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COATED FILM OF CATALYTICALLY ACTIVE OXIDE ON A REFRACTORY SUPPORT

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No Drawing. Continuation-in-part of application Ser. No. 527,511, Feb. 15, 1966, which is a continuation-in-part of application Ser. No. 256,819, Feb. 7, 1963, and also is a continuation-in-part of application Ser. No. 527,494, Feb. 15, 1966, now Patent No. 3,331,787, which is a continuation-in-part of application Ser. No. 256,820, Feb. 7, 1963. This application July 14, 1967, Ser. No. 653,322

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ABSTRACT OF THE DISCLOSURE

A catalyst composition is made having a platinum group metal and a film of catalytically active metal oxide supported on an inert, substantially catalytically inactive refractory support which exhibits a porosity of at least 0.03 cc./gm., say 0.1 to 0.3 cc./gm., and a substantial water pore volume. There are unobstructed openings or channels going through the support through which pass the chemical materials converted by the catalyst, e.g. automobile exhaust gases and oxygen, during its use. Calcined alumina is a suitable film of catalytically active metal oxide and alpha-alumina and zircon-mullite can be used as supports. The support is mainly crystalline and can have a macropore distribution such that over 95% of the pore volume is in pores having a diameter of over 2,000 A. and over 5% of the pore volume is in pores having a diameter of over 20,000 A. One way of making the catalyst is to deposit the film on the support and then impregnate the film with the platinum group metal. The platinum group metal can be fixed on the support by treatment with, for instance, hydrogen sulfide. As a final preparation step the catalyst can be calcined.

This application is a continuation-in-part of application Ser. No. 527,511, filed Feb. 15, 1966, which in turn is a continuation-in-part of application Ser. No. 256,819, filed Feb. 7, 1963; and this application is also a continuation-in-part of application Ser. No. 527,494, filed Feb. 15, 1966, now Pat. 3,331,787, which in turn is a continuation-in-part of application Ser. No. 256,820, filed Feb. 7, 1963. Applications Ser. Nos. 256,819; 256,820, and 527,511 are abandoned.

This invention relates to the manufacture of catalysts and more particularly to catalysts composed of a relatively porous refractory support provided with a thin film or coating of a catalytically-active refractory metal oxide, which film is impregnated with a catalytically-active metal. In a more specific embodiment the present invention is directed to the preparation of catalysts having a catalytic structure that makes them particularly suited for use as oxidation catalysts in the purification of automobile exhaust gases and industrial waste gases.

The metals and metal oxides of Group VIII of the periodic table have long been acknowledged as hydrocarbon oxidation catalysts. They have, for example, been employed per se in pellet or granular form but more commonly have been deposited as the catalytically active component on a support or carrier. While many of these oxidation catalysts perform successfully under relatively mild conditions, there has been current demand for an oxidation catalyst which is active enough chemically and rugged enough physically to withstand extremely severe operating conditions over a long period of time. For example, the use of oxidation catalysts for the purification of exhaust gases from automobiles has been suggested in the past but has not been widely adopted due to the fact that the catalysts available have either been of insufficient activity, exhibited short life and/or were incapable of sustaining the physical stresses and strains involved. This invention concerns the preparation of a catalyst of high activity, long life and extreme durability.

In accordance with the present invention, a film or coating of a refractory metal oxide is provided in a chemically, i.e., catalytically, active form on the external surface of a catalytically-inert, relatively porous refractory material and the film is impregnated with a water-soluble compound of a platinum group metal. The impregnated film, which may be continuous or discontinuous but is usually relatively uniform over the surface, is in the preferred embodiment, treated with, for instance, hydrogen sulfide to fix the active metal impregnant in a relatively water-insoluble form, i.e., the sulfide when hydrogen sulfide is used.

The inert refractory support or carrier of the present invention, onto which an active refractory metal oxide film is deposited, is a solid unitary or monolithic skeletal body having a plurality of unobstructed openings or channels therethrough in a direction of desired fluid flow and is preferably of a size that permits occupancy by one or more of the bodies of at least a major portion of the cross-sectional area of the reaction zone to be employed. Advantageously, the unitary body is shaped to fit the reaction zone into which it is to be disposed.

The support or carrier is constructed of a substantially chemically-inert, substantially catalytically-inactive, rigid, solid material capable of maintaining its shape and strength at high temperatures, for instance up to 1100° C. or more. The material often has a bulk density of about 0.45 to 1.05 grams per cubic centimeter, preferably about 0.5 to 0.9 gram per cubic centimeter, is unglazed, and can contain a major proportion of crystalline material. Preferably the material is essentially crystalline in form and advantageously at least about 90% crystalline material, and is marked by the absence of any significant amount of glassy or amorphous matrices, for instance, of the type found in porcelain materials. Further, the support has considerable accessible porosity as distinguished from the substantially non-porous porcelain utilized for electrical appliances, for instance, spark plug manufacture, characterized by having relatively little accesible porosity, typically about 0.011 cc./gram. The accessible pore volume of the support of this invention, not including the volume of the fluid flow channel, is at least 0.03 cubic centimeter per gram of support, preferably in the range from 0.1 to 0.3 cc./g. Such measurements of accessible pore volume were made by pressurizing the material with Hg from atmosphereic pressure up to about 1200 pounds, which is equivalent to a measument of pores between about 1400 A. and 100,000 A. in diameter. The Hg penetrates the pores without wetting the material. The support exhibits a substantial water pore volume, i.e. when immersed in water and wetted and then when essentially all of the free water is removed from the channels the support retains a considerable amount of absorbed water in its pores. The retained water generally constitutes at least about 10% based on the dry weight of the support before immersion, and often this amount does not exceed about 60% or somewhat more. Preferably, the amount of retained water or water pore volume is about 15 to 50% of the dry support. Many of the supports exhibit water pore volumes in the range of about 20 to 40 or 45%.

The walls of the channels of the unitary skeletal support of the invention can contain macropores in com-