

1

3,104,263

PROCESS FOR THE MANUFACTURE OF
ACETALDEHYDE

Wilhelm Riemenschneider, Frankfurt am Main, Germany, assignor to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Brüning, Frankfurt am Main, Germany, a corporation of Germany
No Drawing. Filed Oct. 6, 1958, Ser. No. 765,272
Claims priority, application Germany Oct. 9, 1957
7 Claims. (Cl. 260-604)

This invention relates to a process for oxidizing olefins to aldehydes, ketones and acids.

A process has already been proposed wherein olefins, such as ethylene, are oxidized continuously with oxygen in the presence of catalysts containing palladium compounds and redox systems. This process is, however, rather expensive in view of the cost for the noble metal compounds which are used as catalysts.

Now I have found that ethylene can also be oxidized to acetaldehyde and/or acetic acid in the absence of noble metal compounds. To this end, an inorganic redox system, in which the metal used is at least monovalent in the reduced stage, is reacted with ethylene at a raised temperature and under a raised pressure in the presence of an oxidizing agent and water. There may be used, for example, redox systems containing metal compounds which may appear in various oxidation stages under the reaction conditions applied, for example compounds of copper, iron, cobalt, nickel, manganese, mercury, cerium, titanium, uranium, bismuth, tantalum, tin, lead, chromium, molybdenum, vanadium, antimony or other metals and, more especially mixtures of these metal compounds. Furthermore, the catalysts may be admixed with silver, zinc or cadmium salts. There may be used, for example catalysts containing mercury sulfate, mercury chloride, copper chloride, vanadyl sulfate, potassium permanganate, cerium nitrate or chromium nitrate or, more especially, mixtures of these salts. It is especially advantageous to use a catalyst which contains mercury sulfate.

The process according to this invention is carried out at a raised temperature and under superatmospheric pressure. The temperatures generally applied are within the range of between 50° and 250°, preferably 100° and 250° C. and, advantageously, 130° and 200° C., and the pressures applied may be as high as 400 atmospheres gauge, preferably 20 to 200 atmospheres gauge and, advantageously, 80 to 120 atmospheres gauge. The invention is, however, not confined to the ranges of temperature and pressure indicated above and may also be conducted, for example, under a pressure of 450 atmospheres gauge, or at temperatures above room temperature up to 150° C. Sometimes, it is especially advantageous to operate at a temperature in the range of 50-100° C.

As oxidation media there may be employed oxygen or gases containing oxygen, for example air. The oxidation medium and ethylene may be contacted with the catalyst either simultaneously or the ethylene is allowed to first react with the catalyst, especially when a liquid catalyst is used, whereby the redox system is converted to the lower valence stage, and then regenerated in a second stage with the aid of the oxidizing medium.

This two-stage process offers the advantage that the composition of the gas mixture need not carefully be controlled and that air may be used as oxidizing medium without a disadvantage being involved, even if the ethylene is recycled. This variant may be carried out by contacting the olefin and the oxidizing medium in periodic alternation with the circulating catalyst liquid in a vessel, or, when the process is carried out continuously, in a reciprocally reversible double-apparatus, or in several reaction spaces. In this variant, the pure ethylene may

2

be replaced by a mixture of oxygen and olefin whose oxygen content is below the explosion limits and which contains for example 1-10%, preferably 3-10% of oxygen, calculated upon the amount of olefin used. For an ethylene-oxygen mixture, for example, the lower explosion limit is at 20.1% of oxygen at atmospheric pressure. In this variant, the catalytic medium is contacted in a further separated stage under the same or another pressure and under known conditions, for example at 50-150° C., with the oxidizing medium, for example oxygen or air, which is used in an amount sufficient to bring about regeneration. This regeneration has the additional effect that ethylene or reaction product which may have dissolved in the catalytic medium depending on the conditions applied, is possibly likewise oxidized or removed from the catalyst by stripping. In order to produce a good stripping effect, regeneration may also be brought about using a mixture of oxygen or air with steam.

