United States Patent Office 3,154,586 Patented Oct. 27, 1964

3,154,586

PROCESS FOR OXIDIZING OLEFINS TO ALDEHYDES AND KETONES

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No Drawing. Filed July 8, 1958, Ser. No. 747,116
Claims priority, application Germany July 10, 1957
19 Claims. (Cl. 260—597)

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 from 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.

Now we have found that acetaldehyde can be obtained from ethylene in a good yield and, if desired, in a continuous manner, by contacting ethylene with an oxidizing agent, a liquid catalyst having an acid to neutral reaction and comprising water, a compound of the noble metals belonging to group VIII of the periodic table and a redox system.

As redox systems there may be used, for example, those that 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, manganese, iron, cobalt, nickel, or osmium, and also in organic redox systems other than specified above, such as sulfite/sulfate, arsenite/arsenate or iodide/iodine systems and/or organic redox systems, for example azobenzene/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, 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. As oxidizing agent there may be used, for example, oxygen, if desired 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 reformation 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. 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 hydrosulfate, 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 catalyst to be propolenged.

The process of this invention is carried out in solution at relatively low temperatures. Preferably a pure aqueous solution is used, but the reaction may likewise be carried out in aqueous solutions in which the water is diluted with a hydrophilic solvent such as acetic acid, ethylene glycol, propylene glycol, glycerol, dioxane or mixtures thereof.

The process of this invention can be carried out with special advantage at temperatures within 50° and 160° C., preferably 50° and 100° C.; since the process is carried out in the liquid phase, it is necessary to operate under a raised pressure provided that the temperature used is above 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, for example, 0.5 may also be used, although such pH-values generally do not involve a special advantage).

It has been found that difficulties which may appear in working in the liquid phase can be overcome by modifying the ratio of olefin to oxygen. Such difficulties may reside in the precipitation of cuprous chloride or other compounds formed which cause cloggings and undesired disturbances in operation. In view of the fact that these precipitated salts are no longer available for the reaction, the yield decreases more or less rapidly. The moment at which the olefin to oxygen ratio must be modified, can be readily determined by continuously measuring the pH.

If the pH decreases, it is easily possible to readjust the optimum pH-range by adding either more oxygen or less olefin, or by combining these two steps. If 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 yielding anions, for example hydrohalic acid or organic compounds splitting off hydrohalic acid under the reaction conditions, or acid salts. 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 olefin-oxygen ratio during the reaction. The pH may of course also be modified during reaction by addition of an acid.

The pH is measured by using a device of known type. 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 then be controlled automatically.

Sometimes the presence of a salt, such as sodium chloride or potassium chloride may prove advantageous. For example, by the presence of these salts—like that of hydrochloric acid itself or of other alkali metal or alkaline earth metal halides such as LiCl, $CaCl_2$, or other salts such as $FeCl_3$, $ZnCl_2$ or $CuCl_2$—the solubility of CuCl, which may be formed in the course of the reaction and which is only very sparingly soluble in water (0.11% at 80° C.) is improved.

The process of the invention 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 and/or—by 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 copper-, iron-, mercury- or iridium compounds, especially halides, or the sulfates, the latter especially when mercury is concerned, or by using organic solvents which are preferably miscible with water, for example acetic acid, mono- or polyhydric alcohols, acyclic ethers of dimethyl formamide. The gases may be circulated; if desired, 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 has also been found that under the conditions specified above under which ethylene yields acetaldehyde, propylene yields preponderantly acetone and propionaldehyde. α and β-butylene yield preponderantly methyl-ethyl 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 modification 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%, or 8–14% 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.

The process of this invention may be carried out for example 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 product, for example acetaldehyde, is separated from the reaction gas, the residual gas which most frequently contains oxygen, is reintroduced, suitably into the lower part of the reactor, and an amount of olefin and oxygen corresponding to that consumed during the reaction is introduced into the reactor separately from the circulating gas. Alternatively, the residual gas is admixed with an amount of ethylene corresponding to that consumed, and the resulting gas mixture, containing, for example, 90–95% of olefin (for example ethylene) and 10–5% of oxygen, is introduced into the reactor. For sake of security the oxidizing agent is suitably introduced separately, especially when no diluting gas is present and about stoichiometric amounts of the reactants are applied. Preferably the oxidizing agent is introduced below the inlet for the residual gas or, if a circulating catalyst is used, into the circulation conduit of the catalyst. The amount of oxygen introduced may be so modified that even in the catalyst solution the explosivity limit is nowhere surpassed. Such modification is generally not necessary; it is rather sufficient to add the oxygen to the residual gas which escapes from the contact solution, in an amount to keep the composition of this residual gas outside the explosive limits.

