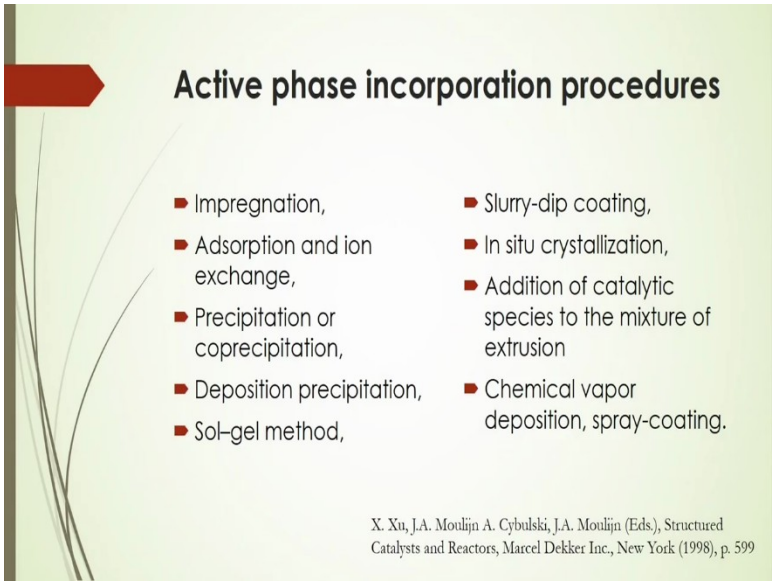

Now active phase incorporation procedures are there are several other procedures to incorporate these active phases like impregnation is one method that we have discussed. Except this impregnation we can get absorption and ion exchange method, precipitation or co-precipitation method, deposition or precipitation method, Sol-gel method, slurry deep coating method, In situ crystallisation method, addition of catalytic spaces to the mixture of extrusion, chemical vapour deposition, even you can say that spray coating is also another important method to incorporate these active phases over the monolithic structure.

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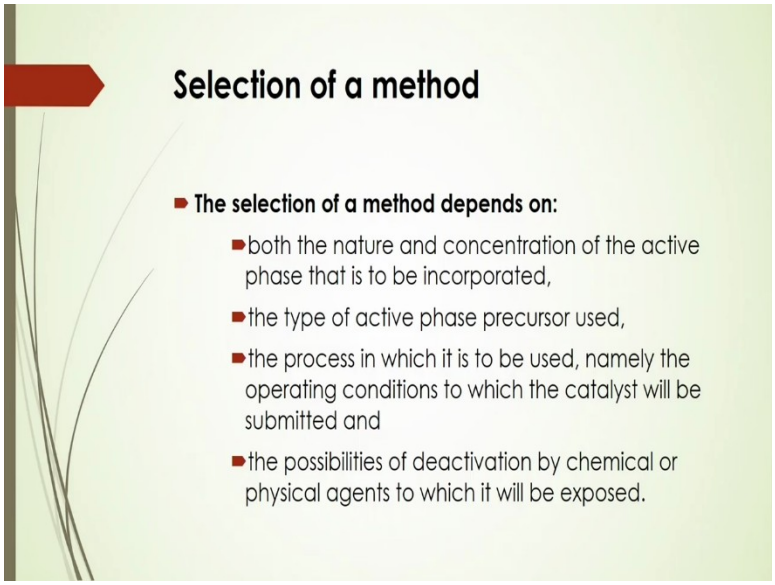

Now, how to select those active phases material there? So both the nature and concentration of the active phase that is to be incorporated, and the type of active phase precursors to be used. And also the process in which it is to be used, namely the operating conditions to which the catalyst will be submitted and also the possibilities of the deactivation by chemical or physical agents to which it will be exposed. So these are the several factors actually which may give you the direction for the selection of a method for this I mean incorporation of the active phases on the monolith surface.

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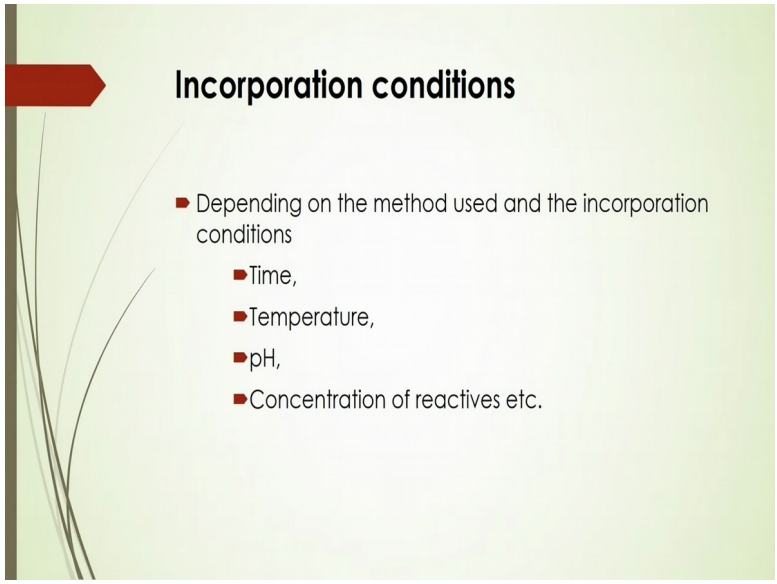

And the conditions that actually effects on the incorporation method, generally time, temperature, pH and concentration of the reactive, et cetera.

