

1

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PROCESS FOR OXIDIZING OLEFINS TO ALDEHYDES, KETONES AND ACIDS

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

It has already been proposed to oxidize ethylene catalytically by means of an argentiferous catalyst to ethylene oxide, or by means of an oxidation catalyst other than a silver-containing catalyst at a raised temperature to obtain mixtures of formaldehyde, acetaldehyde, formic acid, acetic acid and other products. These processes, however, do not produce acetaldehyde or acetic acid in a yield interesting for an economical point of view. Our experiments have revealed that the oxidation carried out under such conditions in the presence of a noble metal catalyst likewise involves small yields of acetaldehyde, and the relative proportion of formaldehyde obtained generally preponderates.

It is also known that compounds of palladium, platinum, silver or copper form complex compounds with ethylene. Furthermore, the formation of acetaldehyde was observed in decomposing a potassium-platinum-complex compound. Other unsaturated compounds may favor the complex formation. In this case stoichiometric reactions are concerned yielding the noble metal as such.

It has also been described to reduce palladous chloride by means of ethylene in the presence of water to palladium metal. In this reduction the formation of acetaldehyde was observed.

Still further, it has been described that palladous chloride dissolved in water can be reduced rapidly and completely to palladium by means of propylene, even if propylene is admixed with nitrogen or air. It has also been described to reduce palladous chloride by means of isobutylene under the same conditions. It is, however, known that carbon dioxide is not evolved either in this latter reduction or in those reductions which are carried out in the presence of ethylene or propylene as a reducing agent.

In application Serial No. 747,115 in which two of the present inventors are co-inventors, a process is described according to which carbonyl compounds can be obtained from the corresponding olefins in a good yield and, if desired, in a continuous manner, by contacting said olefins with gaseous oxygen, water which is present in the vaporous form, and a solid catalyst which contains a compound of the noble metals belonging to group VIII of the periodic table as catalytic substance and a redox system.

In the aforesaid application the term "carbonyl compounds" is used in its broad sense, i.e. it covers not only aldehydes and ketones but also carboxylic acids such as acetic acid.

According to the aforesaid invention there may be used as redox systems, for example, those which contain compounds of metals which under the reaction conditions employed may appear in various oxidation stages, for example compounds of copper, mercury, cerium, thallium, tin, lead, titanium, vanadium, antimony, chromium, molybdenum, uranium, nickel, or osmium, and also inorganic redox systems other than specified above, such as sulfite/sulfate, arsenite/arsenate or iodide/iodine systems and/or organic redox systems, for example azo-

2

benzene/hydrazobenzene, or quinones or hydroquinones of the benzene, anthracene- or phenanthrene series.

As compounds of the noble metals of group VIII of the periodic table there may be used in the process of the aforesaid invention, for example, compounds of palladium, iridium, ruthenium, rhodium or platinum. Compounds of this series of metals are capable of forming addition compounds or complex compounds with ethylene. If desired the oxygen may be used in admixture with an inert gas. The oxygen may be employed, for example, in the form of air, which is the cheapest oxidizing agent. The use of air is, however, confined to certain limits, if the unreacted gases are circulated, inasmuch as nitrogen concentrates as ballast material. Instead of ethylene there may also be used a gas mixture containing ethylene and, for example, saturated hydrocarbons. The reaction may also be carried out in the presence of a noble metal.

The reaction may be supported or carried out by addition of an active oxidizer, such as ozone, peroxidic compounds, especially hydrogen peroxide or sodium peroxide, potassium peroxide, potassium persulfate, ammonium persulfate, alkali percarbonate, alkali perborate, peracetic acid, diacetyl peroxide, benzoyl peroxide, toluyl peroxide, oxygen compounds of nitrogen, such as nitrogen dioxide and nitrogen pentoxide or mixtures of nitrogen oxides containing the same, nitryl halides such as nitryl chloride, free halogen such as chlorine, bromine, or bromotrichloride, halogen-oxygen compounds such as chlorine dioxide, hypochlorous acid, chloric acid, perchloric acid, bromic acid, iodic acid, periodic acid, or compounds of the higher valence stages of metals, such as manganese, cerium, chromium, selenium, lead, vanadium, silver, molybdenum, cobalt, or osmium, for instance potassium permanganate, sodium bichromate, lead tetraacetate, vanadium pentoxide, silver difluoride, selenium dioxide, cerium-(IV)sulfate, osmium tetroxide. The addition of an active oxidizer facilitates the re-formation of the higher oxidation stage of the active catalyst component which is necessary for carrying out the reaction. These oxidizing agents may also be produced during the reaction. If desired, an oxidizing catalyst may be added.