In order to obtain especially high space-time-yields, it is also possible to introduce either olefin or oxidizing agent, preferably 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.

It has also been found that it may be advantageous to

add a dispersant, for example an alkylphenyl sulfonate or a product obtained by the reaction of ethylene oxide, proplyene oxide, or butylene oxide with phenols or aliphatic alcohols, and/or a protective colloid, such as proteins or gum arabic to the liquid catalyst. Finely dispersed solid substances may also be added, if desired. The activity of these substances resides in the fact that free noble metal which has intermediately formed and is reconverted into active compounds by the reactants used in the instant process, cannot aggregate to form large particles. The catalyst is therefore especially finely distributed, and the degree of distribution is stable. As solid pulverulent substances there may be used, for example, coal powder or kieselguhr. It is also possible to use a combination comprising dispersant, protective colloid and finely distributed solid substance.

It has also been found that in many cases the reaction proceeds especially 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 catalysts used in the present reaction may become depleted of halogen in the course of time, a fact which possibly causes a reduction in the rate of conversion. The loss of halogen may be counteracted by addition of halogen or hydrohalic acid or organic substances splitting off halogen or hydrohalic acid under the reaction conditions as already stated.

It has been found that such depletion of halogen must be attributed substantially to the formation of volatile halogenated by-products, for example methyl chloride or ethyl chloride which together with the carbonyl compounds produced entrain the halogen from the catalyst more or less rapidly. It has been ascertained that a certain amount of carboxylic acid corresponding to the olefin, is produced during the reaction, for example acetic acid; such acid concentrates in the liquid and increases the solubility of the reaction products. This favors the formation of halogen-containing volatile by-products and promotes the depletion of halogen. In addition thereto, the carboxylic acids which have concentrated, especially acetic acid, react with the copper ions, which is unfavorable because the copper salts formed, such as copper acetate, are relatively inert towards the olefin oxidation. In many cases it is therefore necessary to counteract such accumulation of carboxylic acids in the reaction space and to take care that these acids appear in as low a concentration as possible. This may be done by suitable continuous or discontinuous measures, for example by distillation, extraction or precipitation. A preferred variant in operating under atmospheric pressure consists for example in that the carboxylic acids formed are allowed to distill over together with the evaporating water; the water consumed is then replaced by a corresponding amount of fresh water. The amount of carboxylc acid removed in this manner is dependent on the surface of the reactor, the temperature used and the amount of gas flowing through, and may be modified by varying these factors. According to another variant the entire contact solution is worked up, carboxylic acid contained in the catalyst is removed, and the contact solution is recirculated into the apparatus.

In order to avoid operative disturbances part of the contact liquid may be withdrawn periodically or continuously and freed from carboxylic acid, partially or substantially, for example by distillation, and the liquid obtained may be added again to the contact medium.

It has also been found that the reaction of the present invention is favourably influenced by irradiation with rays rich in energy, preferably ultraviolet light, especially in the case where oxygen is used as oxidizing medium. Such radiation which may also comprise X-rays activates especially the oxygen, increases its oxidizing 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.

It is known 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 also evident that such reaction proceeds the better, the finer the gaseous components are distributed in the liquid. The catalyst solutions suitable for use in the process of this invention have sometimes the property of foaming after some time. On the one hand this favors the reaction in view of the fact that the gases are finely distributed in the catalyst liquid; sometimes foam-forming agents are intentionally added to the liquid. On the other hand, foaming means that the reaction space available is only insufficiently used, since only part of the contact solution is in the reactor.

The process of this invention may be carried out for example in 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, suitably filled with filling material. The gases may be atomized, for example through a frit, or in another suitable manner, and too voluminous gas bubbles may be divided into smaller ones, for example by means 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 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.

The apparatus used in the process of this invention should be made of a material which is not corroded by the catalyst and preferably has a sufficient thermal conductivity. 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.

