United States Patent Office 3,842,017
Patented Oct. 15, 1974

3,842,017

PROCESS FOR DEPOSITING NOBLE METAL CATALYSTS ON OXIDE CARRIERS

William H. Armistead and Thomas H. Elmer, Corning, and Ivan E. Lichtenstein, Big Flats, N.Y., assignors to Corning Glass Works, Corning, N.Y.

No Drawing. Filed Dec. 13, 1972, Ser. No. 314,704
Int. Cl. B01j 11/08, 11/12, 11/20
U.S. Cl. 252—474 3 Claims

ABSTRACT OF THE DISCLOSURE

A process for depositing selected noble metal catalysts on oxide carriers comprising the step of contacting the oxide carriers with a solution containing selected noble metal ions and a formic acid reductant is described. Reduction of the noble metal ions preferentially occurs at the surface of the oxide carrier, resulting in the deposition of a uniform noble metal dispersion thereon. Sensitization of the carrier with hydrolyzable tin compounds to increase the rate and uniformity of catalyst deposition is also described.

BACKGROUND OF THE INVENTION

The use of catalytically-active noble metals such as plantinum, palladium and rhodium supported on refractory metal oxide carriers such as alumina, magnesia, silica and the like is well known in the field of catalysis. Devices comprising noble metal catalysts on oxide supports are used, for example, in oxidation processes wherein gases comprising oxidizable constituents are treated by contact with the supported catalysts at elevated temperautres to promote the oxidation of these constituents.

A large number of processes for depositing noble metal catalysts on oxide supports are also known. For example, one method of applying platinum or palladium to a porous oxide support structure comprises immersing the structure in a solution containing a platinum or palladium salt, and thereafter drying and firing the structure to pyrolytically convert the resulting noble metal salt coating to the noble metal. Unfortunately, such processes do not always provide uniform results. An important requirement of any such deposition procedure is that it provides a uniform dispersion or coating of the noble metal catalyst on the surface of the oxide carrier in order to maximize the exposed active surface area and thus the efficiency of the catalyst. Technically, processes which optimize catalyst dispersion and uniformity will normally be preferred.

From the commercial viewpoint, many of the processes which are technically suitable for the purpose of depositing noble metal catalysts on oxide supports are undesirable because they require numerous and/or expensive process steps or ingredients. A process which could provide a fine and uniform catalyst dispersion without the need for several different treating solutions, fixing steps, special atmospheres or equipment would be of significant commercial importance.

SUMMARY OF THE INVENTION

We have now discovered a process for depositing noble metal catalysts on refractory metal oxide carriers which is simple yet surprisingly effective in producing a uniform dispersion of noble metal thereon. The process comprises the step of contacting the carrier with an aqueous solution

containing noble metal catalyst ions and a formic acid reductant. The formic acid reductant does not normally reduce the noble metal ions present in the solution to a significant extent in the absence of an oxide carrier. However, in the presence of such a carrier, particularly in the presence of a carrier which effects a localized rise in pH at the carrier-solution interface, the noble metal ions are reduced and preferentially deposited on the carrier suface.

Noble metals which may be effectively deposited on oxide carriers according to the present invention include platinum, palladium, rhodium, gold, silver and mixtures of these metals. The ions of these metals may be introduced into aqueous solution by the addition of soluble compounds of the noble metals such as the noble metal salts, with soluble halide compounds which form halide-complexed noble metal ions in solution being preferred.

Oxide carriers which may be treated according to the invention include alumina, tin oxide, silica and the like, mixtures of oxides such as alumina-silica mixtures, oxide compounds or other phases such as mullite, cordierite, and spodumene, and oxide products of fusion such as glasses. The form of the oxide carrier is not critical for our purposes; powders, coatings and particularly monolithic support structures formed of these carriers may be treated.

Many of the above oxide carriers do not effect a localized rise in pH adjacent to the solution-carrier interface in aqueous solutions, and the catalyst deposition reaction on these carriers typically proceeds quite slowly. In such cases, the addition of urea to the aqueous solution containing the noble metal ions and the formic acid reductant is useful to markedly increase the rate and extent of the catalyst deposition reaction. Additions of urea comprising between about 1–10% by weight of the aqueous solution are suitable for this purpose.

In most cases the rate of the deposition reaction and the uniformity of the dispersed noble metal coating provided by the process as above-described may be further improved through a pretreatment of the catalyst carrier according to a tin-sensitization procedure. This procedure involves the additional steps, prior to contacting the catalyst carrier with the noble metal-containing solution, of coating the carrier with a hydrolyzable tin compound and then hydrolyzing the tin compound to provide a coating containing a hydrous tin oxide on the carrier. Typically, the carrier is contacted with an aqueous solution of a hydrolyzable tin compound such as an acidified stannous chloride solution, and hydrolysis and removal of the chloride are carried out by contacting the solution-coated carrier with hot water. This tin-sensitization pretreatment assures very rapid and uniform deposition of the noble metal onto the carrier upon contact with the noble metal ion-formic acid reductant solution.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention is particularly advantageous in the treatment of oxide carriers which consist of monolithic ceramic catalyst support structures of the honeycomb type, used in the catalytic treatment of flowing fluids, particularly gases. The channeled structure of such suports makes uniform coating with a catalyst using conventional processes difficult, whereas the process of the present invention readily provides a uniform dispersion of catalyst even on the interior channel walls of such supports. Structures which may be suitably treated according to our process may be composed of any of the glasses, oxides, or oxide compounds or solid solutions use-