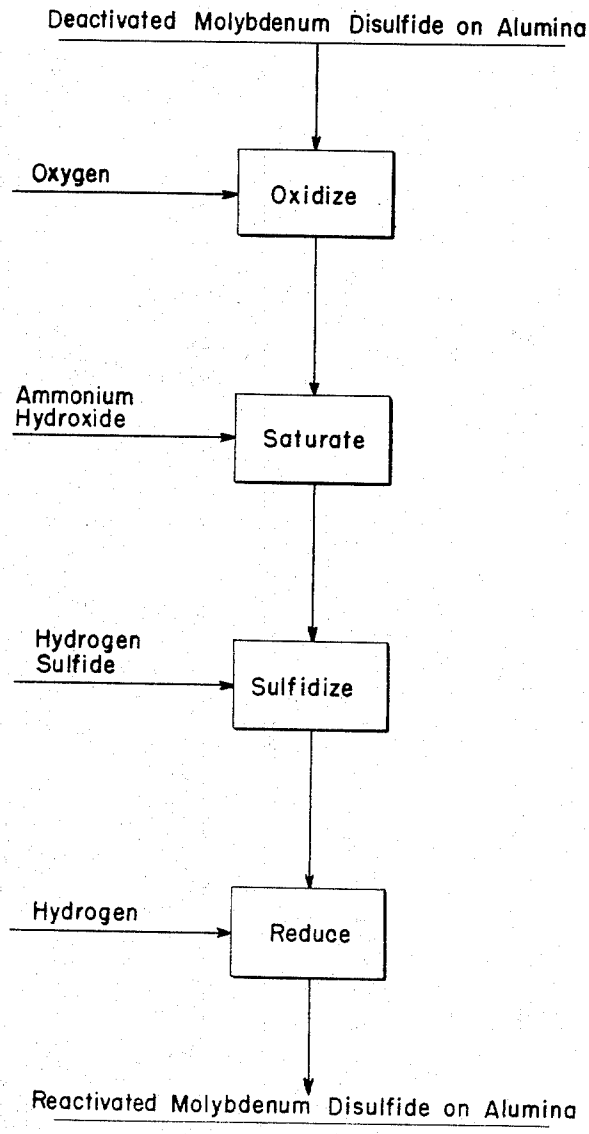
Aug. 17, 1954 H. L. JOHNSON ET AL 2,686,763

REGENERATION OF MOLYBDENUM SULFIDE CATALYST

Filed July 13, 1950



INVENTORS.
HERBERT L. JOHNSON
ARCHIBALD P. STUART

BY Burgess and Hardaj.

ATTORNEYS

Patented Aug. 17, 1954

2,686,763

UNITED STATES PATENT OFFICE

2,686,763

REGENERATION OF MOLYBDENUM SULFIDE CATALYST

Herbert L. Johnson and Archibald P. Stuart, Media, Pa., assignors to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

Application July 13, 1950, Serial No. 173,694

7 Claims. (Cl. 252—412)

1

This invention relates to the activation of spent metal sulfide catalysts. More particularly, the invention relates to the reactivation of molybdenum disulfide deposited on a carrier.

Molybdenum compounds, such as the disulfide, trisulfide, and oxide, have been described as effective in the hydrogenation of hydrocarbon oils. The sulfides have the advantages of high activity toward hydrogenation and resistance to poisoning by sulfur compounds usually found in petroleum, whereas the oxide has low activity as a hydrogenation catalyst and is rapidly deactivated in such processes. Notwithstanding low activity, the oxide is frequently employed since it may be readily regenerated by heating to an elevated temperature in the presence of oxygen or an oxygen contained gas, whereas no commercially feasible process for the regeneration of deactivated molybdenum sulfide catalyst, especially where the sulfide is deposited on a carrier, has been described. For example, the regeneration of molybdenum disulfide by roasting to convert the sulfide to the oxide, and subsequent direct treatment with hydrogen sulfide to convert the oxide to sulfide, has the disadvantage that the direct conversion of the oxide to sulfide is extremely difficult, and requires relatively drastic conditions such as a prohibitively long time of treatment. A further method heretofore described involves dissolution of the catalyst in hot, concentrated sulfuric acid and subsequent precipitation of the sulfide by hydrogen sulfide. This process has the disadvantage of requiring the use of a strong acid under corrosive conditions, and the necessity of removing the catalyst from the hydrogenation apparatus. Prior methods of regeneration, as above described, are not suitable for the regeneration of molybdenum disulfide deposited on a carrier wherein preservation and subsequent use of the carrier is desired. For example, heating to high temperatures, or digestion with hot, concentrated sulfuric acid removes desirable constituents of the carrier, such as moisture, and adversely affects the surface characteristics, and in the event of dissolution completely removes the sulfide from the carrier.