Condensates which separate from the reacted gas, especially aqueous condensates, may also be recirculated 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 rather 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 used as catalysts for the olefin oxidation. 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, silicium 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 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 is used.

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 directly be used as a catalyst for the olefin oxidation in the liquid phase.

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 as a catalyst. If desired the salt of the metals may also partially be converted into the corresponding chlorides and/or acetates.

Palladium chloride or other noble metal chlorides need not be used since 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. These by-products may entrain precipitations, for example of heavy metal oxalates. Foreign substances possibly introduced into the catalyst may derive from, for example, contaminations of the gases, or the corrosion of parts of the apparatus, for example iron parts or the lining of the reactor.

The catalysts 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. 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 olefins or a mixture of several of these precipitating agents. The mixture of cuprous chloride and noble metal is advantageously washed, mixed with water and an acid, suitably hydrogen chloride, if desired in the form of hydrochloric acid, and may then be reused in the reaction in this state, or more suitably after oxidation with oxygen or an oxygen-containing gas, such as air. If a particular oxidation is dispensed with and 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 oxidizing agent, especially 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 catalytically active substance.

The noble metal precipitates quantitatively and so does 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 CuCl+HCl. If the catalyst contains further additions, such as iron salts, it is also suitable to replenish these frequently cheap substances.

The simplest manner of allowing CO and/or olefins and/or hydrogen to act upon the catalyst is to introduce these substances into the catalyst solution. 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 reduring 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 catalyst to entirely or partially neutralize or buffer the acid 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 involve 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 if carbon monoxide is used, may also be subjected to a CO_2 wash. If a larger amount of catalyst is used, it is advantageous in order to avoid operating disturbances to regenerate always a small amount of catalyst and subsequently to add the regenerated portion to the major quantity of said catalyst.

A possibility to recover palladium metal consists in subjecting the catalyst in known manner and in a strong acid medium to the action of acetylene. A palladium-acetylene compound precipitates which can be readily separated and freed from cations and anions by means of a water wash. The palladium-acetylene compound so obtained may be then converted in the air or in the presence of ammonium nitrate to palladium oxide which in turn is capable of being converted directly to the chloride by means of hydrochloric acid. In this variant it is especially advantageous that acetylene can act on the palladium compound in the presence of hydrogen.

A further type of regeneration is important for those catalysts in which a liquid is present, that is to say which are used in the purely liquid phase or contain solid substances as described above, such as active carbon.

More especially such regeneration is important for those catalysts which contain iron- and/or copper compounds and compounds of noble metals of group VIII of the periodic table, and the activity of which has been reduced by precipitation of insoluble compounds, for example in the form of oxalates and/or iron oxide hydrate. These precipitations may be discharged continuously or periodically and taken up, if the desired following a thermal treatment, in a mineral acid, preferably hydrohalic acids, such as hydrochloric acid, and may be then reintroduced into the reaction zone. This enables the initial activity of the catalyst to be restored so that undisturbed operation is possible during a long period of time.

If the catalyst contains copper, copper oxalate generally precipitates. It has been found that it is useful in this case to subject the precipitate first to a thermal treatment at a relatively low temperature, for example at 200–500° C., and then to take up the residue formed in a mineral acid, for example in hydrochloric acid, while passing through oxygen or air, or in nitric acid or in a mixture of hydrochloric acid with nitric acid, and then to add the solution so obtained to the catalyst. In order to avoid too strong an acidification of the catalyst, the residue obtained is suitably taken up in a fairly small amount, i.e. for example the calculated amount of a slight excess of acid. By recirculating this solution the concentration of anions in the catalyzing medium may also be regulated.

If the catalyst contains substantial amounts of iron, it is necessary to effect a possible thermal treatment only at a temperature at which the iron oxide becomes not yet insoluble. If desired, the thermal treatment may be combined with an acid treatment so that the acid is allowed to act at a raised temperature, for example above 100° C., while the whole is radiated with a source rich in energy, for example ultraviolet light, to destroy the oxalate, if any.

If the precipitate contains compounds of copper and iron and possibly compounds of other metals, soluble ingredients may be dissolved in a mineral acid, while the rest is baked at a temperature, at which no acid-insoluble oxides are formed, for example at a weak red heat, and the residue is dissolved in an acid in the manner already described.

In the case where nitric acid is used as a mineral acid, it may be advantageous to admix the solution so obtained with hydrochloric acid in order to regulate the concentration of the chlorine ions in the catalyst solution.