The process of this invention must be carried out in the presence of water. It is therefore possible to carry out the process in an aqueous or water-containing catalyst or in a suspension; the reaction may, however, also be carried out in the presence of a solid catalyst if care is taken that the gas mixture constantly contains water or steam. As catalyst carriers there may be used, for example, silica gel, pumice, silicates, titanium dioxide, kieselguhr, Al_2O_3 and carbon. When the reaction is conducted in the presence of a solid catalyst, it is advantageous to choose from the inorganic redox systems, in which the metal used is at least monovalent in the reduced stage, those which belong to subgroups II to IV of the periodic table. When the process is carried out in water-containing solutions, the latter may also contain a solvent, such as acetic acid, glycol, glycerol, dioxane, methylethyl ketone, acetone, higher ketones or mixtures thereof.

Instead of ethylene there may also be used gases containing ethylene, for example commercial gas mixtures which contain saturated hydrocarbons and may contain carbon monoxide and/or hydrogen as well as other gases inert towards the reaction. As gases inert towards the reaction which may be admixed, there may be mentioned, for example, nitrogen, carbon dioxide, methane, ethane, propane, butane, isobutane or other saturated aliphatic gases, furthermore cyclohexane, benzene or toluene.

The regeneration may be supported by adding active oxidizing agents, such as ozone, peroxide compounds, especially hydrogen peroxide, oxygen compounds of nitrogen, free halogen, halogen-oxygen compounds or compounds of the higher valence stages of metals, such as manganese, cerium, chromium, selenium, lead, vanadium, silver, molybdenum or cobalt. The addition of such active oxidizers facilitates the re-formation of the active catalyst component into the higher oxidation stage which is necessary for the reaction. Oxidation catalysts may also be added, if desired.

When halogen salts are used as redox systems, it is possible that volatile halogen compounds are formed under certain conditions. In order to counteract the halogen depletion of the redox system which is caused by the formation of such volatile compounds, it may be advantageous to continuously or discontinuously admix free halogen, for example chlorine, bromine, or bromine trichloride, suitably in a minor concentration, or hydrogen halide, or inorganic or organic compounds splitting off halogen or hydrogen halide under the reaction conditions applied. Such addition enables a possible depletion of anions to be counteracted and the lifetime of the catalyst to be prolonged.

The aforesaid substances may be added regardless of whether a liquid or solid catalyst is used and they may bring about at the same time the reformation of the catalytic substance into the higher valence stage and the regeneration of the catalyst. As compounds yielding halogen or hydrogen halide there may also be used saturated, low molecular weight, especially aliphatic halogen compounds, such as ethyl, propyl, butyl, acetyl, benzoyl or propionyl chloride, or phosgene.

Due to the presence of oxidizing media acetic acid may be formed in addition to acetaldehyde. If desired, the oxidation of acetaldehyde to acetic acid by known processes may be combined with the oxidation described in the preceding paragraphs so as to omit the aldehyde stage wholly or partially. It is furthermore important to work in an acid to neutral pH. The preferred pH values are between 1 and 5, but the reaction may also be carried out at a pH lower or higher than indicated above, for example at a pH near 0.

It has been found that difficulties which may appear when the reaction is carried out in the liquid phase and especially in the presence of copper, can be overcome by varying the ratio of ethylene to oxygen. Such difficulties may reside in the precipitation of cuprous chloride or other compounds formed during the reaction which cause cloggings. Since these precipitated salts are no longer available for the reaction, the yield decreases more or less rapidly. The moment at which the ethylene to oxygen ratio must be changed, can readily be determined by measuring continuously the pH. When the pH decreases, it is easily possible to readjust the optimum pH range by adding either more oxygen or less ethylene, or by combining these two steps. When the pH increases, the optimum pH-range can be readjusted inversely. This method of controlling the reaction may also be combined with the above described addition of compounds of acid salts which yield anions. It is especially advantageous to adjust the reaction medium to a certain pH at the onset of the reaction, for example by means of hydrochloric acid, and to regulate the ethylene oxygen ratio during the reaction. The pH may of course also be modified during the reaction by adding the necessary amount of an acid.

The pH is measured by using a device of known design. The pH may be measured continuously with electrodes arranged in the reactor, or discontinuously by measuring the pH of samples withdrawn in certain intervals of time.

