

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF OLEFINE OXIDES

Gerardus Hendricus Visser, Amsterdam, The Netherlands; vested in the Alien Property Custodian

No Drawing. Application filed August 14, 1939

This invention relates to a process for the production of olefine oxides which comprises reacting an olefine with an oxygen-containing gas in the presence of a highly active silver metal catalyst prepared by subjecting silver and/or silver compounds while in an aqueous medium to the action of nascent hydrogen.

An object of the present invention is to provide an improved process for converting olefines to olefine oxides by means of an extremely active silver metal catalyst. A further object of the invention resides in a practical, economical and broadly applicable method of effecting the catalytic oxidation of olefines to olefine oxides.

By oxidizing olefines in the presence of the highly active silver metal catalysts prepared in accordance with the invention, high yields of the valuable olefine oxides may be obtained. Although part of the olefines are oxidized in the process to incidental by-products including carbon dioxide, water and aldehydes, the use of my silver metal catalyst permits a high yield of the desired olefine oxide to be obtained and provides a highly desirable method for commercially manufacturing the olefine oxides.

Normally gaseous or readily volatile unsaturated organic compounds such as ethylene, propylene, the butylenes, the amylenes and their homologues and suitable substitution products are preferably employed in the process. A substantially pure olefine may be used or, if desired, a mixture of several olefines is suitable. Furthermore, various diluents may be used with the olefines such as paraffins. Being able to use mixtures of an olefine or olefines with paraffin hydrocarbons is very desirable since fractions containing these constituents may be used without separation therefrom of the paraffins; these fractions being readily obtainable from thermal and catalytic cracking of petroleum and shale oils, destructive distillation of coal, cracking of synthetic hydrocarbon oils and the like. It may be desirable to use other diluents with the olefines such as comparatively inactive gases like carbon dioxide, hydrogen, nitrogen, steam, etc.

The oxygen-containing gas used in the process may be substantially pure oxygen or it may contain one or more other gases such as nitrogen, hydrogen, carbon dioxide, steam and the like. Air is a preferred oxygen-containing gas for use in the process, although other gas mixtures containing oxygen may be especially desirable under some conditions.

The high yields obtained by the process are believed to be due to the very active catalyst em-

ployed and the activity of the catalyst appears to be due to the novel method of preparing the silver. Heretofore silver catalysts have been prepared by several different methods. One commonly used method consists in impregnating an inert spacing material with an aqueous solution of a silver salt, heating the resulting mass under controlled conditions to drive off water and the acid radical with which the metal is combined to produce the oxide of the metal, air being present if necessary to the formation of the oxide, and reducing the oxide at suitable temperatures in the presence of a reducing gas. Another method in use for the preparation of silver metal catalysts consists in thermally decomposing, preferably in a reducing or inert atmosphere, an organic silver compound, for example, a silver salt of a carboxylic acid. Finely divided silver metal catalysts are also prepared, principally for use in liquid phase reactions, by dissolving or suspending decomposable silver compounds in inert liquid media or in liquids intended for subsequent reaction and decomposing the silver compound in situ by the application of heat usually with the passage of hydrogen through the liquid in which the resulting metallic silver is deposited.

Some of the silver catalysts prepared in accordance with the prior art methods under properly controlled temperature conditions have a certain degree of effectiveness in accelerating the normal rate of many chemical reactions, but none of a great number tested have the effectiveness of the silver catalysts of the present invention in accelerating the rate of oxidation reactions. The silver metal catalysts prepared in accordance with the process of the invention are particularly effective in effecting the oxidation of ethylene to ethylene oxide. Their use permits the attainment of better yields, while operating at lower temperatures and thereby decreasing losses due to side reactions, than can be obtained with silver catalysts prepared by the known methods.

In accordance with the present invention silver metal catalysts are prepared by subjecting silver and/or silver compounds while in an aqueous medium to the action of nascent hydrogen. The nascent hydrogen may be generated in the liquid medium in which the silver metal catalyst is being prepared and/or it may be introduced into said medium, during the preparation of the silver metal, from a suitable outside source.

Nascent hydrogen suitable for use in the execution of the process of the invention may be prepared in a variety of manners. For example, nascent hydrogen may be prepared by electroly-

sis, by dissolving non-noble metals in aqueous media, by effecting electrical discharges in a hydrogen atmosphere, by effecting the thermal decomposition of ordinary hydrogen, etc. In the execution of the process of the invention, any one or any combination of the above and other means may be employed to furnish the nascent hydrogen prior to or during its use. For the attainment of the best results, the nascent hydrogen is preferably used as soon as practicable after its preparation. For this reason, it is desirable, in many cases, to prepare the catalyst in such a manner and under such conditions that, in the same media and at the same time, nascent hydrogen is generated and acts on the silver metal during and after its formation.

