This invention relates to hydrogenation catalysts, and, more particularly, to a new class of alloy-skeleton hydrogenating metal sulfide catalysts. More specifically, it relates to alloy-skeleton metal sulfide catalysts characterized by high activity and resistance to poisons and corrosion, and to a process for their preparation.

For many years technical progress and commercial development in the field of catalytic hydrogenation has been largely dependent on the use of the more familiar types of base metal catalysts such as nickel, cobalt, iron, and copper. In general, these catalysts are employed either in the form of finely divided metals, as oxides, or as oxide combinations containing one or more difficultly reducible oxides, such as chromium oxide, which serve as promoters. Catalysts of this type have found increasingly widespread commercial utility owing to their activity towards various hydrogenations such as the saturation of olefinic bonds, reduction of esters, conversion of aromatic compounds to hydroaromatic compounds, and the reduction of nitriles, nitro compounds and the like to amines. It is a familiar fact, however, that all catalysts coming within this classification are sensitive to certain catalyst poisons, such as sulfur, and that their activity is partly or wholly destroyed by the corrosive action of acids and in some cases by strong alkalies as well. These disadvantages have accordingly operated to restrict the utility of these familiar base metal catalysts except in connection with hydrogenations in which the problems of poisoning or corrosion are seldom met.

For the more difficult types of hydrogenations it has been largely necessary to rely on noble metal catalysts of the platinum sub-group in order to accomplish desired hydrogenations for which nickel, cobalt, etc., are unsuited for the reasons set forth above. Although metals of this group, particularly platinum and palladium are valuable catalysts for conducting hydrogenation reactions under adverse conditions, few if any commercial processes based on their use have been developed on account of their relative scarcity and high cost.

It is therefore an object of this invention to provide a new hydrogenation catalyst that is relatively inexpensive, highly active, poison-resistant, and non-corroding. Another object is to provide a process for the manufacture of such a catalyst. Still another object is to provide a more effective method for catalytic hydrogenation. Other objects will be apparent from the following description of the invention.

These objects are accomplished by treating an alloy of an alkali soluble metal and a metal selected from the group consisting of the hydrogenating metals of the 1st, 6th, and 8th groups of the periodic table with an alkali metal sulfide. According to the preferred embodiments of the invention hydrogenation catalysts are prepared by treating alloys of metals selected from the group consisting of the hydrogenating metals of the 1st, 6th, and 8th groups of the periodic table and alkali-soluble metals with solutions of alkali metal sulfides and polysulfides at temperatures in excess of 25° C., thereby preparing an alloy-skeleton metal sulfide catalyst.

A hydrogenating metal of the class referred to above, such as iron, cobalt, nickel, copper, tungsten, or molybdenum is alloyed with aluminum preferably in the proportions of 30 to 50 parts of the former and 70 to 50 parts of the latter, and the alloy is ground to a fine powder by conventional methods. One hundred parts of the alloy powder is suspended in 400 parts of boiling water and a solution of 100 parts of hydrated sodium sulfide (Na2S.9H2O) in approximately 180 parts of water added slowly over a period of 1 to 1.5 hours. The mixture is boiled with efficient stirring for an additional 4 hours and allowed to settle. The supernatant liquid is separated and the sludge washed once or twice with water by decantation to remove soluble salts. The precipitate is then taken up in a solution of 100 parts of hydrated sodium sulfide and 50 parts of caustic soda in 400 parts of water and boiled for 3 to 4 hours to complete the digestion. The product is allowed to settle, the supernatant liquid decanted, and the sludge washed thoroughly with water until free from alkali, salts, and hydrogen sulfide. The resulting product, which comprises an alloy-skeleton metal sulfide catalyst supported on alumina, is obtained as a thick aqueous paste ready for use. In some cases, particularly for employment in non-aqueous hydrogenation systems, it may be desirable to transfer the catalyst to alcohol or some other appropriate organic liquid.

The following examples set forth certain well defined instances of the application of this invention. They are, however, not to be considered as limitations thereof, since many modifications may be made without departing from the spirit and scope of this invention.

