CHAPTER III

WASHCOATING TECHNIQUES

The most widely used method of catalyzing monolithic supports consists of first coating the monolith with a high surface area material (usually an oxide) and then depositing on this layer the active material (usually a noble metal). Most pelleted supports can be made directly with high surface areas because mechanical considerations are not as critical as with monolithic supports. Monoliths are usually made with a surface area of only 0.1-1.0 m^2 gm^{-1}. As a result the monoliths are coated in a variety of ways with 5-20 wt % of high surface area to increase monolith surface area to 2.5-4.0 m^2/g based on total support weight. The surface area per total weight is low when compared with particulate supports, but with washcoated monoliths used in very high severity processes in which pore diffusion may be rate controlling, it is advantageous to have the metal on the external surface [4].

Automotive catalytic converter normally comprises of high surface area γ-Al_2O_3 coating ceramic honeycomb structure. At present, dipping and sol-gel techniques are the main techniques commonly use for applying alumina support on ceramic monolith. Detailed description of each technique is reviewed in sections 3.1 and 3.2 below:

3.1 Dipping Technique

In dipping method, the catalyzed carrier (eg. Pt/γ-Al_2O_3) is dispersed into an acidified aqueous slurry with a solids content of from 30-50 percent by weight. The mixture is ball milled for at least two hours to reduce the particle size (typically 10-25 microns) and generate the proper rheology for the subsequent monolith dipping operation.

The preparation of the finished catalyst involves dipping the monolith into the prepared slurry. The monolith generally has some wall porosity or surface roughness to ensure adhesion of the catalyzed washcoat. The wall porosity and surface roughness also have some influence of adhesion efficiency. After dipping the excess slurry which remain in the coated monolith cell has to be removed to prevent plugging. The cleaning usually performs by blowing compressed air. After cleaning the coated monolith is dried at about 110°C. The final step is calcination, which bounds the catalyzed washcoat securely to the monolith walls and decomposes and volatilizes the excess preparation components such as some binders. Calcinations are performed in hot air at temperatures between 300 and 500 °C. Great care must be taken to avoid rapid heat-up since H_2O trapped in the micropores can build up sufficient pressure to crack the monolith. Furthermore, exothermic reactions due to decomposing salts can cause localized high temperatures within the catalyst material, which can accelerate sintering of the coated alumina .

An alternative approach is to first coat the monolithic honeycomb with the uncatalyzed carrier (i.e. γ-Al_2O_3 only) , followed by drying and calcining. Then, the coated monolith is dipped into a solution containing the catalytic salts. This method relies on the electrostatic adsorption of the salts to the carrier surface. The supported catalyst is then dried and calcined to its final state [1].

The modified process for coating a catalyst support is also disclosed such as European patent number 0152052 dated August 21, 1985 issued to Kraus, Walter,Dr. et al [5]. According to this patent, the monolithic catalyst for purifying exhaust gases was prepared by coating a monolithic support with an aqueous slurry composition comprising a powder of active alumina, at least one compound of platinum-group element selected from the group consisting of platinum, palladium, rhodium ,and a powder of cerium hydroxide. Cerium hydroxide has strikingly increased durability to heat as compared with conventional catalysts prepared by using cerium nitrate and also has increased low-temperature activity, and that particularly when finely devided cerium hydroxide of a specific water content and specific particle size is used,its dispersibility is well controlled, and the presence of a small amount of an acid, the resulting catalyst can be finely pulverized into a slurry form to give a good aqueous slurry.

United States patent number 4,550,034 dated October 29, 1985 issued to Shimrock et al.[6] disclosed a method for impregnating the interior skeletal structure of a ceramic monolithic catalyst support with a slurry of catalyst material, wherein a predetermined amout of catalyst slurry is metered into contact with a first end of the support. In this method, a cover is placed over the periphery of a second, opposite end of the support in sealing relation thereto to define a vacuum chamber adjacent the second end. A vacuum is drawn on the cover to draw catalyst slurry into the skeletal structure from the second end whereby the interior skeletal structure is uniformly impregnated with the catalyst slurry.