In the reaction described in the aforesaid application it is often advantageous to add, prior to or during the reaction, a compound yielding anions under the reaction conditions applied, for example an inorganic acid, preferably a mineral acid such as sulfuric acid, nitric acid or a volatile acid such as hydrochloric acid or hydrobromic acid or a salt such as ammonium chloride, ammonium bromide, zinc chloride, aluminum chloride, iron chloride, chromic chloride, titanium tetrachloride, sodium hydro-sulfate, a halogen or a halogen-oxygen compound, for example those mentioned above, or thionyl or sulfuryl chloride, or also an organic substance, preferably a saturated aliphatic halogen compound of low molecular weight such as ethyl chloride, propyl chloride, butyl chloride, acetyl chloride, benzoyl chloride, propionyl chloride, phosgene. Such addition enables a possible decrease of anions to be counteracted and the lifetime of the catalysts to be prolonged.

In case that non-volatile compounds yielding anions are used as listed above, these substances are, of course, added to the catalyst before the reaction, while the volatile compounds can be added as well before as during the reaction.

The aforesaid process is carried out in the presence of a solid catalyst at relatively low temperatures. Suitable contact supports (carriers) are, for example, silica gel, kieselguhr, pumice, silicates, TiO_2 , Al_2O_3 , active carbon, acid ion exchangers, such as Amberlite IRC 50, Dowex types 50, Permutites, phenol-aldehyde-resins which are substituted by sulfonic acid groups, polystyrene-resins

which are substituted by sulfonic acid groups and cross-linked by divinyl-benzene, etc., or mixtures of such carriers.

The aforesaid process can be carried out with special advantage at temperatures within 50° C. and 160° C., preferably 50° C. and 100° C.; if desired, the process may also be carried out at temperatures outside the ranges indicated above, for example at 170° C. to 180° C., or for example at 40° C., or within a range of, for example, 80° C. and 120° C. It is furthermore of importance to carry out the process in an acid to neutral medium. The preferred pH-values are within 0.8 and 3; higher pH-values between, for example, 0.8 and 5 or 2 and 6, or lower pH-values of, for example, 0.5 may also be used, although such pH-values generally do not involve a special advantage. In the said reaction the solution with which the solid catalyst is impregnated may be adjusted so as to have a pH within the limits indicated above.

In the aforesaid process sometimes the presence of a salt, such as sodium chloride or potassium chloride like that of hydrochloric acid or of other alkali metal or alkaline earth metal halides such as LiCl, CaCl₂ or other salts such as CuCl₂ or ZnCl₂ may prove advantageous. By the presence of these salts, for example the reactivity of CuCl, which may be formed in the course of the reaction, may be improved.

The aforesaid process can be carried out at atmospheric pressure, under a raised pressure and under reduced pressure, that is, under a pressure of up to 100, preferably of up to 50 atmospheres gauge. The process may be carried out under pressure regardless of whether the temperatures used are above or below 100° C.

The reaction may be supported by increasing the ethylene and/or oxygen concentration in the reaction space. This can be achieved, for example, by increasing the pressure. The ethylene concentration at the surface of the catalyst may be considerably increased, for example, by using higher concentrations of metal salts binding ethylene, for instance copper-, iron-, mercury- or iridium-compounds, especially halides, or the sulfates, the latter especially when mercury is concerned. The gases may be circulated, for example a gas containing a few percent of unreacted oxygen.

Due to the presence of oxidizing agents acetic acid may be formed in a small amount in addition to acetaldehyde. If desired, the oxidation of acetaldehyde to acetic acid which is known in the art, may be combined with the reaction described above in order to omit partially or totally the aldehyde stage, or acetaldehyde may be oxidized in a second stage to acetic acid.

It is described in the aforesaid application that under the conditions specified above under which ethylene yields acetaldehyde, propylene yields preponderantly acetone and propionaldehyde. α - and β -butylene yield preponderantly methylethyl ketone, the α -butylene yielding also butyraldehyde, and isobutyraldehyde can be obtained from isobutylene.