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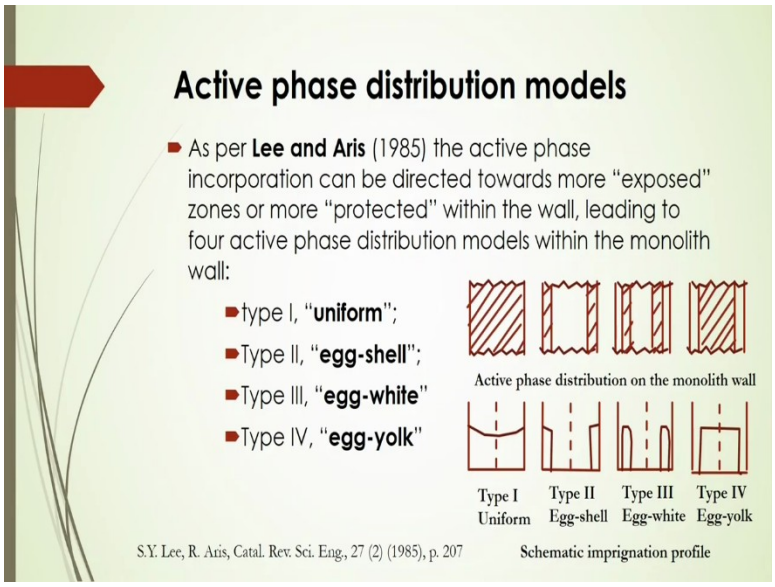

Now, active phase distribution models are there to analyse that exposing of the active phase on the monolithic surface. Now, as per Lee and Aris, they have described actually the certain model according to their experimental observation and also their procurement of the solid material that is monolithic structure material, and they have suggested that on particular models of the distribution for that active phases.

In this case they have actually stated that the active phase incorporation can be directed towards more exposed zones or more protected within the walls that may lead to the four active phase distribution models within the monolithic wall. So as per this structure given in this slides, the active phase distribution of the monolith wall here this figure we will see that how this active phase distribution can be done in the monolith wall.

There are four types of exposing or activating phase distribution there like type I, type II, type III and type IV. Type I is "uniform" distribution model, type II is "egg shell" distribution model, type III is "egg white" distribution model and type IV is "egg yolk" distribution model. And based on these models they have accessed that how we can actually activate that surface of the monolithic surface.

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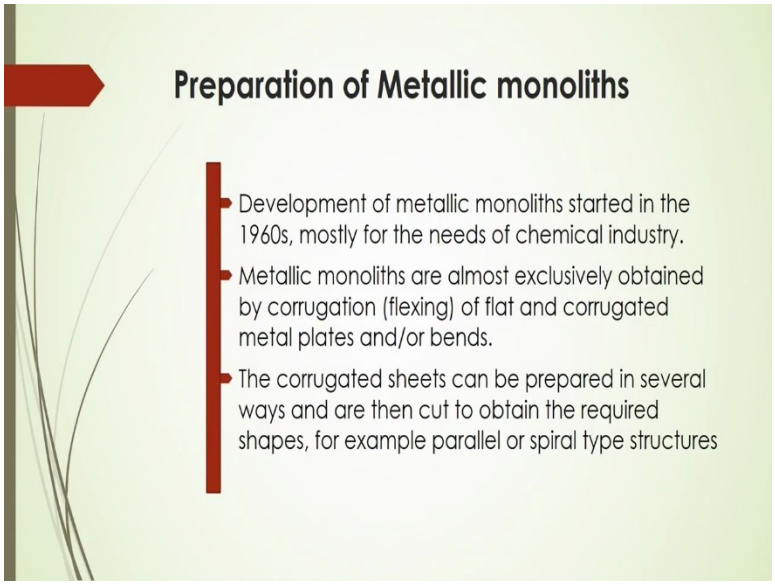

Now, after that we are just considering the metallic monolith how to prepare because we have discussed here how to prepare monolithic ceramic structure and also low surface area, high surface area, different structure by different methods. Now, how to prepare that metallic monolith, this is also one important type of that monolithic catalytic structure. So in this case development of this metallic monolith actually started in 1960s mostly for the needs of chemical industry, and these types of monoliths are almost exclusively obtained by corrugation that means flexing of flat and corrugated metal plates, and also bends.

The corrugated sheets can be prepared in several ways then cut to obtain the required shape. For example, if you are actually preparing parallel or spiral types of structure then you have

to use these corrugated sheets which can be prepared in this particular shapes by particular process there by corrugation method.