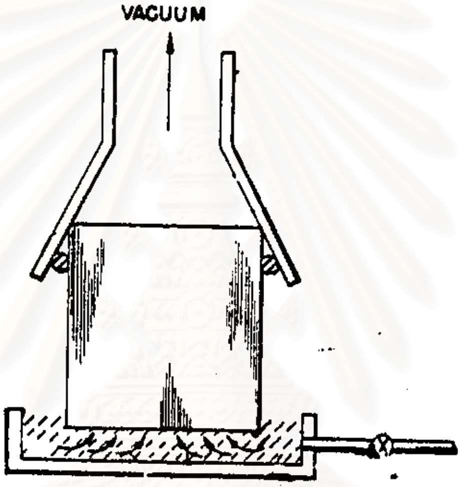

Figure 3.1 A schematic cross sectional view of one embodiment of a simplified system [6].

European patent number 0251708 dated January 7, 1988 issued to Fisher, Adrain John et al.[7] revealed another improved method of making a catalyst composition comprising an activated alumina coating stabilized against thermal degradation by applying a coating of alumina having one or more platinum group metal catalytic components dispersed thereon on to a carrier substrate and calcining the coating. The calcined coating is then impregnated with a solution of a thermal stabilizer-precursor and calcined again to provide a thermal stabilizer in the alumina. Bulk ceria, optionally an aluminum-stabilized bulk ceria, may also be added to the composition.

European patent number 0488515A1 dated March 6, 1992 issued to Messulam, Alec Moses et al. [8] presented a method of making an oxidation catalyst for use in automotive exhaust gas treatment by impregnating with platinum a mechanical carrier having a support comprised substantially of alumina to produce a composite having, by weight, 1-5% platinum, and impregnating (by incipient wetness) in the composite with an organo-titanium compound (titanium butoxide) and decomposing such compound to form a discontinuous titanium oxide phase on or adjacent the exposed portions of the composite in an amount of 0.1-2.5%.

United States patent number 5,212,130 dated May 18, 1993 issued to Addiego et al.[9] showed a method for producing the washcoat on the substrate which comprises steps of forming a slurry comprising at least one ionizable compound of A, where A is selected from barium, strontium, and combinations thereof, and A is in an amount of sufficient to yield AO in an amount of about 0.2-20% by weight of the washcoat, an aluminum oxide yielding species, and a medium wherein at least a portion of the ionizable compound ionizes to form ions of A, contacting the slurry with a substrate to form a green coating containing A and the aluminum oxide yielding species thereon, and heat treating the resulting green-coated substrate at a temperature and for a time sufficient to form a washcoat consisting essencially of AO-Al_2O_3 on the substrate, wherein A is homogeneously distributed throughout the Al_2O_3. The washcoat having a specific area, as measured by the N_2 BET method, of at least about 50 m^2/g, which surface area remains after at least two repeated exposures of the washcoat to temperature of greater than about 500 °C. Additionally, the slurry solid can be removed from the liquid , fired to form a material comprising AO-Al_2O_3 , and another slurry formed of the fired material and a medium. This slurry can then be contacted with a substrate to form the green coating which is then heat treated to form the washcoat.

Some manufactures that use metal substrates precoat them with the washcoat prior to wrapping or forming the metal into the monolithic structure. It is common to pretreat the surface of the metal to generate roughness to ensures good bonding to the washcoat. The metal is then calcined to produce a stable bound between the surface and the washcoat. The major advantage is coating uniformity, with no corners containing high localized amounts of washcoat. According to a current method for providing the washcoat on the substrate, it is repeatedly dipped in a suspension of gamma-alumina to form a coating which is subsequently calcined at an elevated temperature. Initial dippings of the substrate cause large amounts of washcoat to settle in the corners of the honeycomb channels. Additional dippings result in substantially narrowed channels which become circular in shape. The alumina in the corners is not accessible to the exhaust gases during converter operation and hence serves no use to the catalyst. Further, the channels are significantly narrowed. During converter use, this narrowing of the channels is sufficient to cause a back pressure within the converter. This back pressure has a marked detrimental impact on the operation of the converter in that it impedes the flow of the exhaust gases through the converter.