In a special technical variant of this method the pH measuring device has an automatic connection to the dosing device for the supply of ethylene and oxygen. In this case the pH is once adjusted to the optimum value and the reaction can be then controlled automatically.

In a given case it may be advantageous to carry out the reaction in the presence of a salt, such as sodium chloride or potassium chloride, which for example—like hydrochloric acid itself or other alkali metal or alkaline earth metal halides, such as LiCl, CaCl₂, MgCl₂ or other salts, such as FeCl₂, FeCl₃ or CuCl₂—improve the solubility of CuCl, which may form in the course of the reaction and is only very sparingly soluble in water (0.11% at 80° C.). The solubility of CuCl may also be improved by the addition of formic acid; still better dissolving intermediaries are halogenated acetic acids or the salts thereof, especially when a catalyst containing copper chloride is used. These compounds have a very strong dissolving action on CuCl and need only be added in a minor amount, generally 1–50%, calculated upon the amount of copper (CuCl₂·2H₂O) contained in the solution.

Since by this measure the CuCl is kept in solution there is always a high concentration of cuprous ions available for the reaction with the oxygen. This favors the desired rapid oxidation to the readily soluble CuCl₂—this is presumably the velocity—determining step for the entire reaction—and accelerates the entire reaction.

From among the halogenated acetic acids, trichloro-

acetic acid and also dibromoacetic acid are especially active.

Similarly there may also be used the salts of halogenoacetic acids, mixtures of these salts, or mixtures of these salts with free halogenoacetic acids. As salts there may be employed those with inorganic cations or with organic bases. There may be mentioned more especially, salts of alkali metals, ammonia, alkaline earth metals, for example sodium, potassium, lithium, magnesium, calcium, barium, iron, copper or cerium, and also salts of triethylamine, tripropylamine, di- and/or triethanol amine.

The optimum amount of salts to be added is dependent on the composition of the catalyst used in each individual case. When a catalyst is used containing, per liter of water, 100 grams of CuCl₂·2H₂O, it suffices to add 20–25% of trichloroacetic acid or the corresponding amount of its salts, the percentage figures being calculated upon the amount of copper chloride used (CuCl₂·2H₂O).

The reaction may also be supported by increasing the ethylene and/or oxygen concentration in the reaction space. This can be done, for example by increasing the pressure and/or—especially when the reaction is carried out in the liquid phase—by operating in the presence of a solvent. The ethylene concentration in the reaction solution may be considerably increased, for example, by using higher concentrations of metal salts binding ethylene for instance salts of copper, iron or mercury compounds, or more particularly the halides, or the sulfate, especially when mercury is concerned, or by using organic solvents which, advantageously, are miscible with water, for example acetic acid, mono- or polyhydric alcohols, cyclic ethers or dimethyl formamide. After separation of the reaction products, the residual gas may be admixed with a corresponding amount of fresh gas and then recirculated to participate again in the reaction.

For stoichiometric reasons the molar ratio of olefin to oxygen must be 2:1 in the complete oxidation of ethylene to acetaldehyde. To prevent explosions, it is, however, advantageous to use oxygen deficiency, for example in the range of 2.5:1 to 4:1. Still further, it is advantageous to work outside the range of explosivity, for example with a content of oxygen of 8–20% or 8–14% under pressure, to circulate unreacted gas consisting especially of ethylene in excess or of inert gases, such as nitrogen, and to replenish the oxygen and ethylene as they are consumed.

It has also been found that the reaction of the present invention is favorably influenced by irradiation with sources rich in energy, preferably ultraviolet light, especially when oxygen is used as oxidizing medium. Such irradiation, which may also comprise X-rays, activates especially the oxygen, increases its oxidation activity, and promotes both the reaction with the ethylene and possibly the oxidative destruction of by-products, for example oxalic acid. These measures increase the rate of conversion, reduce the formation of undesired by-products and considerably prolong the lifetime of the catalyst, the activity of which may subside after a prolonged time.

A variant of the instant process consists in carrying out the reaction in a homogeneous liquid catalyst solution or in a slime catalyst. It is well established that at a constant volume of the reaction liquid and in the case where the reaction does not run completely in one direction, the rate of conversion is the better the higher and narrower the design of the reactor.

