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PLATINUM CATALYSTS

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1

The present invention relates to improvements in shaped self-supporting platinum and platinum alloy catalysts employed in high temperature reactions such as the catalytic oxidation of ammonia and the cracking of hydrocarbons.

Considerable losses in platinum from the catalysts usually occur at the high temperature at which they are employed such as 650° C. to 1000° C. Such losses, to a great extent, are caused by the change in structure of the catalyst during use which causes considerable roughening and loosening of the surface of the catalyst so that particles thereof are carried off with the reaction gases. These structural changes and losses not only reduce the strength of the catalyst bodies, but also substantially shorten the life thereof. Furthermore, the loss of the precious metal itself represents a substantial monetary loss.

It is an object of the invention to provide platinum catalysts in which the tendency to roughening during use is substantially reduced. It is a further object of the invention to provide platinum catalysts having a substantially longer life than those heretofore employed.

Platinum catalysts are usually used in the form of networks of wires or strips or other structures which are produced from the appropriately worked platinum or platinum alloys such as, for example, platinum-rhodium alloys. The networks required are, for example, woven from drawn unannealed wires, as annealed wires are not well suited to weaving.

In accordance with the invention, it has been unexpectedly discovered that the life of platinum as well as platinum alloy catalysts can be substantially increased by subjecting the finished catalyst structures to an annealing at temperatures at least 150° C. and preferably 300° C.–500° C. over the recrystallization temperature of the platinum or platinum alloy from which they are formed for a sufficient period of time that the crystal structure of the individual catalyst elements, namely, the wires or strips and the like is such that the majority of the individual crystals are so dimensioned that they reach across the smallest dimension of the individual catalyst elements. The annealing temperature, of course, is below the melting point of the platinum or platinum alloy from which the catalyst is formed. Preferably such annealing is continued until the size of the majority of the crystals along the longitudinal axis of the elements is a multiple of the transverse cross-section of the elements.

The temperature of such an annealing depends upon the composition of the catalyst elements

2

and to a slight extent upon the degree the platinum or platinum alloy has been worked. The recrystallization temperature of pure platinum which has been worked about 90% is about 900° C. The recrystallization temperature of platinum alloys is higher, for example, for a platinum rhodium alloy containing 5% of rhodium, it is around 1000° C. The recrystallization temperature can easily be recognized, as it is the temperature at which a decrease in the deformation hardness begins.

The duration of the annealing treatment according to the invention depends upon the cross-section of individual catalyst elements from which the catalysts are formed and can vary between wide limits. As the annealing, according to the invention, is continued until the catalyst elements are substantially composed of crystals of such dimensions that they reach across the entire smallest dimension of such elements, the required duration of the annealing increases with increased thickness of the elements.

The annealing in accordance with the invention is preferably accomplished by direct current resistance heating of the catalyst itself as more easily reproducible results are obtained and the time required for the annealing is considerably shortened. Preferably low voltage such as 10–20 volts are employed for the resistance heating. When indirect heating methods are employed, the catalysts are preferably hung free in the annealing ovens to avoid contact with each other and the oven walls. The time required for such annealing is, however, considerably longer than when electric resistance heating is employed. For example, the crystal structure of catalyst elements formed of pure platinum wires drawn more than 80% and having a diameter of 40–60 microns can be transformed to the desired structure according to the invention by annealing such elements for 3 to 5 hours at 1250° C. On the other hand, similarly suitable results can be obtained by electric resistance heating for about 20 minutes at 1350° C. Wires of larger diameter require longer treatment, for example, wires of 0.1 mm. diameter require 1 hour's electric resistance heating to produce similar results, namely, a crystal structure in which single crystals take up the entire transverse cross-section of the wire.

The following tables illustrate the results obtained by annealing catalysts produced from wires of 60 microns diameter. In each instance substantially all of the crystals obtained are of

such thickness that they take up the entire transverse cross-section of the wires.

CHEMICALLY PURE Pt WIRES

Duration of annealing in minutes	Annealing Temperature, ° C.	Length of crystals along wire axis in microns
2	1,350	17–170
20	1,350	30–270
30	1,350	30–300
300	1,400	480

95% Pt, 5% Rh WIRES

Duration of annealing in minutes	Annealing Temperature, ° C.	Length of individual crystals along wire axis in microns
2	1,400	14–140
30	1,400	30–200

Catalysts produced according to the invention have been found to possess catalytic activity substantially identical with those previously employed. They are employed with extreme advantage in the oxidation of ammonia to nitrogen oxides wherein high temperatures such as about 800° C. are employed, as the amount of platinum lost therefrom is substantially less than from the ordinarily employed catalysts which have not been annealed to provide the crystal structure according to the invention and, consequently, have a considerably longer life.

While it is possible to provide the desired crystal structure in the wires or strips from which the catalysts are produced, for example, by weaving, this has not been found satisfactory. The coarse crystalline structure of such wires or strips effect the mechanical properties in such a way as to render the formation of the catalyst, for example, by weaving, difficult, if not impossible.

On the other hand, it has been found that catalysts, for example, woven networks, which have been annealed according to the invention so that the crystal structure is such that the majority of the individual crystals reach across the smallest dimension of the wires or strips and preferably so that such crystals have a length which is a multiple of the smallest dimension of the wires or strips, will withstand the normal stresses and strains encountered during use as a catalyst.

The term metallic platinum catalyst as used herein and in the appended claims is intended to cover not only pure platinum catalyst, but also platinum alloy catalysts. Accordingly, also the term "platinum metal elements" from which such metallic platinum catalysts are formed is used herein and in the appended claims not only to signify elements formed of pure platinum, but also elements formed of platinum alloys.

The treatment of the catalysts in accordance with the new invention is not merely limited to catalysts formed of physically pure platinum. Surprisingly, it was found that the desired life increasing crystal structure may also be obtained in using chemically pure platinum as such or chemically pure platinum alloys for the manufacture of said catalysts.

We claim:

1. A woven platinum wire network suitable for high temperature catalytic reactions the wires of which are substantially composed of crystals having a cross-section transverse to the longitudinal axis of the wires identical with the transverse cross-section of the wires and whose size in the direction of the longitudinal axis of the wires is a multiple of the diameter of the wires.

2. A self supporting platinum metal catalyst consisting of a network formed of a plurality of relatively thin extended platinum metal elements, wherein the elements are substantially composed of crystals whose size in the direction of the thinnest dimension of such elements is equal to such thinnest dimension and the size of such crystals in the direction transverse to the thinnest dimension of such elements is a multiple of such thinnest dimension.

3. A self supporting platinum-rhodium alloy catalyst consisting of a network formed of a plurality of relatively thin extended platinum-rhodium alloy elements, wherein the elements are substantially composed of crystals whose size in the direction of the thinnest dimension of such elements is equal to such thinnest dimension and the size of such crystals in the direction transverse to the thinnest dimension of such elements is a multiple of such thinnest dimension.

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