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3,380,934

NOBLE METAL CATALYSTS AND THEIR PRODUCTION

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9 Claims. (Cl. 252-462)

This application is a continuation-in-part of application Ser. No. 399,381, filed Sept. 25, 1964 and now abandoned.

This invention relates to a method of making a highly active, finely divided, noble metal catalyst having a high surface area and to the composition of the catalyst itself. In particular, the invention relates to a method of making a highly active, finely divided, noble metal catalyst which comprises: supporting a metallic salt or salts of the desired catalyst upon a support in conjunction with a less noble metallic salt, reducing the metal ions of the supported compounds, removing the support and removing the less noble metal.

The term "noble metal" as used herein refers to a metal which is not easily dissolved by conventional dissolution methods and is not intended to be restricted to the gold, platinum and palladium family of the periodic system. Examples of noble metal contemplated by this invention are platinum, ruthenium, rhodium, palladium, iridium, osmium, rhenium, vanadium, titanium, tungsten, gold, cobalt, nickel, the lanthanide series metals such as cerium, neodymium, samarium, gadolinium, promethium, ytterbium, terbium and mixtures of the above metals.

The term "less noble metal" as used herein refers to a metal which is more easily dissolved by conventional dissolution methods in comparison with the more noble metal or metals with which it is combined. Some "less noble metals" contemplated for use in this invention include chromium, manganese, iron, cobalt, nickel, copper, molybdenum, cadmium, tin, lead, aluminum and silver. Some metals such as cobalt and nickel are classified as both "noble" and "less noble" because metals such as these are more or less readily dissolved depending on the metals with which they are combined. Nickel when combined with aluminum is "noble" because the aluminum is more readily dissolved by conventional techniques than is the nickel, however, when nickel is combined with platinum, it is classified as "less noble" as it is more readily dissolved than the platinum. Silver is classified as a less noble metal as it is relatively easily dissolved, as for example with acid or base or by electrolytic treatment, in comparison with the noble metal or metals with which it is combined. As there are numerous possible combinations of metals one of which is more readily dissolved than the metal or metals with which it is united, a relative physical property such as ease of dissolution must, therefore, be relied upon to properly define "noble" and "less noble." The same metal can be used in either category and the designation "noble" or "less noble" applied depending on whether this metal is later removed or is the catalyst of interest. No identical metals, however, could be used at the same time as both the "noble" and "less noble" constituent.

Heretofore, the art has developed a number of procedures in order to increase the activity of finely divided materials to be used as catalysts. According to one method, a platinum group metal catalyst is prepared by fusing together the platinum group metal with a base metal to form an alloy. The base metal of this alloy is subsequently removed by chemical treatment leaving a platinum metal product active as a catalyst (British Patent No. 606,348). In another prior art method, a

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platinum alloy catalyst is produced by subjecting a platinum alloy, e.g., platinum-rhodium, to a high temperature for a period of time causing the alloy to recrystallize into a catalytically active material (U.S. Patent No. 2,267,753). These methods, together with others in the art, produce active catalysts but the search continues to find more effective catalysts and methods of producing them.

It has been found that the activity of a noble metal catalyst can be significantly increased if prepared by a process wherein the salt of this noble metal catalyst is co-reduced with a salt of a less noble metal on a support. This composition of noble and less noble metal is not an alloy in the true sense of the word, i.e., a product formed by fusing metals together, but rather a co-reduced combination of metals, the noble metal component of which, upon removal of the less noble component, demonstrates improved catalytic activity. Indeed, a spectrographic analysis indicates that the co-reduced combination behaves more like a physical mixture than a true alloy. No sintering of the noble and less noble metal components occurs in this process thus distinguishing it from other processes concerned with alloys.

The less noble metal is removed from the co-reduced combination of metals by either anodization or dissolution by acid or base. This results in a finely divided catalyst having a large surface area. Although an increase in surface area produces a corresponding increase in catalytic activity, it will be shown that the catalytic activity of the noble metal is increased independently of surface area by this process, i.e., the intrinsic activity of the noble metal itself is increased.