**Example 1**

Two hundred twenty-seven parts of finely ground cobalt-aluminum alloy containing ap-
proximately 35% cobalt and 65% aluminum was suspended in 1000 parts of water. The mixture was heated to boiling with vigorous stirring and a solution of 226 parts of hydrated sodium sulfide (Na₂S·9H₂O) in 375 parts of water was added slowly over a period of 1.25 hours. A vigorous reaction accompanied by the evolution of hydrogen and traces of hydrogen sulfide ensued, and the suspended alloy was converted to a gray sludge. After boiling for an additional 4 hours the mixture was allowed to settle, the supernatant liquid decanted and the residue washed twice with water to remove soluble salts. The sludge was then resuspended in a solution containing 1000 parts of water, 226 parts of hydrated sodium sulfide, and 113 parts of sodium hydroxide and boiled during a further period of 4 hours, the water lost by evaporation being replaced from time to time. The catalyst sludge was then allowed to settle and was washed with water by decantation until essentially free from alkali, sodium sulfide, and hydrogen sulfide. The resulting aqueous paste was washed with alcohol and stored under absolute alcohol. The solid catalyst was characterized by an extremely fine state of subdivision, and a remarkable ease of suspensibility in liquids. Analysis for cobalt, sulfur and alumina indicated a weight ratio of 1.94 parts cobalt, 1.0 part sulfur, and 1.8 parts of alumina. The molecular ration of cobalt to sulfur was 1:1 and the composition of the catalyst mixture corresponded to approximately 33 parts of cobalt sulfide supported on 67 parts of hydrated alumina.

**Example II**

A solution of sodium polysulfide was prepared by dissolving 593.3 parts of hydrated sodium polysulfide (Na₂S·9H₂O) in 750 parts of water and adding 142.6 parts of sulfur with vigorous stirring. The resulting red product was mixed with a solution of 440 parts of sodium hydroxide in 500 parts of water. The sodium polysulfide reaction was then added slowly to a stirred boiling suspension of 227 parts of a cobalt-aluminum alloy containing about 35 parts of cobalt and 65 parts of aluminum in 1000 parts of water. A vigorous evolution of gas occurred and the alloy was converted rapidly to a finely divided black powder. The mixture was boiled for 4 hours after completing addition of the sodium polysulfide, and the precipitate was allowed to settle overnight on a steam bath. The black catalyst sludge was washed thoroughly with water until free from soluble salts and stored as a thin aqueous paste. The product was essentially free from alumina, and contained 1.34 moles of sulfur per mole of cobalt.

**Example III**

Two hundred twenty-seven parts of a finely powdered cobalt-aluminum alloy containing about 35 parts of cobalt and 65 parts of aluminum was suspended in 1000 parts of boiling water. The mixture was stirred mechanically while adding slowly a solution of sodium polysulfide containing 84.0 parts of sodium hydroxide and 230 parts of sulfur in 1000 parts of water. On continued boiling, the alloy was transformed to a finely divided black powder, and after 70 hours 600 parts of 30% sodium hydroxide solution was added to complete dissolution of the alloy. The resulting mixture was heated on the steam bath overnight to facilitate sedimentation of this catalyst suspension. The product was separated from the supernatant liquid by decantation and washed several times with water to eliminate caustic and soluble salts, and hydrogen sulfide. The product was an aqueous paste of finely divided catalyst comprising essentially cobalt polysulfide on alumina.

Although in the foregoing examples the use of specific alloys and certain definite procedures for producing supported catalysts, soluble salts and hydrogen sulfide, the use of catalysts produced by the hydrogenation method have been referred to, it is to be understood that these factors are subject to wide variation within the scope of the invention without departing from the spirit thereof.

In general, the process of the invention is applicable to the preparation of a new and highly active class of poison-resistant, non-corrodible hydrogenation catalysts comprising alloy-skeleton sulfides and polysulfides of metals selected from the group comprising the hydrogenating metals of the 1st, 6th, and 8th groups of the periodic table. Typical metals of this class are iron, cobalt, nickel, copper, silver, tungsten, and molybdenum. According to the preferred embodiments of the invention, alloys of these metals with appropriate amounts of carbon and according to the general procedure outlined in the examples. Suitable alkali-soluble components of the alloys are metals such as aluminum and silicon, which are not only readily attacked by caustic solutions but which fail to yield sulfides and polysulfides that are stable in aqueous media. In general, alloys containing as much as 90% or as little as 10% of the hydrogenating metal component and corresponding amounts of the caustic soluble component are satisfactory for activation. It is particularly convenient, however, to employ alloys containing between 30% and 50% by weight of hydrogenating metal and between 70% and 60% of the soluble metal. Within this limits suitable alloys are prepared according to any of the conventional methods of the prior art, either as binary compositions containing only one of the metals, or as multiple compositions containing various combinations of metals coming within the scope of the invention.