In the case where higher olefins are concerned, such as pentene and its homologs, cyclohexene or styrene, the reaction proceeds substantially in a manner analogous to that described and it can be carried out under the same conditions as set forth above. Due to the relatively mild reaction conditions there are almost exclusively obtained those oxidation products which had to be expected in view of their structure, without noteworthy isomerizations or molecule decompositions occurring.

Mixtures of olefins or gases containing olefins or other unsaturated compounds may be reacted in the same manner, provided they are capable of reacting under the reaction conditions, for example diolefins. The reaction of olefins containing 2 to 3 carbon atoms is, however, preferred. Under circumstances, the reaction conditions must be adapted to the compounds used and to their physical properties. The higher boiling points of the reaction products may also require a corresponding modi-

fication of the reaction conditions. Diacetyl may be obtained, for example, from butadiene.

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

Now we have found that in the above process the yield of acids which correspond to the aldehydes, can be considerably increased without the aldehyde yield being reduced, when an olefin is contacted with gaseous oxygen in the presence of water vapor at a solid acid to neutral catalyst comprising a carrier, a compound of a noble metal of group VIII of the periodic system and a redox system containing one or more compounds of one or more metals having an atomic number in the range from 25 to 27, i.e. iron, manganese and/or cobalt. This effect is unexpected inasmuch as it was supposed that part of the aldehyde formed would be oxidized in the catalyst to the corresponding acid; it could not be foreseen, however, that an additional amount of acid would be formed.

The compounds of iron, manganese or cobalt are added to the catalyst in the usual manner. It is possible, for example, to impregnate the catalyst with the soluble salts of these elements and to convert these salts by heating, preferably with air, to the firmly adhering oxides. There may also be used a mixture comprising the aforesaid compounds.

The acid formed can be readily separated from the corresponding aldehyde. According to the present invention, it is preferred to concentrate the acid, which has always a boiling point higher than the aldehyde, in a first separator, and to concentrate the aldehyde which has a boiling point lower than the acid, in a second separator. Both separators are connected in series.

The simultaneous production of carboxylic acids and aldehydes at solid catalysts containing an iron-, manganese- and/or cobalt salt, is preferably carried out in the presence of further redox systems, such as copper compounds.

The process of this invention is generally carried out with the catalysts and under the conditions broadly described in application Ser. No. 747,115 and referred to above, preferably by contacting the olefin and oxygen or air simultaneously with the catalytic substances.

In a frequently useful technical variant of the process of this invention the desired reaction products, for example acetaldehyde and acetic acid, are separated from the reaction gas, the residual gas which may contain inert gases and may be free from oxygen, but may likewise contain some oxygen, is reintroduced and an amount of olefin and oxygen corresponding to that consumed during the reaction is introduced into the reactor through one or more inlets, which may be arranged one above the other or one behind the other or the olefin and/or the oxygen are added to the circulating gas. For example, the residual gas is admixed with an amount of ethylene corresponding to that consumed, and the resulting gas mixture, containing, for example, 90–95 percent of olefin (for example ethylene) and 10–5 percent of oxygen, is introduced into the reactor as well as an amount of oxygen corresponding to that consumed. For the sake of security the oxygen, if desired in admixture with inert gases such as present in air is preferably introduced through separate inlets, especially when no diluting gas is present and about stoichiometric amounts of the reactants are applied.

In order to obtain especially high space-time-yields, it is also possible to introduce either olefin or oxygen, or

olefin and oxygen into the reaction vessel, for example a reaction tower, at various places arranged one above the other or one behind the other. Preferably the inlets for each reactant are locally separated from the other inlets for the same reactant. It is likewise possible that the amount of oxygen introduced is measured so as to keep at all places of the reaction vessel below the lower limits of the explosive range.

In many cases the reaction proceeds likewise smoothly if the catalysts used contain only a small amount of compounds of the noble metals belonging to group VIII of the periodic table. In most cases it is sufficient to use a catalyst in which the ratio of the sum of the redox metals, especially the sum of copper and iron to the noble metal, especially palladium, is at least 15:1, preferably 25-500:1. It is, however, preferred to use a catalyst containing copper salts, in which the ratio of copper to palladium is above 10:1, for example above 15:1 and preferably 50:1 to 500:1, or even above these ranges. This method of operating is more economic in view of the fact that the expensive palladium salt need only be used in a minor amount; it can be used for converting ethylene and olefins other than ethylene, and may be combined as desired with variants hereinbefore or hereinafter described. This embodiment may also be carried out under elevated pressure.