3.2 The Sol-Gel Process

Sol-gel techniques are one of future techniques which will allow elaborating new materials. Already, they are used to form inorganic fibers, ceramic layers, submicronic powders, glasses and monolithic pieces with new compositions. The sol-gel technique can be divided into two main routes depending on the nature of the precursors: metal salts or alkoxides. The technique involves inorganic polymerisation either in aqueous or in organic media. To be more precise, the hydroxylation and polymerisation of hydroxylated molecular species lead to a polymeric oxide species. In gelation processes molecules or particles connect into a three dimensional network. The sol-gel transition consists in clusters growing through condensation reactions, until their clusters collide producing a gel. In the colloidal way, a metal salt or an hydrated oxide reacts with excess water and precipitate of gelatinous hydroxide particles is obtained which is peptised with electrolytes and may then lead to a stable colloidal suspension. The particle size in the sol depends on the process parameters. Very small elementary particles are formed which are bound in larger aggregates (up to 1 micron). With an appropriate treatment, the aggregates can be broken down to a few nanometers. More or less regular and uniform packing results in structures with a mean pore size down to a few nanometers. From alkoxide derived sols, when hydroxide precipitation is avoided, finer structures can be obtained reaching one nanometer in size. This process has been recently explored in reverse microemulsions for the synthesis of titanium and iron alkoxide derived gels as well as for silica and titania particles. The control of the different steps of the process is often empirical and additives are commonly used to optimize the synthesized material and its performance. These additives can be solvent molecules, organic ligands, mineral anions, basic or acid catalysts, stabilising agents, binders, plasticisers of drying control chemical additives. In many cases these additives react chemically with the precursors and modify them at the molecular level.