In the practice of the invention, it is in general preferred to carry out the activation step essentially as described in the examples. However, as mentioned above, this process is subject to considerable variation, and the selection of a particular modification of a particular method will be determined by the composition of the alloy employed as starting material and the type and physical form of the catalyst desired. Broadly speaking, the activation process comprises treating the alloy with solutions containing sufficient alkali metal sulfide or polysulfide to react in equimolecular proportions with the total amount of the hydrogenating metal contained in the alloy. It is preferred to employ soluble sulfides or polysulfides of metals such as the alkali metals which are characterized by a strongly alkaline reaction in solution. The alkali metal sulfides may be employed alone or in combination with caustic alkalies, or a preliminary treatment of the sulfide may be followed by a treatment with caustic alkali solution to facilitate a more rapid and complete solution of the alkali-soluble component of the alloy. In general, the use of alkali metal sulfide solutions alone tends to cause the formation of a supported catalyst carrier is produced in situ from the soluble component of the alloy, whereas the use of caustic alkali favors the production of unsupported cata-
lysts. Variations in the amount of caustic em- 
ployed govern to a certain extent the relative pro-
portions of metal sulfide and support in a fin-
ished catalyst. In accomplishing these results, 
the mode of bringing together the alloy and the 
sulfide solution may also be varied considerably. 
For example, the alkaline reagent may be added 
to a suspension of the alloy or the alloy may be 
added in successive small portions to the sulfide 
solution without materially affecting the quality 
or properties of the catalyst produced. Adjust-
ing to either variation it is preferable to operate with 
solutions at or near the boiling point.

The alloy-skeleton hydrogenating metal sulfide 
catalysts of the invention may be conveniently 
prepared in physical forms adapted for operation 
either in batchwise liquid phase or continuous gas 
phase hydrogenation processes. In the former 
instance, the alloys are preferably reduced me-
chanically to powders prior to the activation pro-
cess in order to produce finely subdivided ma-
terials that are easily suspensible in liquids and 
provide a maximum surface per unit mass of 
catalyst. Catalysts suitable for operation in gas 
phase contact hydrogenation processes may be 
prepared either by briquetting powdered catalysts 
or by surface activation of alloy lumps of suitable 
size. In general, the alloy-skeleton metal sulfide 
catalysts of the invention are characterized by 
their resemblance, by their outstanding re-
sistance to corrosion by strong acids and alkalies 
at elevated temperatures, by their indifference 
to most types of catalyst poisons, and by their 
high activity and efficiency in promoting hydro-
genation reactions under conditions inadver-
table to the familiar metal and metal oxide hydrogen-
genation catalysts.

Alloy-skeleton metal sulfide catalysts are of 
wide-spread utility in the field of hydrogenation, 
not only because they function smoothly to pro-
mote hydrogenation reactions in general, but 
more especially because of their superior activity 
under conditions generally considered unfavor-
able for catalytic reduction processes. This su-
periority is clearly evidenced by the following ex-
pertiments showing various uses for alloy-skele-
ton cobalt sulfide catalysts, which among the 
those coming within the scope of the invention.

A mixture comprising 60 parts of cyclohex-
anone, 30 parts of sulfur, and 7 parts of alloy-
skeleton cobalt sulfide catalyst was charged into 
a high pressure reaction vessel and treated with 
hydrogen under 1000 to 2000 psig. in pressure 
at 150°C. Hydrogen was absorbed smoothly dur-
ing 3 hours. On working up the product accord-
ing to conventional methods there was obtained 
61 parts of pure cyclohexanethiol, which corre-
sponds to a molecular yield of 86% of theory.

In a similar experiment, the hydrogenation of 
heptaldehyde and sulfur with alloy-skeleton co-
balt polysulfide catalyst gave a high yield of 
heptanethiol. These experiments serve to illus-
trate the salutary properties of these catalysts. 
Under similar conditions ordinary nickel or cobalt 
catalysts are subject to severe poisoning and show 
little or no activity. Other types of hydrogena-
tion reactions requiring a sulfatic catalyst and 
in which the catalysts of this invention are par-
ticularly useful are the reduction of aliphatic nitrites to thiols, the cleavage of alkyl aryl disulfides to 
the corresponding thiols, the catalytic 
conversion of certain inorganic salts such as sulfites to a lower valence state.