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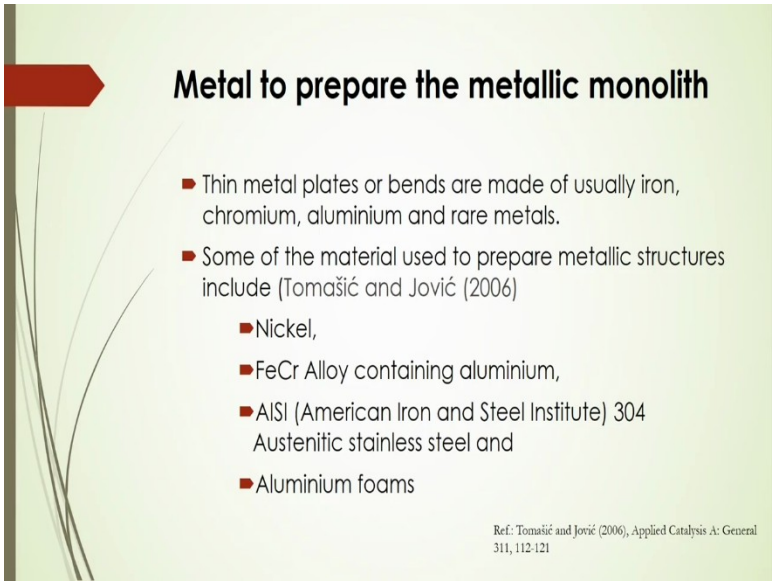

And in this case, what are the metals actually to be used to prepare that metallic monolith? The thin metal plates or bends whatever shapes you are going to make, usually it should be Iron, chromium, aluminium and rare metals. Some of the material that is used to prepare metallic structures include nickel, iron or chromium alloy that may contain aluminium, even some other materials like iron and steel composite material that is called AISI that is American Iron and Steel Institute that is marked as AISI 304, and also aluminium foams can also be used to make these metallic monoliths.

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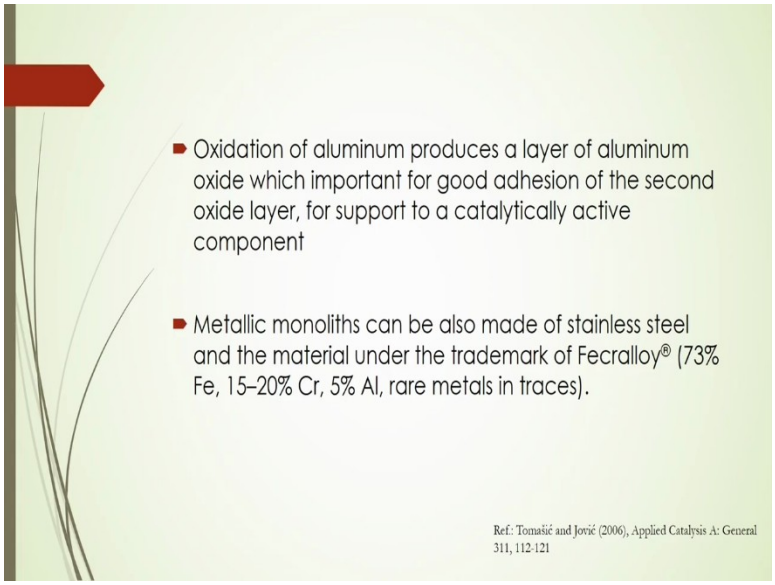

Now, in this case oxidation of aluminium produces a layer of aluminium oxide which is important for good adhesion of the second oxide layer for support to a catalytically active component. And metallic monoliths can also be made of stainless steel and the material under the trademark of ferrochromium alloy, in that case around 73 percent iron and 15 to 20 percent chromium and also 5 percent aluminium should be used. Some trace elements like rare metals to be used there. So for this metallic monolith can also be made this you know composite materials Iron, chromium and aluminium with small amount of rare metals.

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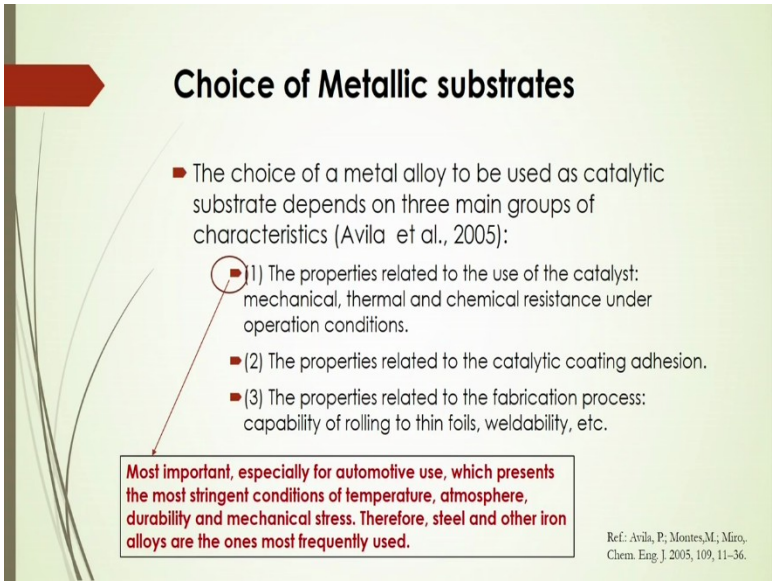