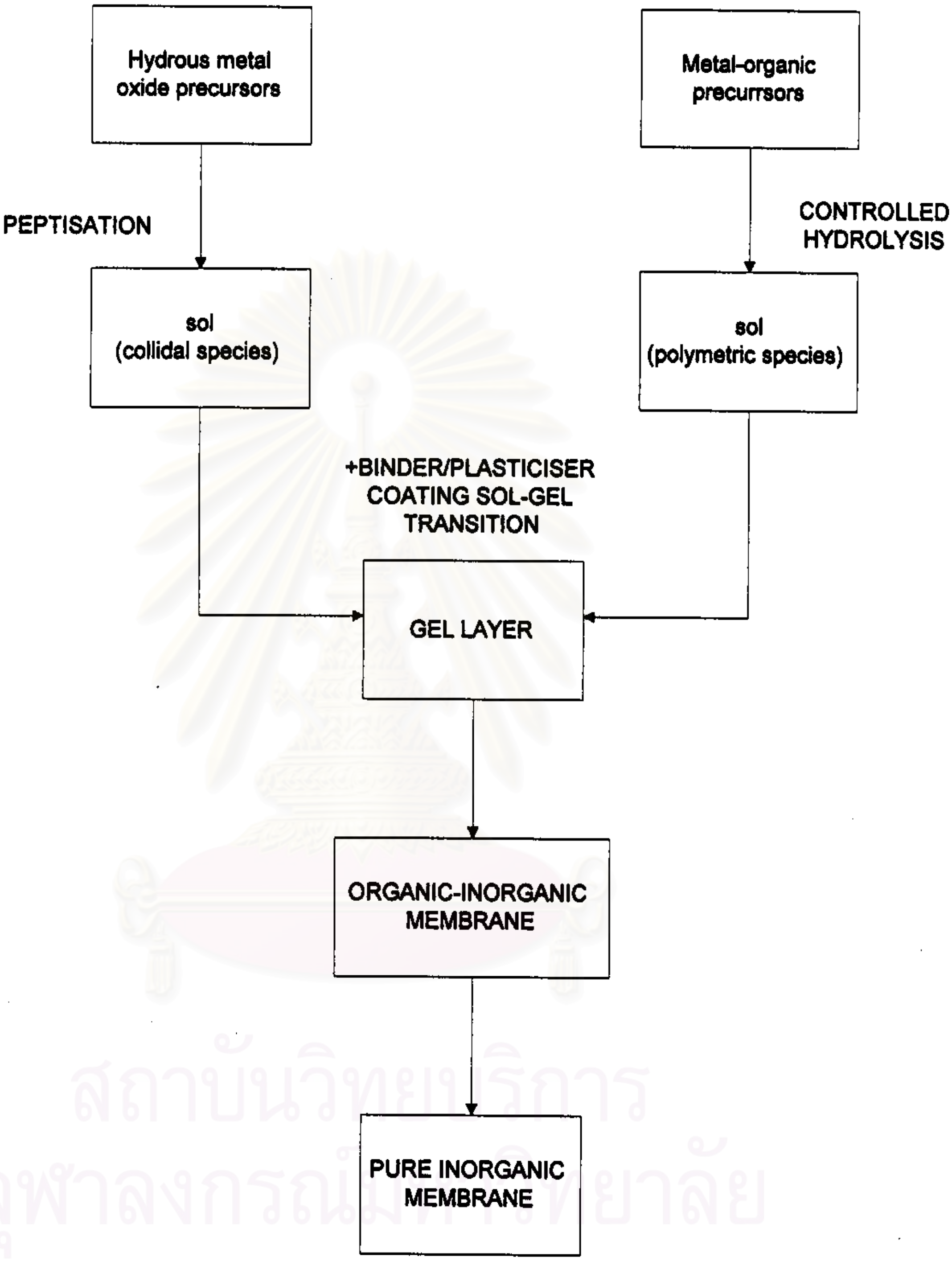

Figure 3.2 Schematic diagram of inorganic membranes preparation by sol-gel processing

Modification of sol-gel technique

The above mentioned procedure is fundamental coating technique of sol-gel process. However, the thickness of coating layer may not uniform enough for some applications. Therefore, some researchs have been set up to overcome this problem.

For example, the international patent number WO 93/03840 dated 4 March 1993 issued to Chaitanya Kumar et al.[10] disclosed a method for preparation aluminum oxide catalyst supports from alumina sols. The patent has revealed coating procedure by sol-gel technique which claimed to be able to provide more uniform washcoat thickness than the standard procedure. The method includes first applying a coating of a reactive mixture on the channeled substrate. Then, the coating on the substrate is dried at a temperature suitable to remove water present in the coating, preferably at or below about 100 °C. After that the dried coating layer is calcined at a temperature greater than about 300 °C, preferably between about 300 °C and 900 °C, to densify the coating and covert it to γ-alumina. The method also comprises repeatedly applying and drying the coating followed by calcining or doing all three steps until a coating of desired surface area is obtained. Preferably, the γ-alumina washcoat additionally comprises barium oxide, cerium oxide or mixtures thereof.

This patent has disclosed two alternative embodiments for applying γ-Al_2O_3 on ceramic monolith. In the first embodiment, a reactive mixture, liquid alumium alkoxide containing hydrolyzable alkoxy groups dissolved in alcohol vaporizable at or below 100 °C, mixed with water and acid is used. The alkoxide used has a chemical formula of $Al(OR)_3$, wherein R comprises an alkyl group, branched alkyl group, or aryl group of between 3 amd 6 carbon atoms. In the second embodiment where in the reactive mixture is made from aluminum alkoxide and alcohol, the coating is exposed to water vapor prior to drying. In either situation, after the step of applying a coating to the channeled substrate the channels are gas blown to remove excess coating

Patent number WO 93/03840 also directed to a method for providing a washcoat comprising γ-alumina on a channeled substrate, e.g., a ceramic honeycomb structure used in catalytic converters. The wascoat is used as a supporting structure for an exhaust gas catalyst.

According to a first embodiment of patent number WO 93/03840, a reactive mixture is made by combining a certain type of liquid aluminum alkoxide containing hydrolyzable alkoxy groups with water and acid, generally with stirring, wherein with this invention has the chemical formula: $Al(OR)_3$, wherein R comprises an alkyl group, branched alkyl group, or aryl group having between 3 and 6 carbon atoms. Exemplary of suitable aluminum alkoxides which may be use in this invention include, but are not limited to, ethoxides, (n-, or iso) propoxides, (n, sec, or tert-) butoxides, or (n, sec, or tert-) amyloxides such as tris(2-proixide), tris(2-amyloxide, tris tert-butoxide), and tris(sec-butoxide), with the latter butoxide being preferred. Compatible mixtures of such alkoxides may also be employed.

The aluminum alkoxide is combined with the water in at least an amount sufficient to allow for essentially complete hydrolysis of the alkoxide. Preferably, the ratio of water to alkoxide employed to form the mixture is between about 1.8 and 2.2 liters of water to moles of alkoxide, more preferably this ratio is about 2. This ratio can be varied, however, outside that disclosed above. Using greater amounts of water per mole of alkoxide results in an alumina of smaller particle size. When the alkoxide is added to water, the alkoxide hydrolyzes. The parent alcohol of the alkoxide may also be employed as a partial solvent in the reaction mixture. After mixing the alkoxide with the water, the mixture is allowed to stand, for example at room temperature, during which time further hydrolysis takes place. It may be desirable to heat the reactive mixture to encourage hydrolysis of the aluminum alkoxide. Preferable the alkoxide is added to water which is at an elevated temperature,. e.g, 80 °C

Acid is added to the reactive mixture preferable in only a minimal amount as is necessary to provide an elevated temperature when the acid is added. Exemplary acids are acetic, trifluoracetic, formic, oxalic, nitric, hydrochloric, and compatible mixtures thereof

Hydrolysis of the aluminum alkoxide in the reactive mixuture generates alcohol in the reactive mixture. It is generally desirable to remove at least a portion, if not substantially all, of the alcohol so formed from the reactive mixture and any parent alcohol which may have been used as solvent. This can be accomplished by subjecting the reactive mixture to heating to boil off the alcohol.

