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3,427,153

METHOD OF PREPARING ALLOY BLACKS

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No Drawing. Filed June 11, 1964, Ser. No. 374,274

U.S. Cl. 75-108

2 Claims

Int. Cl. C22c 1/06, 5/00

ABSTRACT OF THE DISCLOSURE

An improved method of preparing alloy blacks is described. The method comprises admixing salts of the desired metals of the alloy in the proper ratios, forming a co-precipitate of the metals by addition of ammonium hydroxide to the salt solutions, and reducing the co-precipitated hydroxide.

This invention relates to the preparation of alloy blacks in finely divided form. More particularly, the invention relates to a simplified method for the preparation of improved alloy blacks. Basically, the improved method comprises admixing salts of the desired metals of the alloy in the proper ratios, forming a preprecipitate of the metal alloy by addition of ammonium hydroxide and reducing the co-precipitated hydroxide.

It is recognized in the art that many metals, particularly the transition metals of the fifth and sixth series of Group VIII of the Mendelejeff's Periodic Table and the noble metals of Sub-Group I have excellent properties as catalysts particularly in gas-solid reactions. Quite surprisingly, when certain alloys of two or more metals are prepared, the alloys have enhanced catalytic properties in comparison with any of the metals of the alloy taken singly. Therefore, the use of alloys as catalysts has become more prevalent in recent years, particularly as activators in fuel cell electrodes, i.e., cells wherein the energy of reaction between a fuel and an oxidant is converted directly into electrical energy.

Further, it is known that the value of a catalyst, apart from the intrinsic activity of the material, is directly related to the surface area of the catalyst exposed to reactants. For this reason, metals and alloys are used as catalysts in finely divided or spongy form having a high surface area. Although there are several methods of preparing finely divided metals such as electrolytic precipitation of the metal from a suitable salt solution, the preparation of alloy blacks presents more of a problem. Thus, one method of preparing blacks of an alloy is first to form an alloy by known metallurgical means such as melting powders of the different metals together in the proper proportions, preferably above the melting point of the metals and thereafter cooling. The alloy is formed into wires or narrow strips by usual methods known in the art such as drawing, etc. The alloy wires or strips are mounted in ice water as electrodes, i.e., as an anode and cathode. A direct current potential of between 150 and 200 volts is applied to the system and the wires brought into close proximity to establish an arc. The arcing disrupts the metals and forms a fine suspension of alloy particles in the water. The metal particles are filtered out, dried, and employed in known procedures. As apparent, the above-described process is complex and time consuming.

It has now been found that alloy blacks can be prepared by forming admixtures of the desired metal salts in their proper ratio, adding ammonium hydroxide to the admixture to form the co-precipitated metal hydroxides and thereafter reducing the metal hydroxide with a reducing agent, such as hydrazine or bubbling hydrogen, to form the alloy blacks. In addition to the aforesaid process

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being extremely simple, the blacks formed have enhanced activity particularly when used on fuel cell electrodes, possibly due to an increase in the surface area.

Accordingly, it is an object of the present invention to provide an improved method of preparing metal alloy blacks.

It is still a further object of the present invention to provide metal alloy blacks having a large surface area by forming admixtures of the metal salts in the desired ratio, co-precipitating the metal hydroxides by adding ammonium hydroxide and reducing the co-precipitate.

It is a still further object of the present invention to provide gold-palladium alloy blacks by adding a solution of ammonium hydroxide to an aqueous solution of palladium and gold salts to form the co-precipitated hydroxides and thereafter reducing with an aqueous hydrazine solution to form the finely divided metal alloy black.

These and other objects of the invention will become more fully apparent from the following detailed description and illustrative examples.

The alloy blacks of any of the noble metals such as the so-called platinum and palladium metals and gold and silver can be prepared according to the method of the present invention. Thus, it is merely necessary to admix salts of the desired metals in the proper ratio and thereafter form the hydroxides and reduce. However, although metal alloy blacks of ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, and silver can be prepared, gold-palladium alloy blacks are preferred in view of their exceptional activity and stability, particularly when employed as a catalyst on a fuel cell electrode.

