United States Patent Office

3,730,909

Patented May 1, 1973

3,730,909
HYDRAZINE DECOMPOSITION CATALYST

Warren E. Armstrong, Lafayette, and Hervey H. Voge, Berkeley, Calif., assignors to Shell Oil Company, New York, N.Y.

No Drawing. Filed Apr. 5, 1966, Ser. No. 540,413
Int. Cl. B01j *11/82*
U.S. Cl. 252—434 5 Claims

ABSTRACT OF THE DISCLOSURE

Improved catalysts for the decomposition of hydrazine and lower alkyl-substituted hydrazines comprise a platinum group metal catalyst in combination with a solid oxidizer hypergolic on a porous, inorganic solid support.

This invention relates to catalytic decomposition of hydrazine and lower alkyl-substituted hydrazines. It deals with new and improved catalysts for carrying out these decompositions more advantageously, especially in rockets and the like.

Hydrazine and lower alkyl-substituted hydrazines have found extensive application as gas generants in supersonic vehicles. They not only serve as monopropellant fuels for rockets but also are used in operation of auxiliary powder plants for guided missiles and the like. A variety of hydrazine decomposition catalysts have been suggested for use in these devices. Catalysts containing platinum group metals have been proposed in U.S. Pats. 3,081,595 and 3,086,945, for example, and especially effective hydrazine decomposition catalysts of this type are described in our copending application Ser. No. 371,879, filed May 28, 1964. These catalysts have the advantage over previous catalysts of providing repeated cold starts with less than 50 millisecond delay and without appreciable overpressure at the start. The cost of these catalysts is relatively high, but is well warranted because of the infallible operation they provide under the adverse conditions of use in space.

There is need for a cheaper catalyst having the same advantageous low temperature starting characteristics for use where a long effective life or repeated use are not required. An important object of the present invention is the provision of a new type of hydrazine decomposition catalyst which supplies this need. A more particular object is to provide catalysts especially for use in missiles having only a relatively short operating period. A special object is the provision of a reasonably priced catalyst suitable for decomposing hydrazine in the guidance mechanism of missiles where only one low temperature start will be required but having sufficient catalytic activity to sustain decomposition after that start and to give repeated starts at the higher catalyst temperature which will exist during the remainder of the flight. Other objects and advantages of the invention will be apparent from the following description.

The novel and advantageous hdyrazine decomposition catalysts of the invention comprise a platinum group metal catalyst in combination with a solid oxidizer hypergolic with hydrazine and the lower-alkyl hydrazines, the mixture being carried on a porous solid support. It has been found that with combination catalysts of this type only a small amount of platinum group metal is necessary to obtain effective starts at temperatures as low as 0° F. with a liquid hydrazine or blends thereof with other materials.

The catalyst has sufficient permanent activity to sustain the required decomposition and to give repeated starts at the temperatures of about 200° C. or above which are maintained in the catalyst for an appreciable time after stopping the decomposition. As a result the catalyst functions efficiently throughout the entire time required for the missile to complete its trajectory.

Any of the six platinum group metals or mixtures thereof may be used in preparing the new spontaneous catalysts for decomposition of the hydrazines. Ruthenium, rhodium, palladium, osmium, iridium, and/or platinum are all effective decomposition catalysts. It has been found that ruthenium offers special advantages and for this reason it will be emphasized in the following illustrative examples, but this is only for the sake of simplifying the description of the invention, and it will be understood that the other platinum group metals can be similarly used in place of or together with the ruthenium in the catalysts chosen as illustrations.

As solid oxidizing agents for use with the chosen platinum group metal or metal mixture, one will use oxidants which are hypergolic with the hydrazine which is to be decomposed, and stable with respect to the catalyst support which is employed. A variety of suitable oxidants are available. Typical oxidizers are, for instance, chromates, dichromates, manganates, permanganates, chlorates, perchlorates, nitrates, and the like. For the sake of economy these are advantageously used in the form of their alkali metal or ammonium salts, but other salts have been successfully used in hydrazine decomposition. Silver salts, for example silver chlorates, perchlorates, chromates and nitrates have been successfully used in decomposing hydrazine, and other salts such as alkaline earth metal salts, lead salts, zinc salts, etc., can also be used. Solid halo-oxy acids such as iodic acids and the like are another suitable type of oxidizing agents which can be used in the new catalysts. It has been found that there are special advantages in the use of ammonium dichromate and iodic acid as oxidizers because they combine high effectiveness with good stability, freedom from detonation danger, and reasonable cost.

The mixture of platinum group metal and hypergolic oxidizer are used on a porous carrier which should be substantially inert under the hydrazine decomposition conditions used. Carriers which have a moderately high specific area, of the order of 10 or more square meters per gram, are particularly useful. Supports having a pore volume of at least 0.1 cubic centimeter per gram are desirable in order to provide capacity for the desired amounts of platinum group metal catalyst and associated oxidizer. Those with pore volumes between about 0.2 and about 0.8 cubic centimeter per gram are especially advantageous. Alumina supports, especially the highly stable forms derived from gels, such as for instance gelatinous boehmite, are particularly advantageous. However, other porous oxides such, for example, as zirconia, titania, silica gel, and the like, can be used as well as carbides such, for instance, as boron carbide, silicon carbide, zirconium carbide, etc., and nitrides as for example, titanium nitride, zirconium nitride, and boron nitride. Other porous, highly refractory carriers such as carbon, and the like, can also be employed successfully in making the new catalysts, as can ceramic supports of various types.

The proportions of platinum group metal and hypergolic oxidizer to each other and to the weight of carrier