The last mentioned variant of regeneration by treatment with mineral acids may be carried out in certain intervals of time, if possible periodically, or continuously; in this case a small portion of catalyst or a branched-off current of catalyst is treated and then added to the major amount. The regenerated solution may be modified, if desired by addition of catalytically active or catalytically activating substances as set forth above.

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% 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- of 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 but they are not intended to limit it thereto.

It is expressly stated that in the claims of this invention the term carbonyl compounds is used in its broad sense, i.e. it covers also carboxylic acids such as acetic acid.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

Example 1

A reaction vessel having a diameter of 3 cm. and a height of 120 cm. is charged with a solution containing 10 grams of palladium chloride, 30 grams of copper chloride, 20 cc. of concentrated hydrochloric acid and 200 grams of water, and if desired, soda lye in an amount that the solution remains acid. 20 liters of ethylene and 10 liters of oxygen are introduced into the apparatus per hour at 90° C. through a glass frit, and a small amount of hydrochloric acid is occasionally added. The escaping gases contain about 30% by volume of acetaldehyde in addition to unreacted oxygen and ethylene and are capable of being circulated after separation of acetaldehyde.

Example 2

The apparatus described in Example 1 is charged with 2 grams of palladium chloride, 20 grams of copper chloride, 2 grams of ferric chloride, 200 grams of water and 6 cc. of concentrated hydrochloric acid. A 10% sodium hydroxide solution is initially added and hydrochloric acid is occasionally added to keep the content of acetaldehyde at a degree of 20–30% by volume for a charge of 20 liters of ethylene and 10 liters of oxygen per hour.

Example 3

50 liters of a gas mixture containing 66.3% of C_2H_4, 33.2% of O_2 and 0.5% of methyl chloride are passed per hour through a column charged with a solution of 10 grams of $PdCl_2$+40 grams of $CuCl_2$ in 950 grams of a 65% acetic acid. Care is taken to ensure a fairly good and fine gas distribution, for example with the use of a frit, a vibromixer, a rapid agitator or an oscillating agitator. The time of contact may be prolonged by the addition of a foam-forming agent. The solution is kept at a temperature of 75–85° C.

The escaping gas consists of an unreacted portion of the gas mixture used as starting material and the acetaldehyde formed, which may be washed out with water or another known auxiliary. The yield is very high, cal-

culated on the ethylene reacted. The conversion is dependent on the composition of the catalyst solution, the time of contact between gas and liquid, the pressure and temperature applied. Under the conditions indicated, for example at a very short time of contact of only 1–2 seconds at atmospheric pressure and a temperature of 76° C., the conversion is between 5 and 10%; it may be considerably increased by modifying the conditions as stated above.

Example 4

The solution used in the preceding example is circulated over a wash tower in which the gas mixture flows in counter-current to the liquid. The results obtained are the same as those indicated in the preceding example. The conversion is likewise dependent on the catalyst concentration, the time of contact, the temperature and the pressure applied.

Example 5

A mixture of 20 liters of ethylene and 10 liters of oxygen is passed per hour at 90° C. through a tube provided with a glass frit and charged with a solution of 5 grams of $PdCl_2$, 10 grams of $CuCl_2$ and 1 gram of KCl in 225 cc. of 80% acetic acid. The yield of acetaldehyde is initially 15–20%, calculated upon the ethylene used, and increases to 40–60% after addition of 40 cc. of water, which is added in portions of 10 cc.

Example 6

1 part by weight of palladium chloride and 2–5 parts by weight of $CuCl_2.2H_2O$ are dissolved in 50 parts by weight of 65% acetic acid. A solution of a known dispersant stable in an acid medium, for example 1 part by weight of an alkylphenyl sulfonate is then added. A further addition of a small amount, for example 0.2–2 parts by weight of 2 N-hydrochloric acid may be advantageous to reduce or to prevent the separation of the metallic palladium formed.

A mixture of 2 parts by volume of ethylene and 1 part by volume of oxygen is then passed at 80–100° C. through the solution so obtained, and care is taken to ensure a fairly fine distribution of the gas by means of a frit, a rapid agitator, or an oscillating agitator. The acetaldehyde contained in the escaping gas is absorbed in a wash tower while the unreacted gas is circulated. Depending on the height of the liquid column, the gas distribution and the temperature used, the ethylene conversion is between 20 and 50%. It may be further increased by the application of pressure. The formation of by-products is only slight. The yield of acetaldehyde is generally above 90% of the theoretical, calculated upon the ethylene reacted.

