A quantity of reagent grade tin metal or compound, chloride-free, and high-surface-area silica spheres are placed in deionized water, followed by deaerating the mixture by boiling and adding an oxidizing agent, such as nitric acid. The nitric acid oxidizes the tin to metastannic acid which coats the spheres because the acid is adsorbed on the substrate. The metastannic acid becomes tin-oxide upon drying and calcining. The tin-oxide coated silica spheres are then placed in water and boiled. A chloride-free precious metal compound in aqueous solution is then added to the mixture containing the spheres, and the precious metal compound is reduced to a precious metal by use of a suitable reducing agent such as formic acid. Very beneficial results have been obtained using the precious metal compound tetraammine platinum(II) hydroxide.
PROCESS FOR MAKING A NOBLE METAL ON TIN OXIDE CATALYST

ORIGIN OF THE INVENTION

The invention described herein was made jointly in the performance of work under NASA Contract No. NASI-18252 and employees of the United States Government. In accordance with 35 USC 202, the contractor has elected not to retain title.

BACKGROUND OF THE INVENTION

This invention relates to a method of producing a noble metal catalyst, and more particularly, to a method of producing a metal on metal oxide catalyst for use in a carbon dioxide laser.

In a closed cycle carbon dioxide laser, a high voltage discharge is used to initiate laser emission. However, this electrical discharge also causes some of the carbon dioxide in the laser to partially dissociate into carbon monoxide and oxygen in the high voltage discharge region. The continual dissociation of carbon monoxide during laser operation causes the concentration of carbon dioxide to decrease and that of carbon monoxide and oxygen to increase. The loss of carbon dioxide coupled with the gain in oxygen causes a rapid loss in laser power. To maintain laser power, it is necessary to recombine the carbon monoxide and oxygen products.

While different catalysts have been used to effect the recombination of carbon monoxide and oxygen, the CO₂ laser demands a catalyst which is very efficient at room temperature. It has been found that noble metal on tin(IV) oxide catalysts supported on an inert substrate are effective under such conditions. There are several known methods of making such catalysts. However, all of these processes include either time consuming extra drying and calcining steps or the use of chloride-containing materials. The use of chloride containing compounds necessitates thorough washing of the catalyst, because chloride is known to poison and deactivate the catalyst. Consequently, a need continues to exist for a simple, chloride-free method of producing a noble metal on metal oxide catalyst for use in a closed-cycle CO₂ laser.

Accordingly, it is an object of this invention to provide a simple method of producing a noble metal on metal oxide catalyst on an inert support material. A further object of this invention is to provide a one-step method of adding a layer of a metal oxide to an inert support material.

A further object of this invention is to provide a method of producing a noble metal on metal oxide catalyst wherein the reagents used and products formed during the reaction are either volatile or decompose to volatile products during drying.

Other objects and advantages of this invention will become apparent hereinafter in the specification which follows.

SUMMARY OF THE INVENTION

According to the present invention, the foregoing and additional objects are attained by placing a quantity of reagent grade tin metal or compound, chloride-free, and high-surface-area silica spheres in deionized water, deaerating the mixture by boiling, and adding an oxidizing agent, such as nitric acid. The nitric acid oxidizes the tin to metastannic acid which coats the spheres because the metastannic acid will be adsorbed on the substrate. The metastannic acid will become tin-oxide upon drying and calcining. The tin-oxide coated silica spheres are then placed in water and boiled. A chloride-free precious metal compound in aqueous solution is then added to the mixture containing the spheres, and the precious metal compound is reduced to a precious metal by use of a suitable reducing agent such as formic acid. Very beneficial results have been obtained using the precious metal compound tetraammineplatinum(II) hydroxide.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprehends producing a noble metal on metal oxide catalyst on an inert, high-surface-area support material which will function as a catalyst at approximately room temperature using chloride-free reagents. This is accomplished in a two-step process. In the first step, a commercially available, inert, high surface area support material, such as high surface area silica spheres, is coated with a thin layer of metal oxide, a monolayer equivalent. In the second step, the coated support is then coated with a thin layer of a precious metal amounting to a fraction of a monolayer equivalent. The purpose of these thin layers is to maintain the high surface area of the catalyst by not blocking the pores in the support.