Now, how to choice this metallic substrates to prepare that monolithic metallic structure or catalyst? So in this case the choice of a metal alloy to be used as catalytic substrate that depends on 3 main groups of characteristics as per Avila et al. (2005). Now, in this case the properties related to the use of catalyst like mechanical properties, thermal properties, and chemical resistance under operational conditions. And another important characteristics that is very important to be considered for the choice of metal alloy, in this case the properties related to the catalytic coating adhesion and also the properties related to the fabrication process whether it should be capable of rolling to thin foils or whether it should be weldable or not. So that should be also keep in mind whenever you are going to choice the metallic substrates for the procurement of metallic monolithic structure.

Most important point here the properties that is related to the use of catalyst because in this case for automotive use that presents the most stringent conditions where properties related to the use of catalyst that is whether it is mechanical, thermal or chemical resistance or not. So

this point actually being keep in mind for the procurement of that metallic monolithic structure.

In this case that is why it is very important for the automotive uses where these stringent conditions of the temperature, atmosphere, durability and mechanical stresses are to be considered. Therefore, steel and other iron alloys are the ones that is most frequently used for the preparation of this metallic monolithic structure. This is generally for catalytic converter in automotive vehicles.

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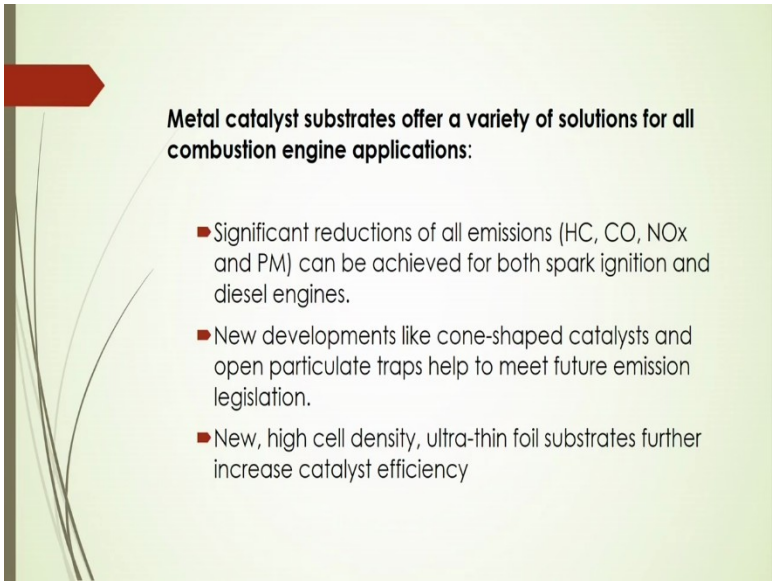

And metal catalyst substrates offer a variety of solutions for all combustion engine applications. In this case you will see that significant reductions of the emissions like hydrocarbon, carbon monoxide, NO_x and even particulate materials there. And in this case reductions of those materials can be achieved for both spark ignition and diesel engines. And also, based on this metal catalyst substrates you can develop cone shaped catalyst and open particulate traps that may help to meet the future emission legislation.

And also based on this metal catalyst substrates, new high-end cell density, and ultra-thin foil substrates that further increases catalyst efficiency for the particular application that you can consider. So these are the variety of solutions for combustion engine applications based on that metallic catalyst substrate.

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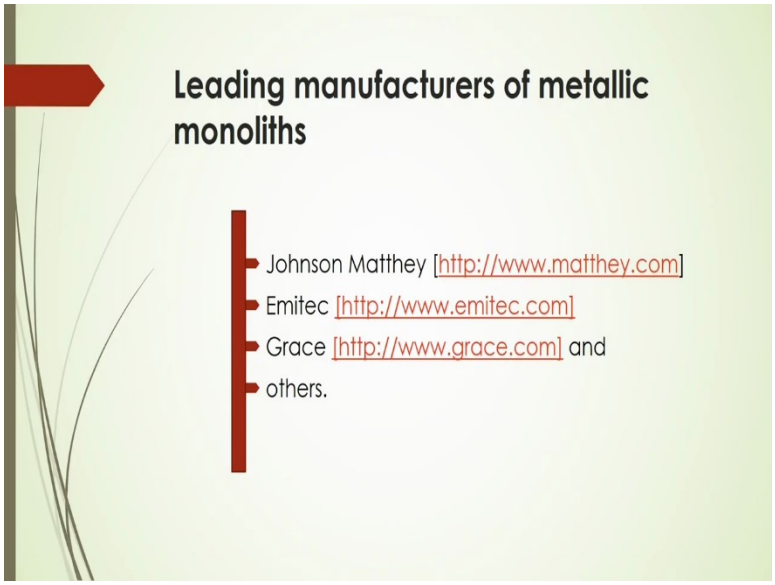

In this case this metallic monolithic structures are manufactured by leading manufacturer of like you know that some companies are given here with websites in the slides; Johnson Matthey, Emitec, Grace, those are leading companies, even potential companies there you know that huge amount of this type of metallic monolithic structure they are procuring and commercialised in the market, they are actually selling in the market.