Example 7

1 part by weight of palladium chloride and 2–5 parts by weight of $CuCl_2.2H_2O$ are dissolved in 100 parts by weight of 65% acetic acid. 1–2 parts by weight of finely pulverized active carbon and 0.1–0.2 part by weight of concentrated hydrochloric acid are then added to the solution so obtained. If desired, there may also be added an additional amount of dispersant and/or of protective colloids as described in Example 6. Through the suspension so produced, a mixture of ethylene and oxygen in a ratio of 2:1 to 4:1 is passed continuously at 80–100° C.; the gas mixture consists of cycle gas and fresh gas. After having passed a cooler, in which the major portion of the entrained water/acetic acid mixture is condensed and from where it flows back into the reaction vessel; the reaction gas containing acetaldehyde, a small amount of water and acetic acid, is freed in a wash tower from reaction product and admixtures; it is then caused to flow back, if desired, after a subsequent treatment, into the reaction tower. The wash liquid is subjected to distillation to obtain acetaldehyde in a yield of between 30–40%, calculated upon the olefin reacted, or in a yield of 90%, calculated upon the ethylene which has undergone conversion.

Example 8

A verticallly arranged reaction tube is charged with a solution of 2 grams of $PdCl_2$, 10 grams of $CuCl_2.2H_2O$ and 1 cc. of concentrated hydrochloric acid in 100 cc. of water. The solution has a pH of about 1. 10 liters of ethylene and 5 liters of oxygen are passed, per hour, at 70° C. through the catalyst solution so prepared. The acetaldehyde formed is obtained by subjecting the escaping gas mixture to a water wash. The conversion is about 30%.

Example 9

A pressure apparatus is charged with 250 cc. of an aqueous catalyst solution containing 5 grams of $PdCl_2$, 25 grams of $CuCl_2.2H_2O$ and 2 cc. of concentrated hydrochloric acid and having a pH of about 1. 15 liters of ethylene and 5 liters of oxygen are then introduced per hour at a bath temperature of 75–80° C. under a pressure of 3 atmospheres gauge. The conversion is 40–50%, calculated upon the ethylene.

Example 10

A vertically arranged reaction tube provided with a glass frit is charged with a catalyst solution consisting of 1 gram of rhodium chloride and 75 grams of $CuCl_2.2H_2O$ in 1 liter of water. Hydrochloric acid was added to the solution to produce a pH of 1.5, and 20 liters of ethylene and 10 liters of oxygen were passed through per hour at 80° C. The acetaldehyde formed can be obtained by washing the escaping gas with water. The conversion is about 15%, calculated upon the ethylene used; it may be increased by the application of pressure. Similar results are obtained under otherwise identical conditions by substituting iridium chloride or ruthenium chloride for rhodium chloride.

Example 11

1.5 parts of palladous chloride are treated in known manner in an aqueous solution in the presence of 10 parts by weight of active carbon powder; the treatment is carried out with the aid of formaldehyde or another reducing agent and lyes, if desired in the presence of a protective colloid, to precipitate about 0.9 part by weight of metallic palladium. The palladium/active carbon/suspension is suction-filtered, washed until neutral and suspended in 1500 parts by weight of water. A mixture of 2 parts by volume of ethylene and 1 part by volume of oxygen is passed in finely distributed form through the suspension so prepared; after a short time, the escaping gas contains a small amount of aldehyde. 200 parts of copper chloride are then added to the suspension and the yield of acetaldehyde is increased within some hours to 20–25% of the theoretical, calculated upon the ethylene used.

Example 12

10 liters of a gaseous mixture comprising 4 parts by volume of ethylene and 1 part by volume of oxygen are introduced in finely dispersed form per hour at 70° C. and through a glass frit into 160 cc. of a catalyst solution containing 12.5 grams of $PdCl_2$ and 12.5 grams of $CuCl_2.2H_2O$ per liter of solution. 1.0 gram of acetaldehyde is formed per hour. The yield of acetaldehyde is doubled by a dropwise addition of 10 cc. of 10% hydrogen peroxide per hour to the catalyst solution. The oxidation may be kept alive by the addition of hydrogen peroxide alone in the absence of oxygen, the yields are however reduced in this case.