The reactive mixture may further comprise other components such as compatible salts of materials like barium and cerium. These components could be, e.g., alkoxides, nitrates, acetylacetonates, etc. of barium and cerium alkoxide or cerium alkoxide. The alkoxide groups would preferable contain 3 to 7 carbon atoms. The presence of barium oxide and cerium oxide in the washcoat improves the high temperature stability of the washcoat and the oxidation efficiency of the catalyst during use.

The mixture may be applied to the substrate by any suitable technique, including spraying or dipping. If the substrate is dipped into the mixture, after withdrawing it from the mixture, the channels of the honeycomb structure would generally be gas (e.g., air/nitrogen) blown to open the channels and remove excess coating. This leaves a very thin coating of the reactive mixture on the substrate. The coating is then subjected to drying at a temperature suitable to evaporate any solvents including water from the coating, that temperature preferably being about 100°C or less. This essentially removes any solvent present in the coating. Thereafter, the coating is calcined to densify the coating and form aluminum oxide. The calcination temperature generally is between about 300°C and 900 °C, often about 600 °C when the catalyst support is to be used for automotive applications. Generally, in order to provided a supporting structure for the catalyst of sufficient surface area, the substrate would be subjected to repeated coating and drying and then afterwards to a final calcining. If the substrate is rested on its side during drying, the substrate is preferably rotated 90°C with each successive drying so that is rested on a different side to obtain the most uniform washcoat. Alternately, the dipping, drying and calcining can be repeated in sequence until a washcoat of desired surface area is obtained. Generally, it is then desirable to subject the resultant coating to a lengthier calcination.

In the second embodiment disclosed in international patent number WO 93/03840 the reactive mixture is made from a certain type of liquid aluminum alkoxide mentioned above dissolved in alcohol vaporizable at or below about 100 °C, preferably being the parent alcohol or the alkoxide. For example, one such reaction mixture comprises aluminum trus-(2-propoxide) dissolved in 2-propanol. The reaction mixture comprises the alkoxide and alcohol preferably in amounts which provide 0.8 to 1.2 molar solutions, more preferably about 1.0 molar solutions of the alkoxide. The reactive mixture may further comprise other components, e.g., compatible salts of materails like barium and cerium as disclosed in the first embodiment. Preferably, in either embodiment if barium and/or cerium are to be incorporated in the γ-alumina washcoat, they would be incorporated by subjecting the calcined γ-alumina washcoat on the substrate to a solution of a barium or cerium salt, e.g., cerium nitrate. Afterwards, the washcoat would again be calcined.

Because the reactive mixture of aluminum alkoxide is sensitive to moisture, its formation is desirably carried out in a substantially moisture free environment. The reactive mixture is applied to a channeled substrate of type described previously wherein by any suitable technique, including spraying or dipping. After application of the reactive mixture, the channels of the structure would preferably be gas blown (e.g., nitrogen) to remove excess reaction mixture. The reactive mixture coating is subsequently exposed to water vapor, e.g., moist air, sufficient to cause hydrolysis of the alkoxide. The coating is then subjected to drying along the lines of the procedure used in the first embodiment disclosed herein. During both exposure to humidity and drying, the substrate is preferably rested on a different consecutive side to encourage uniform coating. Thereafter, the coating is calcined to densify the coating and form aluminum oxide. The calcination temperature generally is between about 300 °C and 900 °C, often about 600 °C when the catalyst support is to be used for automotive applications. The substrate may be subjected to repeated coating, humidity, drying and afterwards to a final calcining. Alternately, the dipping, drying, exposing to water vapor, and calcining can be repeated in sequence until a washcoat of desired surface area is obtained. Generally, it is then desirable to subject the resultant coating to a lengthier calcination.

