

tion products of compounds containing phosphorus, boron, manganese, sulfur, bromine, chlorine, zinc, calcium, iron, and others. It is well known that many of these elements and their compounds are potential catalyst poisons. Several of these poisons may be taken into consideration when designing a catalyst to be used in a normal chemical process. Indeed, for an exhaust gas application many catalyst systems have been discovered which are resistant to several of these contaminants, only to be subject to poisoning by others. Alternatively, in the chemical plant the feed gases may be scrubbed to remove the deleterious constituents. However, because of the required simplicity and economy of space, these alternatives are not practical in an exhaust gas application. Therefore, a practical solution to this problem requires a catalyst which is relatively immune to all the various contaminants present in exhaust gas streams emitted by the modern vehicle.

It is an object of this invention to provide unique catalysts. A further object is to provide catalysts which are particularly resistant to the potential catalyst poisons found in the exhaust gas stream of modern vehicles. A further object is to provide a method of oxidizing substantial amounts of the unburned hydrocarbons and carbon monoxide found in the exhaust gas stream of modern internal combustion engines.

According to the present invention, we provide novel catalysts particularly adapted for conversion of exhaust gas components, said catalysts consisting essentially of a "transitional" activated alumina which has been impregnated, or with which has been mixed, copper oxide in amount such that the catalyst system contains between 0.5 and 25 weight percent of copper as said oxide. The present invention also embodies the method of substantially eliminating and converting unburned hydrocarbons and carbon monoxide from the exhaust stream of internal combustion engines, which comprises passing said exhaust over and through the above catalysts.

In another embodiment of this invention, we provide novel copper catalysts containing one or more promoter metals selected from the group consisting of silver, cobalt and vanadium to improve catalyst performance. The promoter metal(s) may be present in a concentration of from about 0.1 to 10 percent by weight.

We have found the combination of "transitional" aluminas and copper oxide to be critical. In other words, our catalysts are superior to those prepared using "transitional" alumina but using other metals in place of copper, and superior to copper catalysts wherein other catalyst carriers are used in place of the "transitional" aluminas employed in this invention.

By the use of our invention, substantially all of the carbon monoxide is converted to carbon dioxide and a great percentage of the unburned hydrocarbons are completely oxidized to carbon dioxide and water. Further, the catalysts of this invention are active over a wide temperature range and under a variety of engine operating conditions. Other important aspects of our catalysts are: excellent thermal stability at extremely high temperatures; they do not catalyze the oxidation of nitrogen; and they function substantially independently of sulfur content of the gasoline. One of the important properties of the present catalysts is their resistance to the many catalyst poisons in exhaust gas. An outstanding feature is their resistance to the poisoning effects of the many sulfur compounds found in commercial gasolines. The oxidation products of sulfur are well known catalyst poisons. Many materials otherwise suited as catalysts are adversely affected by the oxidation products of sulfur, losing activity with use and eventually being rendered inactive.

Particular attention is called to the alumina used as the carrier material in the catalysts of this invention. Generally, the carrier material serves as a support or a binder for the active catalytic agent, but in itself has little, if

any, catalytic activity for the reaction in question. Other mechanical functions might be to impart physical strength and to serve as an aid in the dissipation of heat to prevent sintering. For such purposes, any one of the well known carrier materials may be equally effective. Aside from purely mechanical functions, a carrier material may serve to give a larger exposure of the catalytic agent, increase thermal stability, modify catalytic selectivity and provide increased resistance to poisoning of the active agent. Also a complex formation may take place between the carrier and the active agent which results in an overall material having better catalytic properties per unit area than the active agent alone. It is because of these non-purely mechanical functions that a carrier material may be specific for a given catalytic agent with respect to a particular reaction; that is, although a catalytic agent on one carrier material may be an excellent catalyst for a specific reaction, it may behave entirely differently and be a poor catalyst if supported by a different carrier material.

We have found that copper oxide on a particular type of transitional alumina, to be described below, is an excellent catalyst for the oxidation of unburned hydrocarbons and carbon monoxide in the exhaust gas streams of internal combustion engines. However, catalysts composed of copper oxide on other well known catalyst carriers and, indeed, even on other types of aluminas, result in inferior catalysts. In other words, a particular type of transitional alumina is specific for copper oxide for the oxidation of the hydrocarbons and carbon monoxide found in the exhaust stream of internal combustion engines.

In general, the transitional aluminas used in this invention are prepared by heating a starting alumina selected from the class consisting of alpha alumina trihydrate, beta alumina trihydrate and alpha alumina monohydrate to a temperature of at least 100-150° C. for a period of time sufficient to permit substantial conversion to a transitional alumina but insufficient to convert a substantial fraction of the transitional aluminas irreversibly to the inactive alpha alumina. Heating alpha alumina trihydrate leads to the formation of partially amorphous and partially crystalline transitional aluminas consisting essentially of a mixture of chi, alpha monohydrate and amorphous forms of alumina, as described in "Alumina Properties," by Allen S. Russell et al., Aluminum Company of America, Pittsburgh, Pa., 1956. The controlled calcination of beta alumina trihydrate leads to mixtures of alpha alumina monohydrate and eta alumina. In general, prolonged heating above about 1000° C. should be avoided. Our carriers in some cases may contain small amounts of either the starting material or alpha aluminas, or both.

The preferred transitional aluminas which we use are those whose surface area/mass ratio is at least 75 square meters per gram ($m^2/g.$) and those having a silica content of from 0.01 to about 5 percent. If the surface is greater than the above minimum but the silica content greater than the above maximum, the alumina does not function well. By the same token, if the silica content is from 0.01 to about 5 percent, but the surface area is below 75 $m^2/g.$, the alumina does not function as efficiently.

In illustration of the importance of the above properties, we have tested aluminas with surface areas as high as 350 $m^2/g.$ but with a silica content greater than 5 percent. These have resulted in catalysts with inferior properties with respect to exhaust gas conversion. Also, an alumina with a silica content less than 5 percent but with a surface area of only 0.5 $m^2/g.$ was ineffective as a support for copper oxide.

Certain aluminas meeting the requisites of this invention are commercially available. Included in these are those sold by Aluminum Company of America as "Desiccant Grade Active Aluminas; Grade F-1, F-3 and F-10" and by Kaiser Aluminum Company as "KA-101."