Example 13

A mixture of 2 liters of ethylene and 1 liter of oxygen is passed per hour at 68–70° C. through 100 cc. of a solution containing, per liter, 2 grams of $PdCl_2$, 10 grams of $CuCl_2.2H_2O$ and 5 cc. of concentrated hydrochloric

acid. The pressure in the apparatus is maintained at 300–320 mm. of mercury. Acetaldehyde is obtained in a yield of about 20%, calculated upon the ethylene used.

Example 14

A pressure apparatus 12 meters high and provided with a catalyst cycle and having a reaction volume of 1 cubic meter, is charged with 800 liters of a catalyst solution containing, per liter of water, 5 grams of $PdCl_2$, 50 grams of $CuCl_2.2H_2O$ and 20 grams of $FeCl_3$. 160 normal cubic meters (measured at N.T.P., i.e. 0° C. and 760 mm. pressure) are introduced per hour under a superpressure of 3 atmospheres gauge. After starting the reaction, the contact temperature is maintained at 112–115° C. without heating. The acetaldehyde is separated by washing and the reacted amount of ethylene of about 30 normal cubic meters per hour is replaced in the escaping gas, and the gas mixture, which now contains about 92% of C_2H_4 and 8% of O_2, is introduced into the reactor at the extreme lower part. The amount of oxygen consumed during the reaction, i.e. about 15 normal cubic meters per hour, is introduced, separately from the circulating gas into the catalyst cycle conduit immediately below the inlet opening of the reactor for said conduit. This apparatus has an average capacity of more than 50 kg. of acetaldehyde per hour.

Example 15

(A) The catalyst used is prepared as follows: 16.5 grams of iron turnings are introduced into a vertically arranged glass tube provided with a glass frit and a heating jacket, and 1000 cc. of and acid solution containing 135 grams of concentrated hydrochloric acid and 76.8 grams of acetic acid of 96% strength in water are added. While passing through nitrogen and heating to 80° C., the iron turnings dissolve within 1–2 hours except for a small residue; the escaping gas contains a considerable amount of hydrogen, hydrogen sulfide and hydrogen phosphide. 51.7 grams of copper turnings and 40 cc. of concentrated hydrochloric acid are added and the batch is gassed with 5 liters of oxygen per hour, and after 3 hours with 10 liters of oxygen per hour. After 12 hours, all has dissolved except for a minor black precipitation of cupric sulfide and carbon. Small amounts of sulfate ions can be detected in the solution. 9 grams of palladium chloride are added and the finished catalyst is gassed at 80° C. in the same tube with 24 liters of ethylene per hour and 6 liters of oxygen per hour. After a short induction period, the escaping gas contains constantly 40% of acetaldehyde.

(B) Similar results are obtained by operating as follows: iron and copper turnings are added together and the aforesaid acid solution of acetic acid and concentrated hydrochloric acid is poured over while passing through nitrogen at 80° C.; after the first vigorous reaction has subsided, the whole is gassed with 5 liters of oxygen per hour, after 4 hours with 10 liters of oxygen per hour, and 40 cc. of concentrated hydrochloric acid are added after 12 hours. The dissolving proces is complete after a further 2 hours. The solution obtained is clear and has a brown-green coloration. Some black flakes of cupric sulfide which swim on the bottom have no detrimental effect. 9 grams of palladium chloride are then added to the solution.

Example 16

A pressure resistant apparatus lined with tantalum heatable by means of a heating jacket and provided with a glass frit for the distribution of the gas, is charged with 300 cc. of a catalyst solution containing, per liter of liquid, 2 grams of $PdCl_2$, 50 grams of $CuCl_2.2H_2O$, 110 grams of $Cu(CH_3COO)_2.H_2O$, 40 grams of $FeCl_3$ and 40 cc. of concentrated hydrochloric acid. The frit serves to introduce into the reactor, per hour, 20 liters of a gas mixture consisting of 15% of oxygen and 85% of propylene. 5–6 grams of oxidation products (substantially acetone and a small amount of propionaldehyde) are obtained per hour at a temperature of 90° C. in the reactor and at atmospheric pressure. If the pressure is raised to 3 atmospheres gauge, while the total amount of gas is the same, the yield of oxidation products increases to 8–10 grams per hour at a temperature of 90° C. By raising the temperature to 100° C., the yield of oxidation products is increased to 15–20 grams per hour (maximum value up to 30 grams). A further increase in temperature and pressure increases the yields of oxidation products, however to a lesser pronounced degree. Similar results are obtained by using the same amount of a catalyst solution containing, per liter of liquid, 5 grams of $PdCl_2$, 50 grams of $CuCl_2.2H_2O$ and 20 grams of $FeCl_3$.

