CARRIER-SUPPORTED CATALYST

This application is a continuation of application Ser. No. 557,925 filed Mar. 13, 1975 now abandoned.

The present invention relates to a carrier-supported catalyst and to a process for making it.

Carbon monoxide and hydrocarbons are oxidized in contact with catalysts, wherein the active ingredients are either noble metals belonging to group VIII of the Periodic System or are mixed oxides, e.g. of copper, manganese and nickel, the mixed oxides, which are less costly, being preferred so as to enable wide use to be made of those catalysts, e.g. for the decontaminations of automobile exhaust gas. The catalysts used to this end are required to be abrasionproof, to be thermally shockproof, to be sinterproof, to have a low starting temperature, if possible lower than 200° C, and to have a constant activity, even if heated for prolonged periods of time to temperatures of at least 800° C.

U.S. Pat. No. 3,493,325 describes a catalyst deposited, e.g. on gel-like or activated alumina, for the catalytic oxidation of exhaust gas of internal combustion engines. The active ingredients applied to the carrier are selected from oxides of copper, nickel, cobalt, iron, chromium, manganese or mixtures thereof.

A further catalyst has been described in German Patent Specification 1 272 896, which is deposited on a carrier containing at least 30 weight % of alumina together with alkali metal and alkaline earth metal oxides, and heat-resistant filler materials. The catalytically active ingredients inter alia include oxides of copper, nickel, cobalt, manganese and cerium.

These prior art catalysts are not fully satisfactory, however, as their activity varies depending on whether they are contacted with an oxidizing or reducing gas. More particularly, they are highly active if contacted with a mixture consisting of the gas to undergo oxidation and a stoichiometric or slightly understoichiometric proportion of oxygen, whilst they are less active if contacted with a mixture containing an excess of oxygen.

In other words, it is necessary for those prior art catalysts to be contacted with a gas mixture containing a stoichiometric proportion of oxygen, based on the carbon monoxide and hydrocarbons present in the gas mixture. This is especially necessary in an attempt (a) to maintain the catalyst active and (b) to ensure complete combustion of the gas to undergo oxidation. It should be borne in mind, however, that the exhaust gases of internal combustion engines always contain variable proportions of carbon monoxide and hydrocarbons so that considerable expenditure in respect of equipment is at least necessary to achieve this, if at all.

It is accordingly an object of the present invention to provide a carrier-supported catalyst whose activity remains unaffected in contact with gas mixtures, irrespective of the oxygen concentration therein, and which additionally has a low starting temperature.

To this end, the invention provides a carrier-supported catalyst, wherein alumina partially converted to α-Al_2O_3 is the carrier and cerium in oxide form is the catalytically active ingredient, the catalytically active ingredient constituting 0.2 to 10 weight % of the carrier being deposited thereon.

Further preferred features provide:

a. for the alumina to be poor in alkalies;

b. for the alumina to contain at most 0.2 weight % of alkalies, and

c. for 0.5 to 8 weight % of cerium in oxide form to be deposited on the carrier.

The invention also provides a process for making the carrier-supported catalyst, which comprises compressing hydrous alumina or unstable anhydrous alumina into shapes; annealing the shapes for periods within the range 10 and 20 hours at temperatures within the range 1000° and 1250° C; impregnating the annealed shapes with an aqueous solution of a cerium salt of a readily decomposable acid; drying the cerium salt so applied to the shapes at temperatures within the range 130° and 150° C.; decomposing the dry cerium salt by gradually heating the shapes to temperatures within the range 200° and 300° C and 450° and 550° C, respectively; and annealing the resulting shapes containing cerium oxide at temperatures within the range 700° and 900° C.

Further preferred features of the present invention for making the carrier-supported catalyst provide:

d. for boehmite to be used as the hydrous alumina;

e. for δ-Al_2O_3 to be used as the unstable anhydrous alumina;

f. for the alumina to be compressed in admixture with graphite;

g. for the alumina to be compressed in admixture with between 3 and 10 weight %, preferably 5 weight %, of graphite;

h. for the graphite to be burnt off prior to the annealing step;

i. for the graphite to be burnt off at temperatures within the range 550° and 750° C, preferably 650° C; and

j. for cerium nitrate to be used as the cerium salt of a readily decomposable acid.

The carrier-supported catalyst of the present invention is particularly useful for the oxidation of carbon monoxide and hydrocarbons with an excess of oxygen to ensure complete combustion thereof.

Vital to the present catalyst is more particularly the alumina carrier, which is partially converted to α-Al_2O_3. Carrier-supported catalysts having the catalytically active cerium oxide applied to incompletely dehydrated aluminum oxide monohydrate or to highly crystalline α-Al_2O_3 are considerably less active catalytically.

In addition to this, it is necessary for the alumina carrier to contain little alkali as alkalies are known to increase the starting temperature of carrier-supported catalysts.

The cerium salt used in aqueous solution for impregnating the carrier and applying the catalytically active ingredient thereonto should have an anion which can be completely removed later, during calcination. The preferred cerium salt is cerium nitrate. Cerium sulfate produces catalysts of reluctant activity.

The carrier should preferably be impregnated with a quantity of cerium salt solution which just corresponds to its volume of pores. In other words, it is the concentration of the cerium salt solution used for impregnation and the volume of pores of the carrier which determine the cerium content of the resulting carrier-supported catalyst.

With respect to catalysts having a low starting temperature, it is necessary for them to be made with the use of very pure cerium salt. So-called cerium mixed metal salts should conveniently not be used.

Qualitatively highly reliable carrier-supported catalysts are obtained in those cases in which the cerium salt