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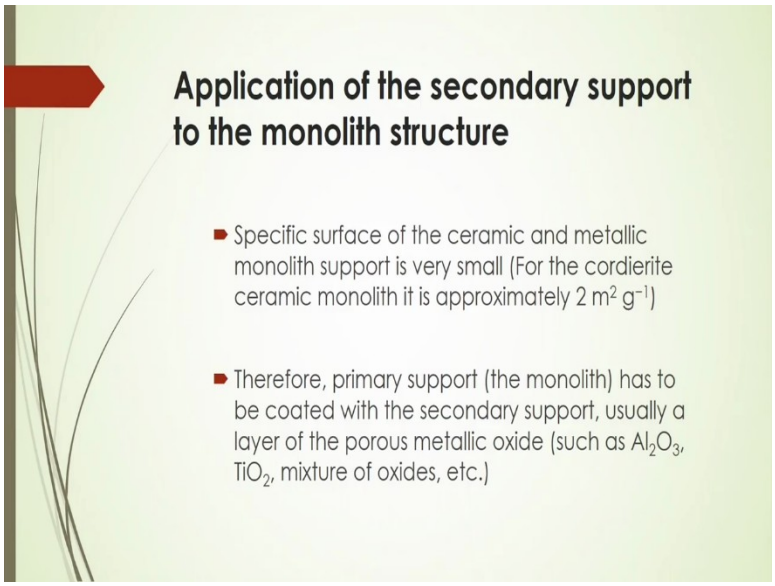

Application of the secondary support to the monolith structure, in that case you know the specific surface of the ceramic and metallic monolith support is very small for the cordierite ceramic monolith, it is approximately 2 meter square per gram. Therefore, primary support

the monolith has to be coated with the secondary support, usually a layer of the porous metallic oxide such as aluminium oxide, Titanum dioxide, Mixer of oxides, etc.

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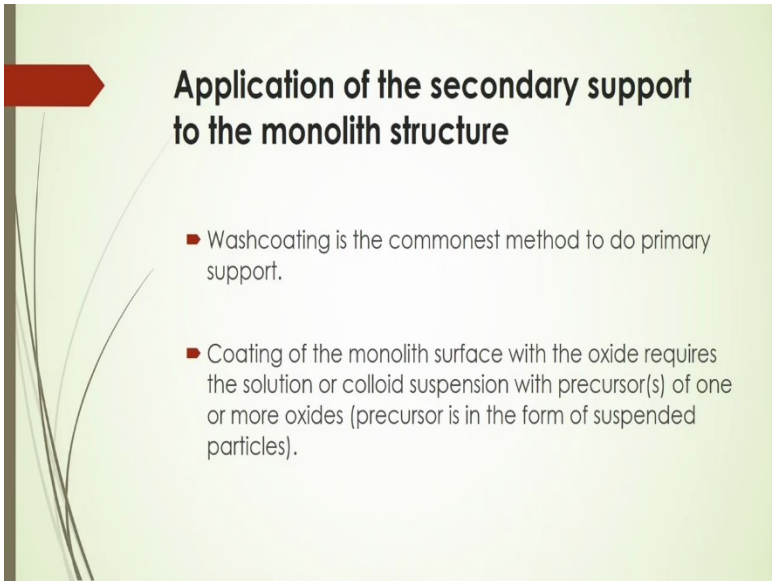

Now, washcoating is very important, in that case it is generally used to do primary support and coating of that monolith surface of the oxides requires the solution or colloid suspension with precursors of one or more oxides, precursor is in the form of suspended particles there.