The admixtures of metal hydroxides can be prepared from aqueous salt solutions of the metals, such as solutions of the chlorides, nitrates, and sulfates. However, it is necessary that the precipitate be prepared from a solution of the two or more metals of the alloy. Thus, quite surprisingly, it was found that when gold and palladium were precipitated separately, and thereafter the precipitates admixed and reduced, an alloy was not obtained but merely an admixture of the two metals. The temperatures at which the precipitated hydroxides are formed or reduced are not critical and can be varied over a substantially wide range.

The alloy blacks can be used in any of the areas where conventional blacks have been employed.

Having described the invention in general terms, the following example is set forth to illustrate a preferred embodiment of the invention.

EXAMPLE

An alloy black was prepared by dissolving gold chloride salt in a concentrated aqueous palladium chloride solution, the concentration in terms of metal being 100 mg./ml., to obtain a gold to palladium ratio of 75:25 on an atomic percent basis. The mixture was introduced slowly into a 3% ammoniacal solution at room temperature with constant stirring. Upon contact of the two solutions, a finely divided yellow precipitate was formed immediately. Thereafter, an excess of dilute hydrazine was added to reduce the precipitated material to the finely divided metallic state. After washing in distilled water and drying, tests showed the finely divided metallic particles to be the gold-palladium alloy.

To demonstrate the utility of the novel alloy black, a reducing electrode was prepared by coating a nickel support screen having a mesh size of 100 on the Tyler scale with a paste prepared from the above-described alloy black and Teflon suspended in water. The Teflon, having an average particle size of 0.3 micron in diameter, and the alloy black were present in a ratio of 3:10. After coating the screen with the paste, the system was stabilized by heating at 300° C. for 30 minutes. After cooling,

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the Teflon gold-palladium alloy coating adhered very well to the support screen.

The structure described as above was employed as the cathode in a fuel cell in conjunction with a similarly constructed anode employing platinum black as the activator. The electrolyte of the cell is a 5 normal aqueous potassium hydroxide solution. The operating temperature is 75° C. The anode is fed with hydrogen at a pressure of 0.15 p.s.i.g. Oxygen is fed to the cathode at a pressure of 0.25 p.s.i.g. Current density versus cell potential data are as follows:

Current density (ma./cm. ²):	Cell potential (volts)
0	1.092
40	.965
80	.945
120	.931
180	.913
240	.894
300	.882
400	.859

In the aforesaid examples, the palladium and gold can be replaced by combinations of other metals such as platinum, ruthenium, osmium, iridium, silver, and rhodium. Such combinations must be capable of forming mixed oxide and/or hydroxide phases and solid metal solutions or an intermetallic phase. Moreover, the percentages of the different metals in the alloy can be varied to obtain substantially different compositions. Other metal salts can be employed in the preparation of the metal hydroxides. It should be appreciated that the invention is not to be limited by the example as it is possible to pro-

duce still other embodiments without departing from the inventive concept herein disclosed and covered by the appended claims.

What is claimed is:

1. The method of preparing a palladium-gold alloy black comprising the steps of (1) adding gold chloride to an aqueous solution of palladium chloride to obtain the desired gold to palladium ratio, (2) forming a precipitate by adding ammonium hydroxide to the solution of (1), and (3) reducing said gold and palladium hydroxide precipitate with hydrazine to form a metal alloy black.

2. The method of preparing a metal alloy black comprising the steps of (1) forming a solution of at least two metal salts; (2) forming a co-precipitate of the metals by adding ammonium hydroxide to the salt solution; and (3) reducing said co-precipitated metal hydroxide with a member of the group consisting of hydrazine and bubbling hydrogen to form a metal alloy black.

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U.S. Cl. X.R.

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