It is evident that the process in this invention can be carried out, inter alia, in known apparatus, through which the gases are passed, for example with high velocity in turbulent flow, or in another suitable device, when a liquid catalyst or slime catalyst is used; as reaction vessel there may be used, for example, a vertically arranged tube provided with a frit or an oscillatory agitator. The process may also be carried out in a usual reaction tower, for example a wash tower which is suitably filled with filling material. The gases may be atomized, for example through a frit, or introduced in another suitable manner,

and too voluminous gas bubbles may be divided into smaller ones, for example with the aid of an agitator. For this purpose there may also be used a vibro-mixer or a turbo-mixer. All these variants enable the reaction to be carried out continuously.

The conversion and the space/time/yield depend substantially on the fine distribution of the gas, the time of stay of the gas in the apparatus, and the composition of the catalyst liquid, the temperature and the pressure used. The optimum time of stay can readily be determined by a simple test.

As anions the catalyst may contain, for example, chlorine ions or halogen ions other than chlorine ions, such as fluorine or bromine ions, nitrate or chlorate or perchlorate radicals, or sulfate or acetate radicals, or mixtures of these anions and also organic anions, such as aromatic sulfonic acid esters.

When it is intended to regenerate a solid bed catalyst, the olefin supply may be arrested for some time and the catalyst may be treated simultaneously with oxygen or oxygen-containing gases, steam and an acid in vapor or gas form, preferably hydrogen chloride. A variant of such regeneration consists, for example, in passing oxygen or an oxygen-containing gas partially or completely and prior to being contacted with the catalyst through aqueous hydrochloric acid, preferably at a raised temperature. Accurately dosing the hydrochloric acid is especially simple when a 20% hydrochloric acid is used.

The apparatus used in the process of this invention are advantageously made from a material which possesses a sufficient heat conductivity and is not corroded by the catalyst.

In order to avoid corrosion in the apparatus used, it is often suitable to use an apparatus lined with titanium or a titanium alloy, for example with a titanium alloy containing at least 30% of titanium or with tantalum. There may also be used glass vessels or enamelled or rubber-lined vessels, especially when the catalyst contains mercury compounds. The reaction may also be conducted in brick-lined vessels or, under suitable reaction conditions, in vessels the insides of which are lined with plastic material, for example polyolefins, polytetrafluoro-ethylene or hardenable unsaturated polyesters, such as phenol, cresol or xylenol formaldehyde resins. As brick lining may be used, for example ceramic material, carbon-bricks impregnated with hardenable artificial resins and similar known materials.

The following examples illustrate the invention.

Example 1

An enamelled shaking autoclave (capacity: 2.5 liters) is charged with 1 liter of a 10% copper chloride solution, ethylene is forced in under a pressure of 50 atmospheres gauge, and the reaction mixture is heated for 30 minutes at 150° C. The internal pressure rises to about 90 atmospheres gauge. The reaction mixture is allowed to cool and expanded by means of a water wash whereby the acetaldehyde formed is collected. The catalyst solution is regenerated by introducing oxygen and can be used again. When the above catalyst solution is used for a prolonged period of time, the loss in chlorine is compensated by adding a small amount of hydrochloric acid.

Example 2

A high pressure tube is charged with a catalyst consisting of 100 cc. of silica gel which has been impregnated with a solution of 50 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 40 cc. of water. The tube is heated to 180° C. and a mixture of 20 normal liters (N.T.P.) of ethylene and 5 normal liters of oxygen is allowed to pass through the catalyst per hour under a pressure of 100 atmospheres gauge. By simultaneous introduction of steam in dosages care is taken that the catalyst has the necessary content of moisture. The escaping gas is cooled and the acetaldehyde

formed is removed by washing. The residual gas can be used again.