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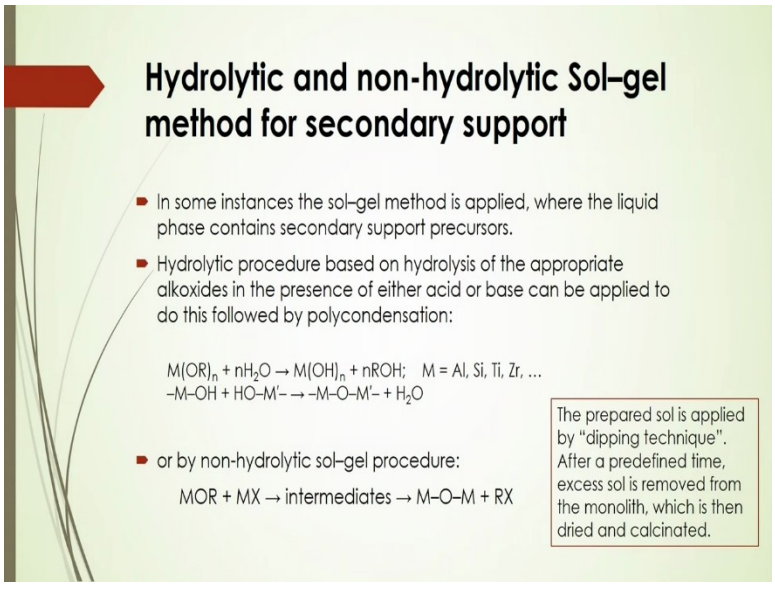

And another important point that should be remembered that for the secondary support also you have to make for getting that stable condition of that monolithic structure, in that case hydraulic and non-hydraulic Sol-gel methods are important. So in some instances the Sol-gel

method is applied where the liquid phase contains secondary support precursors. Hydraulic procedures based on hydrolysis of the appropriate alkoxide in the presence of either acid or base that can be applied to do this that may followed by Poly condensation.

So here this slide this poly condensation process is given and the reaction is given here, you can do either this method or you can do it by non-hydroelectric Sol-gel procedure also that for non-hydroelectric Sol-gel procedure is given here. In this case the prepared Sol is applied by dipping technique, and after a predefined time access Sol is removed from the monolith which is then dried and calcinated to get the secondary support.

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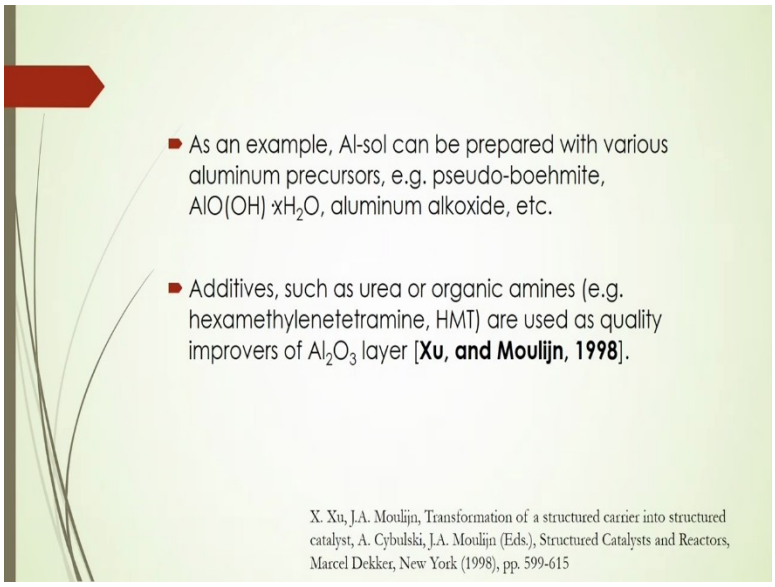

As an example, aluminium sol can be prepared with various aluminium precursors like pseudo-boehmite crystal and also aluminium alkoxide, etc. Additives are such as urea or organic amines like hexamethylenetetramine, and also other materials also you can use as for improve the quality. And in that case quality improvers of aluminium oxide layer should be used there, so this type of additives that you have to use for this making of this secondary support.

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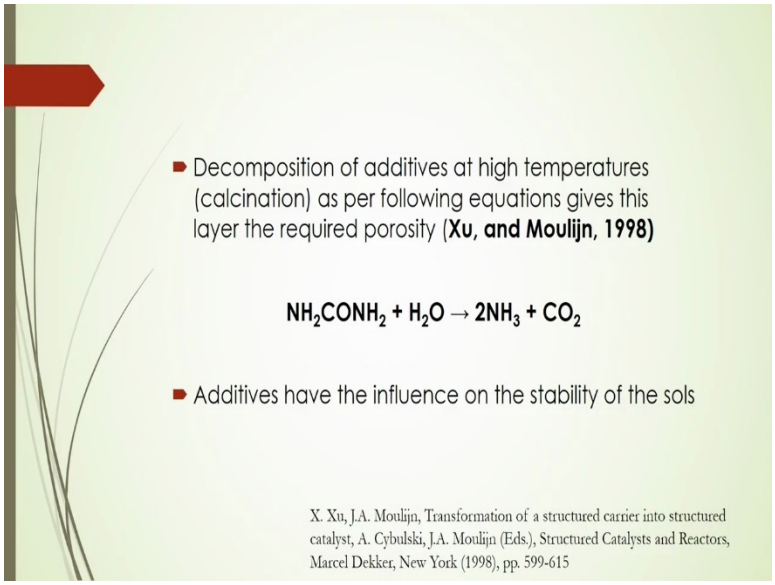

After that decomposition of additives at high temperature that is calcination as per following equations that is give this layer the required porosity as per Xu and Moulijn in 1998. They have given this you know that the reaction procedure to decompose the additives at high temperature. Now, additives have the influence on the stability of the Sols.