Coatings according to the patent have surface areas of at least $25m^2/g$ in order to provide adequate surface area for the catalyst. Advantageously, according to the mentioned invention such high surface area is provided with less loading of washcoat on the substrate. For example while 33% by weight of a conventional washcoat made by dipping the substrate in a dispersion of γ-alumina, baria and ceria is required to achieve a desired surface area of 25-30 m^2/g of total substrate/washcoat weight, a washcoat made according to the present invention method of 14.7% by weight provides the same surface area. Consequently, the invention washcoat provides decreased washcoat material without a corresponding decrease in the surface area of the washcoat. Hence, the channels of a honeycomb substrate uniformly coated according to patent number WO 93/03840 can maintain markedly more of their openness while at the same time providing a desired surface area of washcoat so that catalyst effectiveness is maintained. The back pressure problem associated with the narrowing of the channels thus is substantially eliminated for more efficient operation of the catalytic converter.

It is believed that using the specific sol-gel technique of patent number WO 93/03840 provides a coating on the substrate comprising particles smaller in diameter than those provides from conventional coating system. It is believed that the disclosed techniques allow the formed coating to be thinner and avoid excessive buildup in channel corners experienced with conventional washcoats.

Figure 3.3 shows an optical micrograph of a washcoat on a honeycomb substrate prepared according to the first embodiment of the patent number WO 93/03840. For comparison, figure. 3.4 shows an optical micrograph of a commercial washcoat on a similar honeycomb structure at the same magnification. Figure. 3.3 shows channels which are clearly more open and presents only a thin uniform layer of washcoat. In contrast, the commercial washcoat is non-uniform and thicker so that the channel volume is considerably decreased.

The washcoat formed on the substrate according to the patent number WO. 93/03840 is claimed to be able to advantageously use as a supporting structure for an exhaust gas conversion catalyst, i.e., catalyst to convert exhaust gases to more desirable gases. The catalyst may be provided into the washcoat by any suitable means, e.g., by contacting the porous calcined washcoat with an aqueous solution of a catalyst or mixture of catalysts. Generally, precious metals are used as exhaust gas catalysts. Exemplary of precious metals are palladium, platinum, rhodium and iridium. For example, nitrates of such metals may be used to prepare an aqueous solution of a catalyst used to impregnate the porous washcoat. The exhaust gas to be treated may be that generated by internal combustion engines such as automobile engine.

Figure 3.3 An optical micrograph of a washcoat/catalyst on a honeycomb substrate where the washcoat is provided according to a first embodiment the present in patent number WO 93/03840 [10].

Figure 3.4 An optical micrograph of a commercially available washcoat/catalyst on a similar honeycomb substrate [10].

The improved method of depositing a high surface area alumina as a uniformly thin film on a relatively low surface area refractory support ,and comprises impregnating low surface area refractory support with an alumina sol containing at least about 5 weight percent of a soluble organic plasticizer. was also presented in the United States patent number 3,767,453 dated October 23, 1973 issued to Hoekstra [11]. An aluminum chloride sol prepared by effecting a reduction in the chloride anion concentration of an aqueous aluminum chloride solution to provide an aluminum/chloride ratio of from about 1:1 to about 2:1, said sol containing from about 10 to about 20 weight percent polyethylene glycol characterized by an average molecular weight of from about 200 to about 3000; and calcining the impregnated honeycomb support at temperature of from about 425 to 1100 °C.

United States patent number 3,870,545 dated March 11, 1975 issued to Tabacek et al.[12] presented an improved catalyst composition comprising a catalytic metal on an alkoxide-modified support. The alkoxide-modified support comprises a core support material having on its outer surface a thin layer of a metal oxide produced from a precursor metal alkoxide. The examples of typical precursor metal alkoxides include $Al(OCH(CH_2CH_3)(CH_3))_3$ and $Al(OC_5H_{11})_3$. The alkoxide-modified support is prepared by impregnating the desired core support material with a solution of an alkoxide precursor of the desired metal oxide. The solution used in impregnating the core support material preferably is organic, the only requirement being that an adequate amount of precursor compound for the selected metal oxide is soluble in the solvent used in preparing the impregnating solution. Hydrocarbon or alcohol solutions, preferably hexane solutions, are normally used for convenience. When using the impregnation technique the metal alkoxide impregnating solution is contacted with the core sopport material for a time sufficient to deposit the metal alkoxide precursor material onto the carrier either by selective adsorption. The excess solvent may be evaporated during drying leaving behind the precursor metal alkoxide.