The procedure of the instant invention consists of supporting one or more metal salts and a less noble metal salt upon a selected support; reducing the metal ions by contacting the support either with hydrogen or carbon monoxide at elevated temperatures or another chemical reducing agent; removing the support; and then removing the less noble metal by anodization or by acid or base treatment.

Example of catalysts which may be made by the instant invention include finely divided single metals such as platinum, ruthenium, rhodium, palladium, iridium, osmium, rhenium, vanadium, titanium, tungsten, gold, cobalt, nickel and the lanthanide series metals such as cerium, neodymium, samarium, gadolinium, promethium, ytterbium, terbium, or combinations of the foregoing metals. Examples of mixed catalysts are platinum-iridium, platinum-rhodium, platinum-gold-iridium, platinum-rhenium-vanadium, platinum-gold, and gold-iridium. The procedure will also produce finely divided metal catalysts which are not in the zero valence state but are rather in a lower oxidation state than in the unreduced compound. These catalysts include, either singly or in combination, the oxides of the noble and less noble metals. This invention is not directed to any particular catalyst but only to a procedure for producing a more efficient, more active, finely divided metal catalyst.

The less noble metals which can be used in the practice of this invention are the metals chromium, manganese, iron, cobalt, nickel, copper, molybdenum, cadmium, tin, lead, aluminum and silver. In the practice of this invention, salts of the foregoing metals can be added to a solution comprising a salt or salts of the intended catalyst and subsequent to the addition of a salt of the foregoing less noble metals, a reducing agent is added to the solution thereby precipitating the metals from solution.

Silver, although popularly known as a "noble metal" may be classified as a "less noble metal" if it is combined with a more dissolution resistant noble metal which is of interest as a catalyst. Dissolution of the "less noble

metal" can be carried out by acid or base treatment of the "noble-less noble" combination or by electrolytically removing the "less noble metal."

The supports which can be used in the practice of this invention include silica gel, alumina, calcium carbonate, carbon, ammonium oxalate and ammonium carbonate. The supports can be removed by any convenient means such as treating the silica gel and alumina supports with a strong base. In removing a silica or alumina support, the strength of the base used should be greater than 3 M and the temperature from approximately 0° F. to 212° F. Increasing the temperature will increase the rate of dissolution. The calcium carbonate can be removed by treatment with acid and the ammonium oxalate and carbonate can be removed very efficiently by heating said oxalate or carbonate to about 200° F.

The reducing agents which can be used include the chemical reducing agents such as sodium borohydride, potassium borohydride, formaldehyde, formic acid, diborane, carbon monoxide, hydrogen and the radical anion technique set forth in U.S. Patent No. 2,177,412. The reduction with the chemical reducing agents should not be above approximately 800° F. to 1000° F. so as to avoid sintering the catalyst particles and losing surface area. The temperature at which the reduction takes place will depend upon the metals to be reduced and the particular reducing agent utilized.

The less noble metal is removed from the co-reduced combination of noble and less noble metal by either anodization or treatment with acid or base. Anodization or electrolytic removal of a less noble metal, for instance silver when combined with platinum, can be carried out by either the process of immersing the reduced metal powder resulting from the support removal in a 30% H₂SO₄ bath and holding it at a potential of 1 volt versus standard hydrogen until the current had decreased to zero indicating complete silver dissolution or by a process known as voltage scanning. In the voltage scan procedure the co-reduced combination of metals is immersed in 30% H₂SO₄ and using a potentiostat, the potential of the electrode is fixed at 0 volt versus standard hydrogen. The potential is then moved anodically (voltage scanning) to 1.5 volts versus standard hydrogen. The presence of silver in the co-reduced combination is indicated by the difference in the current noted during this scan when compared with a plain platinum electrode. Less current in the hydrogen oxidation region (0 to 0.3 volt) and a relatively large anodic current beginning at about 0.9 volt indicates silver dissolution. A preferred scan rate is 10 millivolts/second but is not critical. The system is returned to 0 volt versus hydrogen by moving the potential at the same rate in the reverse direction. This "voltage scanning" from 0 volt to 1.5 volts to 0 volt is repeated for a number of cycles, each time the silver contribution becoming less as the silver dissolves, until the scan becomes the same as a pure platinum scan indicating that the silver is completely dissolved. The removal of silver by this technique is easily monitored by the changing shape of the current trace. Also during the cathodic scan, the platinum reduction peak grows, indicating the surface area of the platinum available for electrochemical reaction.