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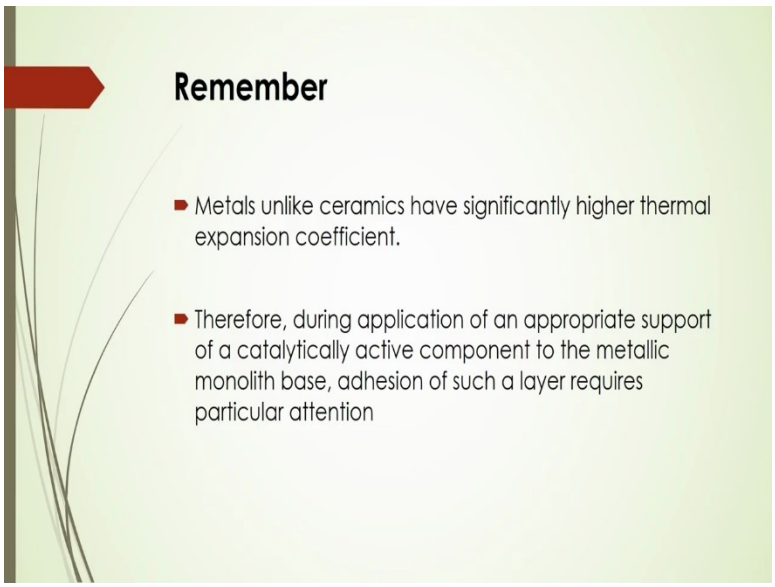

So in this case remember that metals unlike ceramics have significantly higher thermal expansion coefficient therefore, during the application of an appropriate support of a catalytically active component to the metallic monolith base, the adhesion of such layer that may require particular attention.

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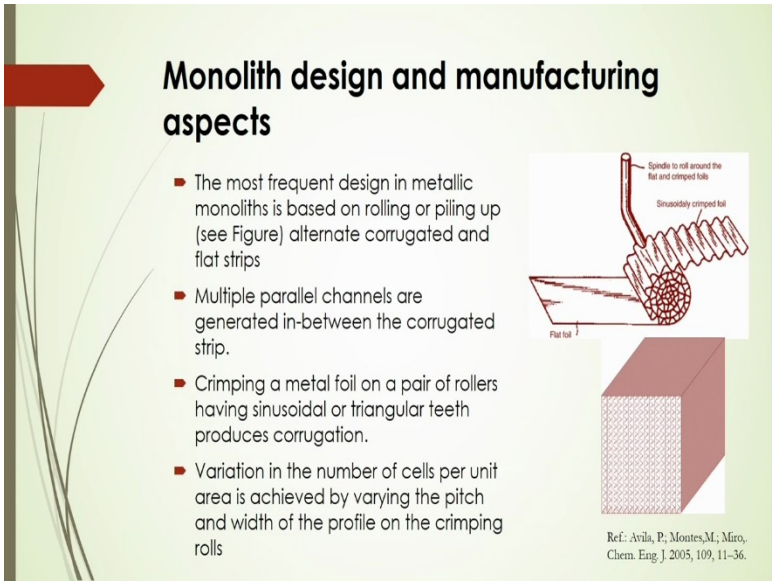

Now then how to design and manufacture of that monolith there? So some aspects are given here, the most frequent design in metallic monolith is based on the rolling or piling of, in this case see the figure you know alternate corrugated and flat strips are there. And also multiple parallel channels are generated in between the corrugated strip. Crimping a metal foil on a pair of rollers that have sinusoidal or triangular teeths that produces that corrugation. And variation in the number of sales per unit area is achieved by varying the pitch and width of the profile on the crimping rolls.

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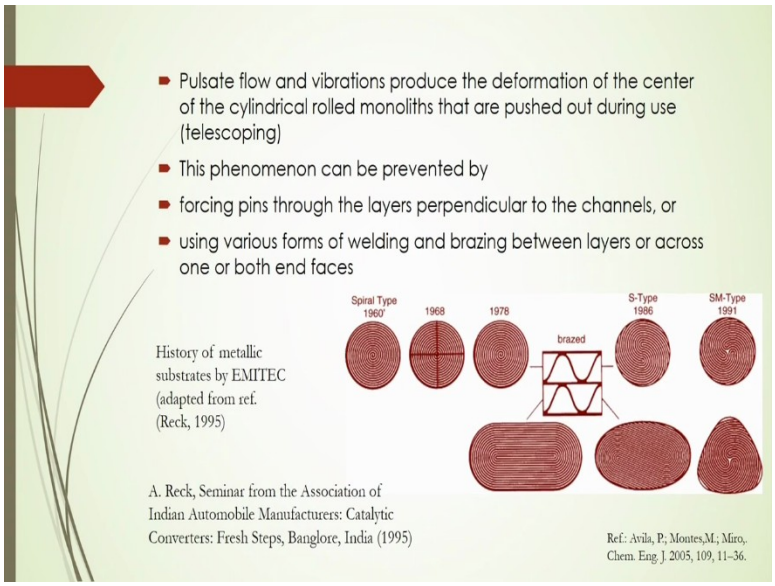

And then pulsate flow and vibrations produce the deformation of the centre of the cylindrical rolled monoliths that are pushed out during use there like telescoping application. This

phenomenon can be prevented by forcing pins through the layers that may be perpendicular to the channels or using various forms of welding and brazing between layers or across one or both end faces of this structure.