The following experiment demonstrates the re-
sistance of alloy-skeleton metal sulfide catalysts 
to the corrosive action of strong acids at elevated 
temperatures: Fifty parts of 45% sulfuric acid and 1 part of alloy-
skeleton cobalt sulfide catalyst were charged into 
a corrosion-resistant high pressure autoclave and 
treated with hydrogen under 500 psig. pressure at 
a temperature of 135° to 140°C. for a period of 3 
hours. On working up the crude hydrogenation 
product there was obtained 10 parts of unreacted 
nitrobenzene, 19 parts of aniline and 8 parts of 
p-aminophenol. Conversely, alloy-skeleton cobalt 
sulfide catalysts promote the hydrogenation of 
organic nitro compounds such as nitrobenzene 
smoothly in caustic alkaline media at temperatures 
below about 150°C. at hydrogen pressures as 
low as 500 psig. From nitrobenzene the products 
are azobenzene, azoxybenzene, and 
aniline.

Having described in detail the preferred em-
bodyments of my invention, it is to be understood 
that I do not limit myself to the specific embodi-
ments thereof except as defined in the following 
claims.

1. A process for the manufacture of a highly 
active, poison-resistant, non-corrodible hydrogen-
ation catalyst which comprises treating an alloy 
of an alkali soluble metal and a metal selected 
from the group consisting of the hydrogenating 
mets of the 1st, 6th and 8th groups of the 
periodic table with an alkali metal sulfide.

2. A process for the manufacture of a highly 
active, poison-resistant, non-corrodible hydrogen-
ation catalyst which comprises treating an alloy 
of an alkali soluble metal and a metal selected 
from the group consisting of the hydrogenating 
mets of the 1st, 6th and 8th groups of the 
periodic table in finely divided form with an 
aqueous solution comprising an alkali metal sul-
hide and obtaining alloy-skeleton metal sulfide 
hydrogenation catalysts.

3. A process for the preparation of a hydrogena-
tion catalyst which comprises treating an alloy 
in finely divided form and in suspension in an 
aqueous medium containing an alkali metal sulfide, 
said reaction being carried out within the 
temperature range of from 25° to 100° C, and said 
alloy consisting of from 10 to 90% of a hydro-
genating metal of the 1st, 6th and 8th groups of 
the periodic table and 90 to 10% of an alkali 
soluble metal.

4. A process in accordance with claim 3 
characterized in that the alkali metal sulfide is 
an alkali metal polysulfide.

5. A process for the preparation of a hydrogena-
tion catalyst which comprises treating an alloy 
in finely divided form and in suspension in an 
aqueous medium containing an alkali metal sulfide 
and a caustic alkali, said reaction being car-
rried out within the temperature range of from 25° to 100° C, and said alloy consisting of from 
10 to 90% of a hydrogenating metal of the 1st, 
6th and 8th groups of the periodic table and 90 
10% of an alkali soluble metal.

6. A process for the production of a hydrogena-
tion catalyst which comprises treating a finely 
divided alloy with an aqueous solution of an alkali 
metal sulfide at a temperature near the boiling 
point of said solution, said alloy consisting to 50 
5% of a hydrogenating metal of the 1st, 6th and 
8th groups of the periodic table and 70 to 50% of 
an alkali soluble metal.

7. A process in accordance with claim 6
characterized in that the hydrogenating metal in said alloy is cobalt and the alkali soluble metal is aluminum.

8. A metal sulfide hydrogenation catalyst prepared by a process consisting of treating an alloy of an alkali soluble metal and a metal selected from the group consisting of the hydrogenating metals of the 1st, 6th and 8th groups of the periodic table with an alkali metal sulfide.

9. A metal sulfide hydrogenation catalyst prepared by a process consisting of treating an alloy in finely divided form and in suspension in an aqueous medium containing an alkali metal sulfide and a caustic alkali, said reaction being carried out within the temperature range of from 25° C. to 100° C., and said alloy consisting of from 10 to 90% of a hydrogenating metal of the 1st, 6th and 8th groups of the periodic table and 0 to 10% of an alkali soluble metal.

10. The catalyst of claim 9 characterized in that the hydrogenating metal is cobalt.

11. The catalyst of claim 8 characterized in that the alloy is an alloy of cobalt and aluminum.

12. The catalyst of claim 8 characterized in that the hydrogenating metal is copper.

13. The catalyst of claim 8 characterized in that the hydrogenating metal is molybdenum.

14. The catalyst of claim 9 characterized in that the alloy is an alloy of cobalt and aluminum.

BENJAMIN W. HOWK.