As stated above the escaping reaction gases may be reused or circulated. Furthermore the reactants may be diluted by gases inert towards the reaction, for example by nitrogen, carbon dioxide, methane, ethane, propane, butane, isobutane and other saturated aliphatic compounds, and furthermore by other compounds, such as cyclohexane, benzene or toluene.

The reaction of the present invention is favourably influenced by irradiation with rays rich in energy, preferably ultraviolet light. Such irradiation which may also comprise X-rays activates especially the oxygen, increases its oxidation activity, and promotes both the reaction with the olefin and a possible oxidative destruction of by-products, for example oxalic acid. These measures increase the conversion, reduce the formation of by-products and considerably prolong the lifetime of the catalyst, the activity of which may subside after a prolonged time.

In practice it is advantageous to use a mercury quartz lamp as source of radiation arranged in the catalyst so that the light energy is fairly substantially utilized. If the reaction is carried out with an apparatus into which oxygen or an oxygen-containing gas is introduced separately from the olefin or olefin-containing gas or even an olefin-oxygen mixture, it is preferred to arrange the source of radiation in the vicinity of the oxygen inlet, so that that part which is rich in oxygen is especially well irradiated. The oxygen is thereby activated as long as it has a high partial pressure. In an apparatus in which the catalyst circulates, it is advantageous to arrange the source of radiation at the lower end of the contact line, immediately above the oxygen inlet. Activation may also be brought about by adding a compound of a radio-active element to the catalyst solution.

The conversion and the space-time-yield in the present reaction depend, for example, on the residence time in the apparatus and the composition of the catalyst, the temperature and the pressure used. The most suitable residence time can readily be determined by a simple test.

In the process of this invention advisable care is to be taken that the heat evolved during the process (high heat effect: about 60 kcal. per mol of aldehyde) is dissipated to the exterior.

The reaction of the present invention may be carried out in a manner known per se, for example by passing the gases through a tube which is filled with the catalyst, or with the use of a fluidized bed catalyst. Condensates which separate from the reacted gas, especially aqueous condensates, may also be recirculated after vaporization to again participate in the reaction, for example as such

or after separation of higher and/or lower boiling reaction products.

It is not necessary that the catalysts used are made of fine chemicals; they may likewise be produced from suitable metals of commercial purity. Metals, such as copper and iron may be readily dissolved even by not-oxidizing acids, such as hydrochloric acid and acetic acid, if desired by addition of an oxidizing agent if copper is used, or by passing through during the dissolving process a gaseous oxidizing medium, such as oxygen or air enriched with oxygen. The contaminations contained in commercially pure metals do not affect the reaction if the solutions obtained are worked up to the solid bed catalysts used in the process of the present invention. More especially the catalytic activity remains practically unaffected by small amounts of foreign metals which may appear in copper or iron of commercial purity. The anion forming agents contained in metals, such as sulfur, phosphorus, carbon, silicon, etc., are converted upon being dissolved to either hydrogen compounds, for example H_2S , which escape together with the reaction gases, or oxidized to acids of a higher valence stage, for example H_2SO_4 , which do not affect the reaction, or are converted partially into insoluble compounds, for example CuS , which appear only in minor amounts and, if necessary, can readily be separated from the catalyst, for example by filtration, before the catalyst solution is applied to the carrier.

The solutions so obtained are then admixed with the noble metal compound which is added in substance or in the dissolved state, if desired diluted with water, and the concentration of hydrogen ions is adjusted to the degree desired; the solutions so prepared may then be concentrated and are applied to a carrier, for instance those mentioned above.

Solvents suitable for dissolving the metals are chiefly hydrochloric acid and acetic acid in view of the fact that the presence of these acids proves especially advantageous in oxidizing olefins to aldehydes, ketones and acids. Acids other than those indicated above may, however, also be used, for example nitric acid. In this case, it is preferred to remove the acid in excess in order to adjust the solution to the pH desired and to use the solution so treated for impregnating the carrier. If desired the salt of the metals may partially be converted into the corresponding chlorides and/or acetates.