In the case of dissolution with acid, the co-reduced combination of metals is simply stirred with the acid until the less noble metal dissolves. In the case of silver, complete dissolution is tested by placing the catalyst in fresh acid and testing for the presence of silver ion by adding sodium chloride.

The catalysts produced in accordance with the instant invention are quite suitable for use as catalysts in chemical reactions as initiators and accelerators. Examples of chemical processes which can utilize a catalyst produced in accordance with the instant invention include hydrogenation, dehydrogenation, polymerization, anodic oxidation, cathodic reduction and hydrocracking.

The following examples are submitted for the purpose of illustration only and are not to be construed as a limitation upon the scope of the invention as set forth in the appended claims.

EXAMPLE 1

40 grams of silica gel (Davison 40 to 100 mesh) were mixed with 242 milligrams of AgNO₃ dissolved in 40 ml. of H₂O. This mixture was constantly mixed and dried at about 95° C. (not over 100° C.). When dried this mixture was impregnated with 2.11 grams of H₂PtCl₆ dissolved in 40 ml. of H₂O. Again the material was dried at about 95° C. with constant mixing. Reduction of the metal salts was carried out by treating the material with a stream of hydrogen at 500° F. for 3 hours.

The product resulting from this reduction step was stirred in 6 M potassium hydroxide for 16 hours at room temperature (approx. 70° F.) to remove the silica. The resulting mixture was centrifuged leaving a metal powder which was washed with water.

Eighty milligrams of this resulting metal powder which was approximately 75 atom percent platinum and 25 atom percent silver was mixed with 8 milligrams of polytetrafluoroethylene powder and pressed at 3,000 p.s.i.g. into a platinum screen to form a flag electrode. This electrode was immersed in 30% H₂SO₄ and held at a potential of 1 volt versus the standard hydrogen electrode until the current had decreased to approximately 0 indicating complete silver dissolution. The electrolyte was changed several times during this anodic dissolution process.

A test of the surface area of the platinum indicated that the surface area of the platinum prepared in accordance with the instant invention was 50% greater than the platinum produced by the prior art procedure of reducing its salt from solution. The activity of the catalyst was tested during the anodic oxidation of methanol. The activity of the platinum produced in accordance with this invention was 2.0 ma./mg. compared to 1.2 for the commercial platinum.

EXAMPLE 2

Two high surface preparations of platinum were compared to commercial platinum black in both methanol activity and surface area as measured by the scan technique. A 75 atom percent platinum-25 atom percent silver preparation reduced on silica with H₂ was prepared as per Example 1 and divided into two portions. A first portion was voltage scanned according to the technique explained above, until the electrochemical contribution of the silver was eliminated. The number of scanning cycles required to eliminate the silver was 12. A second portion was treated with warm 25 vol. percent HNO₃ to remove the silver. The two catalysts were then tested as anode catalysts in a fuel cell utilizing methanol as the fuel, 30 wt. percent sulfuric acid as the electrolyte at 60° F. and a driven cathode. The results are set forth in Table I with accompanying explanations of the terms used therein. All preparations had surface areas and methanol activities which were superior to commercial platinum black.

TABLE I

Platinum	Surface Area, mc./mg.	Platinum Util. percent	Methanol Activity	
			Specific ma./mg. at 0.45 volts	Intrinsic ¹ ma./cm. ² at 0.45 volts
Commercial	100	10	1.2	25
Pt-25 Ag, Anodized	160	16	2.0	33
Pt-25 Ag, HNO ₃	177	17.7	4.0	40

¹ Normalized to equivalent surface area.

