METHOD OF DEPOSITING A HIGH SURFACE AREA ALUMINA FILM ON A RELATIVELY LOW SURFACE AREA SUPPORT

This invention relates to a novel method of catalyst manufacture. More particularly, this invention relates to a method of depositing a high surface area alumina as a uniform thin film on a relatively low surface area ceramic support. The present invention is particularly adapted to the manufacture of a rigid, unitary, catalytic element useful to catalyze the oxidation of carbon monoxide and unburned hydrocarbons contained in exhaust gases of an internal combustion engine.

Certain refractory materials, for example, the various high surface area refractory inorganic oxides such as alumina, silica, zirconia, alumina-silica, alumina-zirconia, etc., are efficient supports for any number of catalytically active materials when utilized in a particulate form. Such refractory supports are readily manufactured and commonly employed in the form of powders, pills, pellets, extrudates, or other particulate form including micro and macro spheroids resulting from spray-drying or dropping techniques. However, the described refractory materials, which embody the high surface area characteristics so essential to efficient catalyst support material, exhibit a physical instability under conditions of thermal stress which makes them generally unsuitable for use as a larger unitary support structure for catalytic components in the conversion, for example, of automobile exhaust gases.

On the other hand, the desired physical stability is realized by utilizing certain ceramic materials such as sillimanite, petalite, cordierite, mullite, zircon, zircon mullite, spodumene, magnesium silicates, aluminum silicates, etc., as a unitary catalyst support. However, although such ceramic materials are characterized by a low coefficient of thermal expansion — a particularly desirable feature in the larger unitary catalyst structures herein contemplated, they are invariably also characterized by a relatively low surface area which makes them generally unsuitable as an efficient catalyst support material. It has therefore been the practice to deposit a high surface area film or coating on the surface of the ceramic material, e.g., a thin, high surface area refractory inorganic oxide film or coating.

It is an object of this invention to present a novel method of applying a high surface area alumina as a uniform thin film on a rigid, low surface area, unitary support. The method of this invention is particularly directed to the manufacture of catalysts characterized by a rigid, unitary or homogenous skeletal structure, frequently referred to as a monolithic structure, comprising thin laminated sheets of a corrugated ceramic material providing a plurality of adjacent, parallel and uni-directional channels therethrough, and commonly referred to as a honeycomb. While the method of this invention can also be used to apply high surface area coatings on particulate, finely divided catalyst supports, the real advantage is in the application of high surface area coatings to the larger, unitary support structures in the manufacture of catalytic elements for inclusion in an exhaust gas converter system.

In one of its broad aspects, the present invention embodies a method of depositing a high surface area alumina as a uniformly thin film on a relatively low surface area refractory support, and comprises impregnating said low surface area refractory support with an alumina sol containing at least about 5 wt. percent of a soluble organic plasticizer; and calcining the impregnated refractory support at a temperature of at least about 425°C.

One of the more specific embodiments is in a method of depositing a high surface area alumina as a uniformly thin film on a cordierite honeycomb support which comprises impregnating said support with 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 wt. percent polyethylene glycol characterized by an average molecular weight of from about 200 to about 3,000; and calcining the impregnated honeycomb support at a temperature of from about 425° to about 1100°C.

Other objects and embodiments of this invention will become apparent in the following more detailed specification.

The alumina sols herein contemplated are such as are formed by reducing the acid anion concentration of an aqueous solution of an acid salt of aluminum whereby olation occurs with the formation of inorganic polymers of colloidal dimension suspended in the remaining liquid. Such sols are in contrast to a colloidal suspension of discrete, minute particles of a preformed alumina. Suitable acid salts of aluminum include aluminum chloride, aluminum sulfate, aluminum nitrate, aluminum acetate, and the like.

Reduction in the acid anion concentration of said solution can be accomplished in any conventional or otherwise convenient manner. For example, an aqueous aluminum chloride solution can be subjected to electrolysis utilizing an electrolytic cell with a porous partition between the anode and cathode whereby acid anions are removed from the cathode compartment with the formation of an alumina sol therein. In some cases, as with an aqueous aluminum acetate solution, where the anion is sufficiently volatile, the desired reduction in anion concentration can be effected simply by heating. A particularly suitable method of preparing a sol involves the use of aluminum metal as a neutralizing agent in conjunction with, for example, an aqueous aluminum chloride solution. In this instance, the salt of neutralization is itself a hydrolyzable aluminum salt subject to ultimate sol formation.

One convenient and preferred method, particularly suitable for the preparation of an aluminum sol comprises digesting aluminum pellets or slugs in aqueous hydrochloric acid, and reducing the chloride anion concentration of the resulting aluminum chloride solution through use of an excess of aluminum reactant as a neutralizing agent. The described sols are preferably prepared to contain about 15 wt. percent aluminum, preferably from about 12 to about 15 wt. percent, with an aluminum/chloride atom ratio of from about 1:1 to about 2:1. Generally, the sols will contain from about 8 to about 12 wt. percent chloride.

Pursuant to the present invention, the aforesaid sol further contains an organic plasticizer dissolved therein. The organic plasticizer is selected to improve the flexibility characteristics of the sol whereby blistering and cracking of the surface coating is minimized during the initial drying and calcining stages of the impregnated support material, and a durable, thin, uniform film of alumina is formed thereon. The organic plasticizer is suitably a polyethylene glycol with an av-