Palladium chloride or other noble metal chlorides need not be used; there may also be employed the metals themselves, e.g. metallic palladium, suitably in a finely divided and finely distributed state, which reacts, for example, with copper chloride, and is converted to palladium chloride or a compound other than palladium chloride.

For example, the catalyst may contain as anion chlorine ions or halogen ions other than chlorine, such as fluorine or bromine ions, nitrates or chlorate- or perchlorate radicals, or mixtures of these anions, for example, with sulfate or acetate radicals. Sometimes it is especially advantageous to use a catalyst which contains perchlorate ions.

Although the catalysts have generally a good activity even after a prolonged time of reaction, especially when anions are added during the reaction, it may be advantageous to regenerate the catalyst from time to time. Some variants for such regeneration are described hereinafter.

It may be that the activity of the catalyst, especially when the catalyst is used for a very long period of time, is more or less reduced by the formation of a minor amount of by-products, or by foreign substances which may have been introduced. The by-products formed consist partially of organic compounds which are water-soluble at least to a certain degree, such as acetic acid, oxalic acid, higher aldehydes or ketones or chlorinated organic compounds. Foreign substances possibly introduced into the catalyst may derive from, for example, con-

taminations of the gases, or the corrosion of parts of the apparatus, for example, of iron parts or of the lining of the reactor.

The catalyst may be freed from these contaminations and regenerated in a simple manner by precipitating the cupric chloride as cuprous chloride and the noble metal compound as elementary metal. The precipitation may be effected directly on the carrier or the catalytic compounds may be dissolved therefrom. Precipitation is preferably carried out with the exclusion of substantial amounts of oxygen by the action of carbon monoxide, hydrogen or one or more olefins, for example ethylene, propylene or the butylenes, or of any other olefin or a mixture of several of these precipitating agents. The mixture of cuprous chloride and noble metal or the solid catalyst in which these substances are precipitated are advantageously washed, e.g. with water. If a solution of the catalytic agents had been prepared it is mixed with water and an acid, suitably hydrogen chloride, if desired in the form of hydrochloric acid, and may, after a salt of iron, manganese and/or cobalt has been added, be reused in the impregnation in this state or, if desired, after oxidation with oxygen or an oxygen-containing gas, such as air. If the cuprous chloride and the noble metal are precipitated in the carrier, the washed carrier is treated with a solution of a salt of iron, manganese and/or cobalt and with an acid, such as hydrochloric acid and, if desired, is additionally oxidized, e.g. by means of oxygen or chlorine, and then reused. If a separate oxidation is dispensed with an olefin and oxidation agent are allowed to act simultaneously upon the catalyst to be reused, oxidation is brought about in the following reaction by the oxygen contained in the reaction gas. After the regenerated but not yet oxidized catalyst has been reintroduced into the reactor, the amount of oxygen contained in the reaction gas may temporarily be increased, if desired. If in reducing the catalyst oxygen is not completely excluded, it is only necessary to use a somewhat larger amount of reducing agent.

This mode of execution is especially interesting if in addition to the noble metal the catalyst contains substantial amounts of copper salts, since these two rather expensive components of the catalyst—CuCl and noble metal—precipitate, while all other impurities or additions, for example iron salts, remain in the solution and are thus separated from the expensive noble metal and copper compound.

The noble metal is quantitatively precipitated as well as CuCl, except for a minor amount thereof which is soluble in water. In reusing the catalyst it is therefore advisable to add the corresponding amount of fresh CuCl_2 and/or $\text{CuCl} + \text{HCl}$. The further well soluble and frequently cheap additions, such as iron salts, are suitable to be replenished.

The simplest manner of allowing CO and/or olefins and/or hydrogen to act upon the catalyst is to introduce these substances upon the catalyst or into the solution prepared as described above. In most cases this may be done under normal conditions, but it may be advantageous to use a higher temperature and/or a raised pressure. More severe conditions are opportune, especially when hydrogen is used, which is the weakest reducing agent among the substances mentioned above. In using olefins as reducing agents the oxidizing activity of the catalyst may be used for a further formation of aldehydes, ketones and acids.

