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METHOD FOR THE PRODUCTION OF A NOBLE METAL CATALYST

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This invention relates to the production of a noble metal catalyst, and particularly to the production of a noble metal in a form possessing high catalytic activity.

Noble metal catalysts are, as is well known, variously employed in effecting chemical reactions, as hydrogenation, oxidation, etc., and have been prepared in various ways. Broadly, however, the noble metals as, for example, platinum, palladium, etc., have been prepared for use in catalysis either in a colloidal form, which may be used in suspension or supported on a carrier, or in massive form, as gauzes, rods, plates, etc.

Now in accordance with this invention, it has been found possible to prepare a coating or film of noble metal as platinum, palladium, etc. in a highly active state upon a suitable support, which itself may be, for example, a noble metal. The coating of noble metal deposited in accordance with this invention will be found to be exceedingly active, and when the catalyst becomes inert after long use it may be easily reactivated by simply depositing a fresh coating over the old one.

The method in accordance with this invention involves broadly the formation, as by electrolysis, upon a suitable support, of a mechanically stable layer of noble metal oxide, as platinum trioxide, palladium oxide (Pd_2O_3), etc., and the subsequent reduction of the oxide to an active stable form of the noble metal. When the oxide is deposited by electrolysis, the electrolyte used is an alkaline solution of the noble metal hydroxide, as platinic hydroxide ($Pt(OH)_4$), palladium hydroxide, or in some cases an acidic solution of the noble metal as, for example, an acid solution of palladium nitrate. The cathode may be, for example, a rod or wire of the noble metal to be deposited. As an anode any material capable of resisting oxidation may be employed, as for example, carbon, a noble metal, which may be the same as that to be deposited or another, or a noble metal alloy. In place of an anode comprising solely a noble metal or noble metal alloy, a material, such as a base metal, carbon, or even a non-conductor, as cloth, etc., coated with an impervious layer of noble metal or noble metal alloy may be used.

It is very important that the surface of the anode be properly prepared in order to give an adherent film of noble metal oxide upon electrolysis. For example, laboratory investigators many years ago (see "Platinum Trioxide, a New Stage of Platinum Oxidation" by L. Wohler and F. Martin, Berichte, vol. 42, pp. 3326–33 (1909), and "A New Stage of Palladium Oxidation" by the same authors, Zeit. anorg. Chem., vol 57, pp. 398—413 (1908)), learned how to prepare these noble metal oxides by electrolysis. However, they produced no useful catalytic material because they were unable to deposit an adherent film on the anode. In accordance with this invention it has been discovered that adherent films of satisfactory thickness can be obtained only if the anode has an unpolished, matte surface. If the anodic surface is bright or polished, continued electrolysis will give an oxide film which easily and readily peels off.

The necessary matte surface may be, for example, conveniently produced upon a polished anode in this manner. The polished anode is set in place in the electrolytic cell prepared in accordance with this invention as described in detail hereafter, and electrolysis is continued until the anode is just covered with the noble metal oxide. The anode is then removed, and the oxide layer reduced in accordance with this invention as described in detail hereafter. The reduction produces a very thin matte layer of noble metal upon the anode, and upon this layer the stable, adherent films of noble metal oxide are laid down by further electrolysis.

The primary material deposited upon the anode during electrolysis has been referred to above as a noble metal oxide. However, when an alkaline solution of platinic hydroxide ($Pt(OH)_4$) is electrolyzed, a complex platinum-alkali oxide of the probable composition $3PtO_3.K_2$(or Na_2)O is deposited on the anode. This deposit, when washed with, for example, acetic acid, loses alkali and becomes the simple platinum oxide (PtO_3), which may then be reduced to form the catalytically active platinum surface.

As illustrative of the method in accordance with this invention, the electrolyte may be prepared by dissolving, for example, chlorplatinic acid in a small amount of water, making the solution strongly alkaline with a 50% solution of, say, sodium hydroxide, and pouring the alkaline solution together with any precipitate that may have formed into an excess of acetic acid and cracked ice. A cream colored precipitate corresponding to the formula ($Pt(OH)_4$) is thrown down. This precipitate after being well washed with water is dissolved on a, say, 2 N solution of sodium or potassium hydroxide, to give a solution having a platinum concentration of 10 g. per liter. This solution is placed in the anode chamber of the electrolytic cell, and the cathode chamber, separated from the anode chamber by a porous diaphragm, is filled with an alkali solution of about the concentration used in making up the

anode solution, in this case, about 2 N. A platinum cathode and a platinum anode with a matte surface are then introduced and electrolysis continued for about 2 hours at room temperature and at a current density of 2 amperes per square decimeter.

The anode with its adherent layer of platinum-alkali oxide is then removed and thoroughly washed with acetic acid to remove the alkali, and then with distilled water to remove all acetic acid. The anode, which is now coated with an adherent layer of platinum oxide (PtO_3), is then, for example, placed in an atmosphere of hydrogen to effect reduction of the oxide to the metal. There is accordingly formed a mass of any desired shape and surface area, which, because of its surface coating of platinum in a highly active form, is a highly advantageous catalyst for use in catalytic hydrogenations, oxidations, etc.