An object of the present invention is to provide a rapid and convenient method for the reactivation of molybdenum disulfide hydrogenation catalyst. A further object is to reactivate a molybdenum disulfide catalyst deposited on a carrier, wherein the carrier is not adversely affected by the treatment. A still further object is to provide a process for the reactivation of molybdenum disulfide deposited on a carrier wherein the sulfide catalyst is not removed from the carrier in the regenerative process. Other objects appear hereinafter.

2

It has now been discovered that a molybdenum disulfide hydrogenation catalyst deposited upon a carrier, and which has become deactivated through use in a process involving the hydrogenation of hydrocarbon oils, may be reactivated without destroying or adversely affecting the carrier. According to the present invention, deactivated molybdenum disulfide deposited on a carrier is heated in the presence of oxygen to remove at least a portion of the volatile carbonaceous materials, and to convert the disulfide to the oxide; the oxide is then treated with ammonium hydroxide to form ammonium molybdate; hydrogen sulfide is then contacted with the molybdate to form molybdenum thiomolybdate; the so-formed thiomolybdate is then heated in the presence of hydrogen to produce, in active form, molybdenum disulfide. Throughout all of the above steps, the molybdenum compound remains deposited on the carrier, the final product consituting molybdenum disulfide deposited on the carrier. In the following descriptions and illustrations of the process, the term "catalyst," unless otherwise qualified, is used to include the present active hydrogenation catalyst deposited on a carrier. Although molybdenum disulfide without a carrier, usually in the form of pellets, is usually employed, deposition thereof on a carrier enhances its activity toward hydrogenation, and hence reactivation of the catalyst-carrier composition is especially desirable.

The drawing is a diagrammatic illustration of an embodiment of the invention and indicates the sequence of steps in the regeneration of molydenum sulfide catalysts in accordance with the process of the present invention.

In the initial step, the spent catalyst is heated to a temperature of from 300° C. to 500° C. and preferably not above 400° C. for from 1 to 4 hours in the presence of oxygen or an oxygen containing gas, preferably air. Higher temperatures cause deactivation of the catalyst, probably due to removal of the moisture bound to the carrier, and to alterations in the surface of the carrier.

The carrier containing molybdic oxide is then treated with ammonium hydroxide and preferably is saturated with a concentrated aqueous solution of ammonium hydroxide, 12 normal ammonium hydroxide being suitable. It is preferred to use a quantity of ammonium hydroxide sufficient to saturate the catalyst; if an excess is employed so that a portion thereof is not ab-

sorbed, molybdenum in the form of ammonium molybdate may be removed from the catalyst, whereas a paucity of ammonium hydroxide results in incomplete conversion of the oxide to the thiomolybdate. This step is conveniently accomplished by admixing the catalyst with ammonium hydroxide until it is saturated. At this point, especially if relatively dilute ammonium hydroxide has been used, the catalyst may be subjected to mild drying, such as by heating to not over 150° C.

The treatment with hydrogen sulfide is preferably performed under relatively mild conditions, whereby the molybdate is converted to ammonium thiomolybdate; the temperature of treatment is advantageously ambient, i. e., atmospheric temperature is employed and control thereover is unnecessary, a temperature within the range of from 10° C. to 100° C. being suitable. The time of treatment is not critical, and usually is from ½ to 4 hours. Atmospheric pressure is suitable and is preferred, but elevated pressures may be employed if desired. The so-treated mass is then heated to from 200° C. to 400° C. for from 1 to 4 hours, preferably in the presence of hydrogen or other reducing gas to convert any trisulfide to disulfide. The product resulting from this treatment consists of molybdenum disulfide in active form deposited on the original carrier.

An advantage of the present process is that it may be accomplished without removing the catalyst from the hydrogenation apparatus. To illustrate this latter embodiment, when a hydrogenation catalyst consisting of molybdenum disulfide deposited on a carrier has become deactivated through use in a process wherein hydrocarbon oils are hydrogenated under elevated pressures of hydrogen, the process is discontinued and the fluids drained from the catalyst chamber, which is flushed with an inert gas, such as nitrogen or steam. The catalyst bed is then heated to a temperature of from 300° C. to 500° C. for from 1 to 4 hours, while passing a stream of air therethrough. An aqueous solution of ammonium hydroxide is then introduced into the chamber to saturate the catalyst; as an alternative to this step, ammonia and steam may be simultaneously injected into the catalyst chamber. Hydrogen sulfide, which may be diluted with an inert gas if desired, is then passed through the catalyst bed at ambient temperature. The catalyst is then heated to about 300° C. for 4 hours or less, preferably in the presence of hydrogen or a reducing gas. The catalyst is then ready to be employed in the hydrogenation process.

Where necessary or desirable, the catalyst may be removed from the hydrogenation apparatus for regeneration in accordance with the present process.

Aluminum oxide, bauxite, silica gel, comparable carrier materials, and mixtures thereof, are the preferred carriers to employ, in conjunction with molybdenum disulfide, in the process of the present invention, and which are not adversely affected by the process.