² Yield indicated complete removal of silver.

The term Pt-25 Ag, Anodized, represents the platinum catalyst produced by removing the silver from the co-reduced combination of 75 atom percent platinum and 25 atom percent silver by the anodization technique. The term Pt-25 Ag, HNO₃ represents the platinum catalyst

produced by dissolving the silver of a like coreduced combination with acid.

Surface area (millicoulombs per milligram) is a relative measure of the surface area derived from the cathodic scan. As there is no convenient way of measuring the surface area of the finely divided particles of catalyst, it must be measured indirectly. This can be done by measuring the size of the reduction peak of a pre-oxidized platinum catalyst using a cathodic scan. As the measured units are current (milliamps) and time (seconds), the area of the peak is derived in millicoulombs, which can then be divided by the mass of the catalyst in milligrams. The magnitude of the resulting number is directly related to the surface area. Table I shows the surface area per unit mass increasing as the various catalysts are tested in this manner. For example, the 75 atom percent platinum-25 atom percent silver combination treated with HNO_3 shows a surface area greater than the commercial catalyst used in the experiment. This means that the catalyst formed by treating this combination with HNO_3 has a proportionally greater surface area than the commercial catalyst, i.e., by a ratio of 177/100.

The term Platinum Util. percent, is that percent of the platinum which is actually available for use as a catalyst, and is a calculated number illustrative of the percent of the platinum atoms actually in the surface. The total number of platinum atoms in the electrode as determined by weighing, is compared with the number of electrochemically active atoms in the surface to find the percentage of platinum exhibiting catalytic activity. Note that as the surface area increases, the percent of platinum utilized also increases indicating that more platinum atoms are available for use as catalyst.

Methanol activity is listed in two ways. Specific activity is the number of milliamps obtained per milligram of catalyst measured at 0.45 volt polarized and is thus a measure of the inherent activity of the catalyst. It takes into account both the intrinsic activity of the catalyst and the larger surface area available. Table I indicates that the catalyst prepared by this process has a much greater inherent activity than the catalyst prepared by the commercial process. For instance, the catalyst prepared by nitric acid leaching is almost four times as active as the commercial material. Intrinsic activity, as defined here, is the measured activity of the catalyst corrected for surface area differences, and thus indicates that the activity of the platinum atoms themselves, produced by the instant process, is also greater. This is a truly unique feature of this method. One would expect that an increase in surface area would increase catalytic activity, but it has been found by this process that, in addition to increasing the activity by increasing surface area, the activity of the platinum per unit surface area is also increased.

EXAMPLE 3

10 grams of silica gel (Davison 40 to 100 mesh) were mixed with a solution of 170 milligrams of silver nitrate in 10 ml. of H_2O . This mixture was constantly mixed and dried at about 95°C . (not over 100°C .) on a hot plate. When dried this mixture was impregnated with a solution of 740 milligrams of chloroplatinic acid and 260 milligrams of ruthenium chloride in 10 cc. H_2O . The resulting material was again dried at about 95°C . and stored in a desiccator overnight. Reduction of the metal salts was accomplished by treating the material with a stream of hydrogen at 500°F . for 3 hours.

The product resulting from this reduction step was stirred in 6 M potassium hydroxide for approximately 16 hours at room temperature (approximately 70°F .) to remove the silica. The resulting mixture was centrifuged leaving a metal powder which was washed with water.

The metal powder which was a coreduced combination of platinum, ruthenium, and silver was divided into two portions. One portion of this powder was made into an

electrode and the silver was removed as per the anodization process of Example 1. The other portion of powder was stirred for approximately 1 hour in 25 wt. percent HNO_3 to dissolve the silver. The platinum-ruthenium catalyst resulting from this acid treatment was washed successively with H_2O , H_2SO_4 , and H_2O , and subsequently made into an electrode. The catalysts produced by the above two silver removal procedures were approximately 60 atom percent platinum and 40 atom percent ruthenium.