It will be appreciated that in the electrolysis a cell of such size and such quantities of electrolyte will be used as will enable the anode selected to be wetted to the desired degree. The platinum concentration of the electrolyte may vary from about 2 to about 30 grams per liter, although it is desirable to use a concentration of about 10 grams per liter to effect a sufficiently rapid deposition of the oxide. Concentrations lower than 5 g./liter when employed require a longer electrolysis period. The alkali concentration of the electrolyte may vary from about 0.1 normal to about 5.0 normal. When the platinum concentration is high the alkali concentration should also be high for best results. It is preferable, however, to keep both the platinum and alkali concentrations fairly low to secure the most adherent films of oxide. The current density may vary from about 1 to 3 amperes per sq. decimeter. In general too high current densities are to be avoided since they tend to make the oxide film mechanically unstable. The only effect of a very low current density will be to unduly prolong the time of electrolysis. The time of electrolysis will vary with varying platinum concentrations and current densities from 1 to 4 hours. With the platinum concentration of 10 g./liter or higher and a current density of 2 amperes per sq. decimeter or more, electrolysis will be complete in 2 hours or less. The temperature of electrolysis is relatively unimportant, although elevated temperatures may be used if desired.

As further illustrative of the method in accordance with this invention, an electrolyte containing palladium may be formed by dissolving hydrated palladium dioxide in sodium hydroxide or sodium carbonate. This electrolyte is then placed in the anode compartment of the cell and electrolysis carried out exactly as in the example given above. In this case palladium oxide (Pd_2O_3), and not a complex oxide, is deposited on the anode, and consequently the anode after electrolysis may be directly reduced by, for example, heating in hydrogen.

The limited solubility of hydrated palladium dioxide in alkali renders the procedure described above somewhat unsatisfactory, however, and the following method is to be preferred. Palladium nitrate is dissolved in 2 N nitric acid to give a palladium concentration of 15 g./liter. This solution is placed in the anode compartment of the diaphragm cell, and the cathode compartment is filled with 2 N nitric acid. Electrolysis is carried out at 2 amperes per sq. decimeter for about 2 hours. The cell is preferably cooled to about 4°–10° C. The anode is reduced after electrolysis as described above.

The concentration of palladium, the current density, and the time of electrolysis may be varied within substantially the limits given above for operation with platinum. The temperature of electrolysis with palladium should always be kept about 4–10° C. however.

It will be apparent that this invention relates broadly to the formation of a catalyst suitable for hydrogenation, oxidation, etc. formed of a continuous surface layer of catalytically active noble metal, as platinum, palladium, etc. superposed on a base or support of any type or shape formed of any material substantially unattacked under the conditions of deposition, as, for example, carbon, one of the noble metals, or an alloy thereof, or any material coated or plated with one of the noble metals or alloys thereof. And that the method in accordance with this invention involves broadly the formation on such a base or support of an adherent, mechanically stable film of a noble metal oxide, for example, by electrolysis, and the reduction of such oxide film to the noble metal, for example, by the action of hydrogen gas.

The catalyst prepared in accordance with this invention will be found highly advantageous and economical for use in oxidations, hydrogenations, etc. for because of the large surfaces which can be obtained upon a relatively inexpensive supporting base, and the activity of these surfaces it will be low in cost and yet possess great catalytic efficiency. It will be found especially suitable for use in continuous hydrogenations where the material to be hydrogenated flows over the catalyst in an atmosphere of hydrogen. It may also be used advantageously in batch hydrogenations where hydrogen is bubbled through a material in contact with the catalyst. Typical operations in which the catalyst in accordance with this invention may be used to advantage are: the hydrogenation of oils and fats, the hydrogenation of rosin and its compounds, the oxidation of ammonia to nitric acid, the oxidation of sulfur dioxide to sulfuric acid, etc.

What I claim and desire to protect by Letters Patent is:

1. The process of making a catalyst which includes forming by electrolysis of an alkaline solution containing platinum upon a suitable base employed as the anode an adherent coating of a complex platinum oxide, converting the complex oxide to a simple platinum oxide, and reducing the simple oxide to metallic platinum.

2. The process of making a catalyst which includes forming by electrolysis at a current density of from 1–3 amperes per square decimeter of an alkaline solution containing from 2–30 g. platinum per liter, upon a suitable base employed as the anode, an adherent coating of a complex platinum oxide, converting the complex oxide to a simple platinum oxide, and reducing the simple oxide to metallic platinum.

3. The process of making a catalyst which includes forming by electrolysis at a current density of from 1–3 amperes per square decimeter of a solution containing 1.0–10.0 g. palladium per liter, upon a suitable base employed as the anode, an adherent coating of palladium oxide, and reducing the oxide to metallic palladium.

4. The process of making a catalyst which includes forming by electrolysis at a current density of from 1–3 amperes per square decimeter of an alkaline solution containing from 2–30 g. plati-

num per liter, upon a suitable base employed as the anode, an adherent coating of a complex platinum oxide, converting the complex oxide to a simple platinum oxide by treatment with dilute acid, and reducing the simple oxide to metallic platinum.

5. The process of making a catalyst which includes forming by electrolysis, at a temperature of about 4°–10° C. and a current density of 1–3 amperes per square decimeter, of a solution containing 1.0–10.0 grams of palladium per liter, upon a suitable base employed as the anode an adherent coating of palladium oxide and reducing the oxide to metallic palladium.

6. The process of making a catalyst which includes forming by electrolysis of an alkaline solution containing platinum upon a suitable base employed as the anode an adherent coating of a complex platinum oxide, converting the complex oxide to a simple platinum oxide and reducing the simple oxide to metallic platinum by treatment with hydrogen.

7. The process of making a catalyst which includes forming by electrolysis of an alkaline solution containing platinum upon a support, at least the surface layer of which is resistant to oxidation, employed as the anode, an adherent coating of a complex platinum oxide, converting the complex oxide to a simple platinum oxide, and reducing the simple oxide to metallic platinum.

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