Example 3

A shaking autoclave provided with a silver lining (capacity: 0.5 liter) is charged with 200 cc. of a 10% FeCl_3 solution and ethylene is forced in under a pressure of 75 atmospheres gauge. The reaction mixture is heated to 200° C. and the pressure increases to about 310 atmospheres gauge. The supply of heat is arrested after 10 minutes, the reaction mixture is allowed to cool and worked up in the manner described in Example 1. 3% of the ethylene used has been converted to acetaldehyde. When the pure ethylene used is replaced by a mixture of 90% of ethylene and 10% of oxygen while the conditions are otherwise the same, the rate of conversion increases to 5%.

Example 4

An apparatus as that used in Example 3 is charged with 200 cc. of a 40% FeCl_3 -solution, ethylene is forced in under a pressure of 80 atmospheres gauge, and the reaction mixture is heated for 10 minutes at 250° C. The internal pressure increases to 396 atmospheres gauge. After cooling and expansion by means of a water wash, the acetaldehyde formed is titrated. 5% of the ethylene used has been converted to acetaldehyde. The catalyst solution is regenerated by introducing air.

Example 5

An autoclave (capacity: 1 liter) provided with a glass insert is charged with a 20% mercurichloride solution and ethylene is forced in under a pressure of 50 atmospheres gauge. After heating for 1 hour at 180° C. during which time the pressure increases to 88 atmospheres gauge, the reaction mixture is expanded by means of water wash flanges. 2.5% of the ethylene used has been converted into acetaldehyde. The residual ethylene can be used again. About the same rate of conversion is obtained under the same conditions by using a solution of bismuth trichloride, tin tetrachloride or antimony pentachloride.

Example 6

When the apparatus used in Example 5 is charged while the conditions are otherwise the same as described in that example with a suspension of 10 grams of tungstic acid in 500 cc. of normal hydrochloric acid, there is obtained 0.6% of acetaldehyde.

I claim:

1. A process for the manufacture of acetaldehyde which comprises contacting ethylene with molecular oxygen at a temperature above room temperature and up to about 250° C. and under superatmospheric pressure up to about 450 atmospheres gauge at a pH between 0 and 7 in the presence of water and of an inorganic redox system consisting essentially of at least one water-soluble salt of a metal selected from the group consisting of copper, iron, cobalt, nickel, manganese, mercury, cerium, titanium, uranium, bismuth, tantalum, tin, lead, chromium, molybdenum, vanadium, and antimony.

2. A process as in claim 1 wherein the reaction is carried out in the presence of halide ions selected from the group consisting of chloride ions and bromide ions and wherein additional halide ions selected from the group consisting of chloride ions and bromide ions are supplied during the reaction to a liquid catalyst formed by combination of said water and said inorganic redox system.

3. A process as in claim 1 wherein said water and inorganic redox system are combined to form a liquid catalyst, and said catalyst has a pH between 1 and 5.

4. A process as defined in claim 1 wherein said metal is copper.

5. A process as defined in claim 1 wherein said metal is mercury.

6. A process for the manufacture of acetaldehyde which comprises contacting ethylene at a temperature above room temperature and up to about 250° C. and under superatmospheric pressure up to about 450 atmospheres gauge in a first stage with a liquid catalyst having a pH between 0 and 7 and consisting essentially of water and an inorganic redox system consisting essentially of at least one water-soluble salt of a metal selected from the group consisting of copper, iron, cobalt, nickel, manganese, mercury, cerium, titanium, uranium, bismuth, tantalum, tin, lead, chromium, molybdenum, vanadium, and antimony, and then contacting said liquid catalyst with oxygen in a second stage.

7. A process as in claim 6 wherein said liquid catalyst is stripped between said first and second stages.

5

10

15

References Cited in the file of this patent

UNITED STATES PATENTS

1,999,620	Van Peski et al. -----	Apr. 30, 1935
2,055,269	Van Peski et al. -----	Sept. 22, 1936
2,333,216	Trieschmann et al. -----	Nov. 2, 1943
2,451,485	Hearne et al. -----	Oct. 19, 1948
2,486,842	Hearne et al. -----	Nov. 1, 1949
2,690,457	Hackmann -----	Sept. 28, 1954
2,776,316	Baldwin -----	Jan. 1, 1957

FOREIGN PATENTS

575,571	Great Britain -----	Feb. 25, 1946
664,879	Germany -----	Sept. 16, 1938
722,707	Germany -----	July 27, 1942