The first step is accomplished by first preparing a mixture of a commercially available, inert, high-surface-area support material, such as high-surface area silica spheres, and an oxidizing agent. Very beneficial results have been obtained using nitric acid as an oxidizing agent since it leaves no residue. It is also helpful if the spheres are first deaerated by boiling in water to allow the entire surface to be coated. A metal, such as tin, is then dissolved in the oxidizing agent/support material mixture to yield, in the case of tin, metastannic acid. Although tin has proven especially beneficial for use in a closed-cycle CO₂ laser, in general any metal with two valence states, such as most transition metals and antimony, may be used. The metastannic acid will be adsorbed onto the high-surface-area spheres and coat the spheres. Any excess oxidizing agent is then evaporated and the resulting metastannic acid-coated spheres are dried and calcined, whereby the metastannic acid becomes tin(IV) oxide.

The second step is accomplished by preparing an aqueous mixture of the tin(IV) oxide coated spheres and a soluble, chloride-free salt of at least one catalyst metal. The catalyst metal may be selected from the group consisting of platinum, palladium, ruthenium, gold and rhodium or other platinum group metals. Extremely beneficial results have been obtained using chloride-free salts of platinum, palladium, or a combination thereof, such as tetraammine platinum(II) hydroxide (Pt(NH₃)₄(OH)₂) or tetraammine palladium nitrate (Pd(NH₃)₄(NO₃)₂). It is also beneficial if the coated spheres are first deaerated by boiling. The platinum salt will be adsorbed onto the high surface area and coat the spheres. A chloride-free reducing agent is then added to the aqueous mixture whereby the catalyst metal is deposited on the tin(IV) oxide coated spheres. Any reducing agent which decomposes to volatile products and
because the method of forming and applying tin oxide to a substrate is a one-step process that results in a more uniform application than other methods. Similarly, the method of forming and applying a precious metal to either tin oxide or an inert substrate is a one-step process and occurs at a lower temperature than that commonly used by other processes. Most importantly, the present invention is inherently clean because excess reagents, such as nitric acid and formic acid, as well as unwanted products, such as nitrates and formates, all decompose and are removed from the system by simple evaporation without the necessity to separate them by filtration or washing. Furthermore, as it is possible to apply extremely thin layers of the tin oxide and precious metals, the present invention is able to coat high-surface area substrates without appreciably blocking small pores, which greatly increases the efficiency of the catalyst. For example, prior methods have yielded a catalyst with a B.E.T. surface area between approximately 65 m²/g and 70 m²/g. By contrast, the present invention has yielded the same catalyst with an increased B.E.T. surface area of approximately 170 m²/g.

It should become obvious to those skilled in the art that this invention is not limited to the examples herein described.

**EXAMPLE**

Ten grams of commercially available, high surface area silica spheres, 10 microns in diameter, having a B.E.T. surface area of 167 m²/g, were placed in deionized water. Two grams of reagent grade tin powder were added. This was an amount sufficient to coat the spheres with one monolayer equivalent of tin(IV) oxide. The water was boiled for 4 minutes to deaerate the acid absorbed on the support is converted to tin(IV) oxide at a lower temperature than that commonly used by other processes. Most importantly, the present invention is inherently clean because excess reagents, such as nitric acid and formic acid, as well as unwanted products, such as nitrates and formates, all decompose and are removed from the system by simple evaporation without the necessity to separate them by filtration or washing. Furthermore, as it is possible to apply extremely thin layers of the tin oxide and precious metals, the present invention is able to coat high-surface area substrates without appreciably blocking small pores, which greatly increases the efficiency of the catalyst. For example, prior methods have yielded a catalyst with a B.E.T. surface area between approximately 65 m²/g and 70 m²/g. By contrast, the present invention has yielded the same catalyst with an increased B.E.T. surface area of approximately 170 m²/g.

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