Now here some historical aspects of structure of this monolith are given here, from the beginning of 1960s spiral type even in 1968 a spiral and then there will be cross connection and then 1978 you know the spiral again and then brazed connections and then what is that S type in 1986 they have even SM-type 1991. So these types of several structures are manufactured by metallic substrates for this monolithic catalytic structure.

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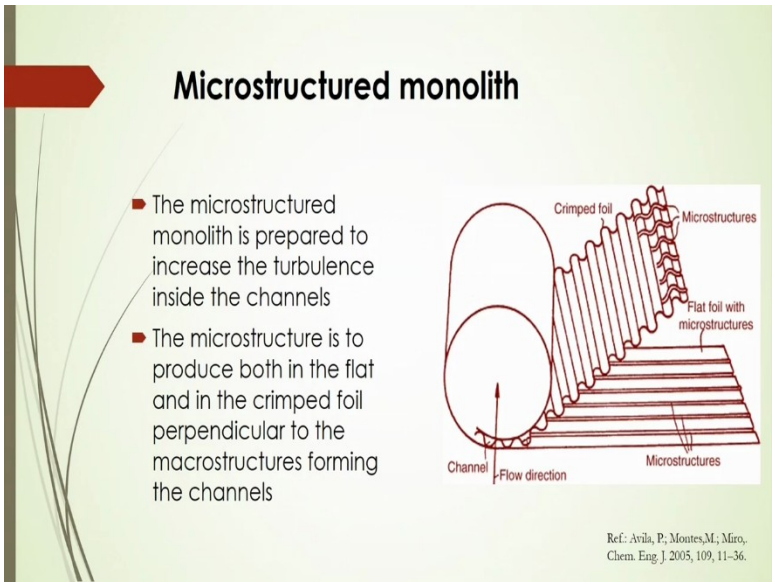

And other structure may be microstructure, Micron in size like channel based that may be micro channel based that monolithic structure is also there that is microstructure monolith is actually prepared to increase the turbulence inside the channels there. So to increase that turbulence you have to make this microstructure in channel base, a microstructure is to produce both in the flat as well as that crimped the foil that may be perpendicular to the macrostructure forming the channels there as per the figure shown here as per reported by Avila in 2005.

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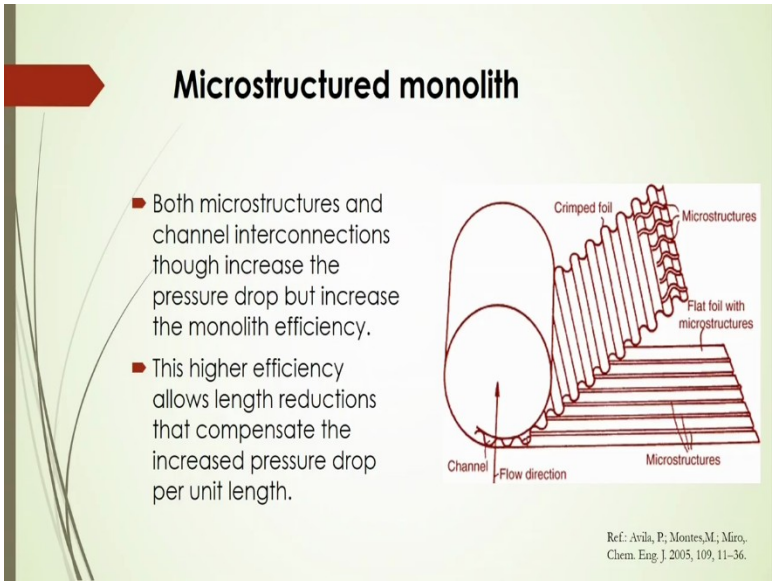

Now, these both microstructure and channel interconnection though increase the pressure drop, but it may increase the monolith efficiency. And this efficiency allows the length reduction that may compensate the increased pressure per unit length.

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So we have discussed that several aspects of that preparation methodology of different types of monolithic structures that is by extrusion, by Sol-gel method, by other methods also even for low surface how to produce that and also for high surface area, how to make that macro-porous structure, how to make the foam structure also and also what are the different conditions for making different types of monolithic structure that we have discussed in this lecture. I think you got some information about the preparation methods, for getting more

information of this preparation method you can go through these references for further reading, so I think it will be helpful for you, so thank you for this lecture.