The catalyst may, for example, be prepared in the desired form in aqueous medium and while being subjected to the action of nascent hydrogen generated in situ by resorting to methods of electrolysis. A variety of conventional electrolysis cells may be used, and the active silver metal catalysts prepared by electrolytic reduction of a wide variety of inorganic and/or organic silver compounds. In one embodiment of the invention, both the anode and the cathode are silver. The silver electrodes are placed in a cell of suitable size and containing the required amount of electrolyte, and the current applied. Silver metal, which has been subjected to the action of nascent hydrogen formed in the cell, deposits on the cathode in the form of a spongy, grey precipitate. The precipitated silver metal can from time to time be scraped from the cathode and removed from the cell without interrupting the operation. During the electrolysis, it is, in general, advantageous to keep the electrolyte in the cell in motion by mechanical stirring or other suitable means. The electrolysis is conveniently effected at about room temperature, but higher or lower temperatures may be used when necessary or desirable.

The electrolyte used comprises water to which has been added in the desired amount an acid, salt or base which ionizes and makes the aqueous medium a conductor. If desired, the electrolyte may be an aqueous solution of a silver salt, such as silver nitrate. Other conveniently employed electrolytes are the aqueous solutions of the alkali metal salts. The current density applied may vary considerably. In general, current densities of from about 0.75 to about 3 amperes per square decimeter are suitable.

In removing the electrolytically reduced silver metal catalyst from the cell and preparing it for subsequent use by washing and drying, it is desirable to preserve the activity of the catalyst by avoiding contact with the air as much as possible. This may be done by effecting such operations in an inert atmosphere, for example, in an atmosphere of nitrogen or hydrogen.

Another convenient method of executing the process of the invention to obtain a highly active silver metal catalyst comprises reducing a silver compound in an aqueous medium by means of nascent hydrogen generated in said aqueous medium by dissolving therein a metal less noble than silver. The aqueous medium in which the reduction of the dissolved or suspended inorganic or organic silver compound is effected may be acidic, neutral or alkaline depending upon the particular silver compound to be reduced and upon the particular metal which is to be dissolved therein to furnish the nascent hydrogen for the reduction. The reduction may be effected at any

suitable temperature. In many cases, it may be effected at about room temperature. A wide variety of metals may be employed for generating the nascent hydrogen in situ. It is only necessary that the metal selected be less noble than silver so that the aqueous medium in which the reduction is effected be incapable of dissolving silver but be capable of dissolving the added metal to generate the nascent hydrogen at the required rate. The reduction of the silver compound is conveniently effected in an aqueous alkaline medium in which a cheap and readily available metal such as zinc or aluminum is dissolved to generate the nascent hydrogen. These metals are preferably applied in a suitable finely divided form. During the reduction, the reaction mixture is preferably agitated, as by mechanical stirring or other suitable means, to insure even generation of the nascent hydrogen and efficient contact of the hydrogen and the material undergoing reduction. The reduction may, if desired, be effected in a closed vessel under superatmospheric pressure, preferably under a pressure of nascent hydrogen generated in the system or introduced into the system from an outside source.

After the reduction is complete, the precipitated silver is separated from the reaction mixture, washed free of salts and any of the added metal which did not react, and dried. To avoid loss of activity of the catalyst due to contact with the air, these operations are preferably conducted in a hydrogen atmosphere.

The catalysts prepared in accordance with the process of the invention may be used per se or in conjunction with one or more other metal or metal compound catalysts. They may, if desired, be supported on suitable catalyst carriers and supports such as charcoal, pumice, alumina, clay, etc. In some cases, the activity of the catalysts may be enhanced by incorporating therewith small amounts of promoter substances. Suitable substances for this purpose are platinum, gold, manganese, etc.

The silver metal and silver metal containing catalysts prepared in accordance with the process of this invention will be found highly advantageous and economical for use in a wide variety of chemical reactions, such as hydrogenations, oxidations, dehydrogenations, etc., conducted either the liquid or the vapor phase because of their ease of preparation and their great activity at relatively low temperatures. Typical operations wherein the catalysts may be used to particular advantage are the hydrogenation of unsaturated hydrocarbons and unsaturated oxygen compounds, and the oxidation of saturated and unsaturated organic compounds.

In executing the process of the invention the olefine or olefines together with such diluents as may be present and the oxygen-containing gases are passed over the silver catalyst at a predetermined desirable rate and temperature. In general, the molecular ratio of olefine to oxygen passed to the catalyst is maintained greater than one to one although the ratio may vary widely depending upon the specific operating conditions. Excellent results are obtained when about 1.5 to 2.5 mols of olefine to one mol of oxygen are employed.