It is furthermore advisable prior to allowing the above gases to act upon the solution which is obtained by dissolving the active components from the carrier to entirely or partially neutralize or buffer the acid contained therein to a relatively low pH which is preferably in the range between 2 and 4. At too strong an acidity the reaction proceeds too slowly or is incomplete after the usual time of reduction. In addition thereto, CuCl is remarkably soluble in concentrated hydrochloric acid, which may in-

volve losses of copper. It should be noted that a further amount of hydrochloric acid is formed during the reduction of the copper or noble metal chloride, and this amount of acid must possibly also be neutralized or buffered. Reduction at a pH higher than 4 is often regarded to be disadvantageous since hydroxides are likewise precipitated, though a regeneration by precipitating the hydroxides or basic salts of the metals used is likewise possible.

Neutralization or buffering may be made in the usual manner with alkaline reacting substances, such as sodium hydroxide solution, sodium carbonate, sodium acetate, chalk, lime, and similar compounds. The said reducing gases may be circulated for reasons of economy and, especially if carbon monoxide is used, may also be subjected to a CO_2 wash.

According to another method of regeneration of the solid bed catalyst, the olefin supply may be arrested for a short while and the catalyst may be treated simultaneously with oxygen or oxygen-containing gases and steam and an acid in vapor form or gas form, preferably hydrogen chloride or hydrogen bromide. A variant of such regeneration consists, for example, in passing oxygen or an oxygen-containing gas partially or completely and prior to contacting the catalyst through aqueous hydrochloric acid, preferably at a raised temperature. Accurately dosing the hydrochloric acid is especially simple, if a 20 percent hydrochloric acid is used.

The catalyst which prior to this treatment has possibly a metallic glance turns again brown and regains its initial activity, possibly after an induction period of several hours.

The apparatus used in the process of this invention should be made of a material which has a sufficient thermal conductivity and is not corroded by the catalyst. Since the catalysts used contain noble metal compounds, for example palladium compounds, it is less suitable to use the usual metals and alloys as construction material, since there is the risk that these less noble metals, in the presence of water and at the indicated temperatures, precipitate the noble metal salt used in the catalyst, and that they themselves are converted into salt form.

In order to avoid corrosion in the apparatus used, it is often suitable to use an apparatus lined with titanium or titanium alloys containing at least 30 percent of titanium, or with tantalum. There may also be used glass vessels or enamelled or rubber-lined vessels. The reaction may also be carried out in brick-lined vessels or, under suitable reaction conditions, in vessels, the insides of which are lined with plastic material, for example polyolefins, polytetrafluorethylene or hardenable unsaturated polyesters, or phenol-, cresol- or xylenol-formaldehyde resins. As brick lining there may be used, for example, ceramic material, carbon bricks impregnated with hardenable artificial resins and similar known materials.

The following examples illustrate the invention but they are not intended to limit it thereto.

Example 1

3.3 grams of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are dissolved in 30 cc. of water and the solution so obtained is used to impregnate 100 cc. of silica gel. Silica gel so pretreated is heated for about 3 hours at $250\text{--}300^\circ \text{C}$. in a furnace in the presence of a weak current of air. The cooled catalyst is impregnated with a solution of 2 grams of PdCl_2 and 19.5 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 30 cc. of water, and is ready for use after having been dried for about 1 hour at 80°C .

80 cc. of the catalyst prepared as described above are heated at 80°C . in a contact tube and a mixture of 10 liters of ethylene and 3.3–4.0 liters of oxygen is passed through per hour. The gases introduced into the furnace are saturated with water at a temperature of $80\text{--}85^\circ \text{C}$., or water is added dropwise in an amount corresponding to that entrained by the escaping gases. Acetaldehyde is obtained in a yield of 45–50 percent and acetic acid in a yield of 15–20 percent, calculated upon the ethylene used.

The escaping gases consist of unreacted ethylene and a minor amount of oxygen; they are capable of being circulated.

Example 2

10 liters of ethylene and 3.5 liters of oxygen are passed, at a contact temperature of about 90° C., through 240 cc. of a catalyst containing 10 grams of PdCl₂, 38 grams of CuCl₂ and 18.3 grams of FeCl₃ per liter of silica gel (carrier). The gas mixture used has previously been saturated with steam at about 70° C.