The following example illustrates the process of the present invention and its efficacy in the regeneration of molybdenum disulfide deposited on a carrier:

About 1300 grams of a hydrogenation catalyst consisting of 21% molybdenum disulfide deposited on 4–8 mesh activated alumina was prepared by means known to the art, namely, by impregnating 4–8 mesh alumina with an aqueous solution of a water soluble molybdenum salt, drying under mild conditions, treating with H_2S, and heating to from 300° C. to 400° C. in an atmosphere of hydrogen. This catalyst was employed for the hydrogenation of one pass catalytic gas oil containing about 31% aromatics, principally naphthalenes; operation was at about 340° C. and 1200 p. s. i. After about 4 months operation, the activity of the catalyst had decreased 21% as measured by the change of refractive index caused by the hydrogenation of the aromatic compounds.

The operation was discontinued, the catalyst removed from the hydrogenation apparatus, and heated to about 400° C. in an atmosphere of air for about 3 hours. About 12 normal ammonium hydroxide was added to substantially saturate the catalyst, which was then treated with H_2S at ambient temperature for about 1 hour. The so-treated mass was then heated to about 300° C. in the presence of hydrogen for about 3 hours to form the regenerated catalyst.

The regenerated catalyst was placed in service under the original conditions; it was found that the activity thereof, as compared to the activity of the catalyst as originally employed, varied only by about 3%, and no loss of mechanical strength was observed.

The process of the present invention, as above described, is directed primarily to the regeneration of molybdenum disulfide deposited on a carrier, which is a preferred embodiment of the present invention. Various modifications will be apparent and are included within the scope of the present invention. For example, molybdenum disulfide not deposited on a carrier may be regenerated in the present process, in which case it is usually in pellet or lump form, and molybdenum trisulfide may be regenerated by omitting the reducing gas from the final step of the process.

The present process is applicable for the regeneration of molybdenum disulfide catalysts which have become relatively inefficient in hydrogenation processes generally, especially those involving the hydrogenation of carbonaceous materials, such as aromatic hydrocarbons, as above described, the hydrogenation of unsaturated non-aromatic hydrocarbons such as olefins, and the like.

The invention claimed is:

1. Process for the regeneration of a catalyst comprising molybdenum disulfide deposited on a carrier which has become relatively inefficient for the hydrogenation of carbonaceous materials which comprises heating said catalyst to a temperature of from 300° C. to 500° C. in contact with oxygen to convert the disulfide to the oxide, saturating the resulting oxide-carrier composition with about 12 normal ammonium hydroxide to convert the oxide to ammonium molybdate while maintaining the composition in solid form, treating with hydrogen sulfide at ambient temperature and atmospheric pressure to convert the ammonium molybdate to ammonium thiomolybdate while maintaining the composition in solid form, and then heating to a temperature of from 200° C. to 400° C. in contact with hydrogen to convert said thiomolybdate to molybdenum disulfide, whereby reactivated molybdenum disulfide deposited on the original carrier having essentially the same activity toward the hydrogenation of aromatic hydrocarbons as when initially prepared is formed.

2. Process according to claim 1 wherein the carrier consists essentially of aluminum oxide.

3. Process according to claim 1 wherein the carrier consists essentially of bauxite.

4. Process according to claim 1 wherein the carrier consists essentially of silica gel.

5. Process for the treatment of molybdenum sulfide catalysts which have become relatively inefficient for the hydrogenation of carbonaceous materials which comprises heating the catalyst to a temperature of from 300° C. to 500° C. in contact with oxygen to convert the sulfide to the oxide, absorbing ammonium hydroxide on the solid oxide composition in amount just sufficient to convert the oxide to ammonium molybdate while maintaining the composition in solid form, treating with hydrogen sulfide to convert the ammonium molybdate to ammonium thiomolybdate while maintaining the composition in solid form, and then heating to a temperature of from 200° C. to 400° C. in contact with hydrogen to convert the thiomolybdate to molybdenum disulfide.

6. Process for the treatment of molybdenum sulfide catalysts which have become relatively inefficient for the hydrogenation of carbonaceous materials which comprises heating the catalyst

to a temperature of from 300° C. to 400° C. in contact with oxygen to convert the sulfide to the oxide, absorbing a concentrated aqueous solution of ammonium hydroxide on the solid oxide composition in amount just sufficient to convert the oxide to ammonium molybdate while maintaining the composition in solid form, treating with hydrogen sulfide at a temperature of from 10° C. to 100° C. for from ½ to 4 hours to convert the ammonium molybdate to ammonium thiomolybdate while maintaining the composition in solid form, and then heating to a temperature of from 200° C. to 400° C. in contact with hydrogen to convert the thiomolybdate to molybdenum sulfide.

7. Process according to claim 6 wherein the molybdenum sulfide is deposited on a carrier.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,904,218	Franceway	Apr. 18, 1933
2,123,623	Brown	July 12, 1938
2,398,175	Cole	Apr. 9, 1946