The two resulting platinum-ruthenium catalysts were then tested for activity as anode catalysts in a fuel cell utilizing methanol as a fuel with 30 wt. percent H_2SO_4 as an electrolyte and compared with a platinum-ruthenium catalyst prepared by a prior art method. The temperature was 60°F . The results are set forth in Table II.

TABLE II

	Current density in ma./cm. ² at indicated volts polarization			
	0.20 v.	0.25 v.	0.30 v.	0.35 v.
Pt-Ru Catalyst:				
A -----	0.3	2.1	14	90
B -----	2.5	12.2	63	300
C -----	1.7	9.2	50	290

A is a standard 60 atom percent Pt-40 atom percent Ru catalyst prepared by reducing platinum and ruthenium salts in solution.

B is a 60 atom percent Pt-40 atom percent Ru catalyst prepared by the instant process with the silver removed by anodization.

C is a 60 atom percent Pt-40 atom percent Ru catalyst prepared by the instant process with the silver removed by treatment with HNO_3 .

In connection with Table II it is important to note that the current increases logarithmically with potential. The higher the current density at any given polarization, the higher the activity of the catalyst. Thus, at 0.30 volt polarized, the activity of the catalyst prepared by the present process is approximately 4 to 5 times that of the catalyst prepared by the prior art procedure. The activity of the catalyst prepared by the instant method, as indicated in Table II, is the summation of the contribution of activity attributed to an increase in surface area and the contribution of activity attributed to the increase in the intrinsic catalytic effect of the platinum-ruthenium catalyst.

In summary, the examples and other foregoing explanations disclose a novel method of making a noble metal catalyst which demonstrate improved catalytic activity over catalysts produced by prior art procedures. The unique combination of steps described above each contribute an unknown quantity of activity to the final product. Describing a catalyst produced by this method merely in terms of one percentage of metal to another would not reveal the increased activity attributed to this process. The proportion of noble to less noble metal is not critical; catalysts of varying degrees of activity may be desired necessitating different proportions of one metal to the other.

What is claimed is:

1. A method of making a highly active noble metal catalyst which comprises the steps of:

- impregnating a support with a salt of a noble metal and a salt of a less noble metal;
- reducing the metal ions of said salts;
- removing said support; and
- removing said less noble metal by anodization, said less noble metal always being different from the noble metal and always having the property of being more readily dissolved than said noble metal.

2. A method as claimed in claim 1 wherein the noble metal is selected from the group consisting of platinum, ruthenium, rhodium, palladium, iridium, osmium, rhenium, vanadium, titanium, tungsten, gold, cobalt, nickel

and the lanthanide series metals such as cerium, neodymium, samarium, gadolinium, promethium, ytterbium, terbium and combinations of the foregoing metals and the less noble metal is selected from the group consisting of chromium, manganese, iron, cobalt, nickel, copper, molybdenum, cadmium, tin, lead, aluminum and silver, said less noble metal always being different from the noble metal and always having the property of being more readily dissolved than said noble metal.

3. The catalyst produced according to claim 1.

4. A method as claimed in claim 1 wherein the less noble metal is silver.

5. A method as claimed in claim 1 wherein the support is selected from the group consisting of silica gel, alumina, calcium carbonate, ammonium carbonate, and ammonium oxalate.

6. A method as claimed in claim 1 wherein the noble metal is a combination of platinum and ruthenium and the less noble metal is silver.

7. The catalyst produced according to claim 6.

8. A method of making a highly active noble metal catalyst which comprises the steps of:

(a) impregnating a support with chloroplatinic acid and salt of a metal less noble than platinum;

(b) reducing the metal ions of said acid and salt;

(c) removing said support; and

(d) removing said less noble metal by anodization.

9. A method as in claim 8 wherein the less noble metal is silver.

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