The temperatures which may be used in the process may vary considerably depending upon the olefine being oxidized, the rate of flow being used, the condition of the catalyst and other factors. The silver metal catalyst prepared in accordance with the invention permits the oxida-

tion to be conducted at temperatures as low as 125°C. or lower. It is ordinarily preferred to employ a temperature of from about 100°C. to about 500°C. It is usually desirable to employ as low a temperature as may be conducive to obtaining good conversions of the olefine to olefine oxide since undesirable side reactions are lessened at lower temperatures. The highest temperature beyond which it is not desirable to conduct the reaction is governed largely by the tendency of the particular olefine oxide produced to undergo further oxidation, rearrangement, and decomposition as well as the character of the olefine being oxidized, the activity of the catalyst, the rate of flow of the reactants and the pressure on the reaction system. In general, the temperature should be maintained at a point lower than temperatures at which pyrolytic side reactions are favored.

In general it is preferred to execute the process at atmospheric pressure or at slightly in excess thereof. However, if desired, substantially higher or lower pressures than atmospheric may be utilized.

The heat of the reactions which occur when the olefine is oxidized may be advantageously used to maintain the catalyst mass at the desired temperature. This may be done by suitably arranging the apparatus for such a purpose by methods well known to the art. For example, the reaction zone wherein the oxidation reactions occur may be fitted to heat the incoming reactants. By the use of such an arrangement a considerable economy of operation may be effected.

The exit products from the reactor may be passed to suitable condensing, absorption or adsorption equipment. Thus the olefine oxide and more non-volatile constituents may be separated from the unreacted olefine and other gaseous constituents. After removal of the olefine oxide, the unreacted olefine may be mixed with the desired amount of oxygen-containing gas and again introduced into the reaction zone.

The following examples illustrate suitable modes of executing the process of the invention. It is to be understood that the invention is not to be regarded as limited to the particular compounds, methods of operation and conditions shown in the examples.

Example I

Two silver plate electrodes were immersed in a 5% aqueous solution of potassium nitrate, and electrolysis effected by applying a current density of about 1 ampere/sq. decimeter. During the electrolysis, the liquid in the cell was kept in constant motion by vigorous mechanical stirring. As the electrolysis proceeded, the silver metal deposited on the cathode was washed and dried, while being kept out of contact with the air as much as possible.

The resulting silver metal catalyst was found to be particularly effective for catalyzing the oxidation of ethylene to ethylene oxide at relatively low temperatures. A mixture of two liters of ethylene and about six and a quarter liters of air was passed per hour over the heated catalyst contained in a pyrex glass reaction tube at a temperature of about 200°C. The effluent gas was found to contain ethylene oxide in an amount

corresponding to about 20% by weight of the ethylene treated. Thus, with the catalysts prepared in accordance with the invention, good conversions of ethylene to ethylene oxide can be obtained at lower temperatures than are required by the silver catalysts prepared by the known methods. The use of lower temperatures decreases the loss of applied ethylene caused by side reactions.

Example II

A silver nitrate solution having a concentration of about 0.04N was electrolyzed employing two silver metal plates, each of which had a surface of about 100 sq. cm., as electrodes and using a current intensity of about 1 ampere. Silver metal was deposited on the cathode in the form of a spongy, grey colored precipitate which was intermittently removed during the course of the electrolysis. The precipitated silver was washed with water to remove silver nitrate, subsequently washed with acetone, and then dried in a stream of nitrogen. During the separation, washing and drying of the catalyst, contact with the air was avoided as much as possible by working in a nitrogen atmosphere.

The powdered silver metal, prepared as above-described in the presence of nascent hydrogen was found to possess high catalytic activity for converting olefines to olefine oxides like the silver metal catalyst prepared in Example I.

Example III

To a solution of about 80 gm. of potassium hydroxide in 1500 c.c. of water was added drop by drop, while stirring vigorously, a solution of silver nitrate consisting of about 63 gm. of silver nitrate in 1000 c.c. of water. While the silver nitrate solution was being added, a total of about 6.6 gm. of aluminum metal grit was simultaneously introduced into the stirred mixture intermittently in small proportions.

The liquid was decanted from the resulting precipitate and the precipitate treated with about 1 liter of a 1 N potassium hydroxide solution for about half an hour at room temperature. The precipitate was then separated by filtration, washed with a 2 N potassium hydroxide solution until free of aluminum, washed with water until free of hydroxide, and subsequently washed with acetone.

A small quantity of the resulting catalyst product was freed of acetone by passing ethylene over it, and its activity as a catalyst for the oxidation of ethylene to ethylene oxide tested. A mixture consisting of ethylene and air in the volume ratio of 1 to 2 was passed over the heated silver catalyst. Oxidation of the ethylene to ethylene oxide was effected at temperatures as low as 125°C.

The present application is a continuation in part of my application Serial No. 218,635, filed July 11, 1938.

While I have described my invention in a detailed manner and provide examples illustrating suitable modes of executing the same, it is to be understood that modifications may be made and that no limitations other than those imposed by the scope of the appended claims are intended.

GERARDUS HENDRICUS VISSER.