Highly concentrated acetic acid is obtained in a heatable separator provided with a reflux condenser and connected in series with the contact tube. Acetaldehyde is separated from the gas current by a water wash. The conversion, calculated upon the amount of ethylene used, is 30–35 percent of acetaldehyde and 10–15 percent of acetic acid.

Similar results are obtained by using the same amount of granular active carbon as a carrier instead of silica gel.

Example 3

3.3 grams of Mn(NO₃)₂·6H₂O and 3.5 grams of Co(NO₃)₂·6H₂O are dissolved in 25 cc. of water and the solution obtained is used to impregnate 100 cc. of silica gel. The silica gel is then treated for 2 to 3 hours in a furnace at 250–300° C. with a current of air to form the manganese and cobalt oxides on the carrier. The catalyst so pretreated is impregnated with a solution of 2 grams of PdCl₂ and 19.5 grams of CuCl₂·2H₂O in 30 cc. of water and dried for a short period at 80° C.

A gas mixture of 10 liters of ethylene and 5 liters of oxygen which has previously been saturated with water at 80–82° C. is passed per hour over the catalyst while the outer temperature of the contact furnace is maintained at 80° C. The reaction gases are condensed and washed to yield 40–50 percent of acetaldehyde and 10–13 percent of acetic acid, calculated upon the ethylene used. A fresh catalyst yields initially only acetaldehyde. The formation of acetic acid sets in only after 10–12 hours and reaches the above rate after a further 3–5 hours. The conversion rate decreases after a period of some days and reaches the initial height by an incidental or continuous addition of hydrogen chloride, if desired in the form of evaporated hydrochloric acid.

Example 4

1.76 grams of Co(NO₃)₂·6H₂O are dissolved in 30 cc. of water and the solution obtained is used to impregnate 100 cc. of silica gel. The cobalt oxide is produced as indicated in Example 2 and the catalyst is treated in the manner described in the preceding example with 2 grams of PdCl₂, 19.5 grams of CuCl₂·2H₂O and 4.6 grams of MgCl₂·6H₂O.

A mixture of 10 normal liters of ethylene and 2.5 normal liters of oxygen (N.T.P.) is passed per hour over the catalyst under a pressure of 1 atmosphere gauge and at a furnace temperature of 80° C. The fresh gas current is simultaneously admixed per hour with 5–10 cc. of water. The conversion, calculated upon the ethylene used, is about 30 percent for acetaldehyde and about 10 percent for acetic acid. In this example, too, acetic acid

is only formed after a period of about 10 hours. The rate of conversion remains constant for a prolonged time and is later kept at this level by cautious addition of dilute hydrochloric acid instead of water.

We claim:

1. In the process for the conversion of ethylene into a carbonyl compound selected from the group consisting of acetaldehyde and acetic acid by contacting ethylene in a reaction zone in the presence of water vapor with gaseous oxygen at an acid-to-neutral solid catalyst comprising a carrier, a salt of a noble metal of group VIII of the periodic system the stable valence of which is at most 4, and cupric chloride, the improvement of contacting the reactants with a catalyst which additionally contains an oxide of at least one metal having an atomic number from 25 to 27.

2. A process as defined in claim 1 wherein strong vaporizable inorganic acids are supplied to the catalyst during the reaction.

3. A process as defined in claim 1 wherein said salt of a noble metal is a palladium salt.

4. A process as defined in claim 1 wherein the reaction is carried out at a temperature in the range between 40° and 180° C. and the catalyst comprises a carrier, palladium chloride, cupric chloride, and an oxide of at least one metal having an atomic number from 25 to 27, wherein a compound yielding chloride ions under the reaction conditions is supplied to the catalyst during the reaction, and wherein non-converted gaseous compounds are recycled from the reaction zone back into the reaction zone after the substantial separation therefrom of carbonyl compounds produced and with the addition of more ethylene and oxygen thereto.

5. A process as defined in claim 1 wherein the oxygen and the ethylene are reacted in the presence of a diluent consisting of a member selected from the group excess ethylene, gases inert under the reaction conditions applied, and mixtures thereof.

6. A process as defined in claim 1 wherein ethylene is intermittently introduced into the reaction zone and the catalyst is contacted with oxygen, steam and vaporized acid when ethylene is absent.

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, 1958
722,707	Germany	July 27, 1942

OTHER REFERENCES

Karrer: Organic Chemistry, 4th ed. (1950), page 504.