Example 17

(A) 2.0 grams of $PdCl_2$, 50 grams of $CuCl_2.2H_2O$ and 110 grams of $Cu(CH_3COO)_2.H_2O$ are dissolved with 50 cc. of concentrated hydrochloric acid in distilled water (end volume: 1000 cc.). The solution so prepared is introduced into a vertically arranged glass tube having a diameter of 3 cm. and a gas inlet frit at its lower end. The catalyst is heated to 80° C. with a water jacket and then gassed with a mixture of 40 liters of ethylene per hour and 10 liters of oxygen per hour at atmospheric pressure. The conversion of the ethylene used is in the first hour at 30% (corresponding to 60% calculated upon the oxygen) decreases slightly and finally remained at a constant degree, which may be maintained for a long period (some hundred hours) by incidental addition of small amounts of hydrochloric acid.

(B) The conversion is considerably higher, if the catalyst used contains additionally 40 grams of $FeCl_3$.

(C) The conditions are the same as described above with the exception that 79 grams of green chromic chloride are substituted for 40 grams of iron chloride; a better stationary state is reached, i.e. a conversion of about 25–30%, calculated upon the ethylene (corresponding to 50–60%, calculated upon the oxygen), which can be maintained for a long period by an incidental addition of hydrochloric acid.

(D) 59 grams of manganic chloride are substituted for iron chloride or chromic chloride and added to the catalyst prepared as described above. Ethylene and oxygen are reacted under the conditions described. About 50% of the ethylene are converted (corresponding to 100%, calculated upon oxygen, and corresponding to the theoretical yield); the yield decreases slowly and finally remains at a constant degree of likewise 25–30%, calculated upon ethylene.

Similar results are obtained, if the same amount of a catalyst solution is used which contains per liter in

Experiment A: 5 grams of palladium chloride and 50 grams $CuCl_2.2H_2O$

Experiment B: in addition to the compounds of A 24 grams of $FeCl_3$

Experiment C: the same ingredients as sub B, but instead of $FeCl_3$ 40 grams of green chromic chloride

Experiment D: the same ingredients as sub B, but instead of $FeCl_3$ 30 grams of manganous chloride.

Example 18

A catalyst solution is prepared from 5 grams of $PdCl_2$, 34 grams of $CuCl_2 \cdot H_2O$, 50 grams of copper acetate. H_2O and 73 grams of cerous chloride and 30 cc. of concentrated hydrochloric acid, and made up to 1 liter by the addition of water. The catalyst solution so prepared is introduced into a glass tube provided with a gas inlet frit, and gassed at 80° C. with 40 liters of ethylene per hour and 10 liters of oxygen per hour. 25% of the ethylene used are converted to acetaldehyde, corresponding to 50%, calculated upon oxygen.

Example 19

A glass tube provided with a frit is charged with 5 grams of $PdCl_2$, 17 grams of $CuCl_2 \cdot 2H_2O$, 24 grams of

$FeCl_3$, 70 grams of copper acetate·H_2O, 40 cc. of concentral nitric acid, and 500 cc. of water; 30 liters of a gas containing 82% of ethylene and 18% of oxygen were then introduced per hour at 90° C. at atmospheric pressure. 15 grams of acetaldehyde are obtained per hour. The catalyst retains its activity by continuous addition of hydrochloric acid.

Example 20

A pressure apparatus having the dimensions of that used in the preceding example is charged with 5 grams of $PdCl_2$, 17 grams of $CuCl_2 \cdot 2H_2O$, 60 grams of

$$Fe(NO_3)_3 \cdot 9H_2O$$

70 grams of copper acetate·H_2O, 35 cc. of concentrated hydrochloric acid and 500 cc. of water, and gassed at 110° C., under a pressure of 2 atmospheres gauge with 60 normal liters of a mixture consisting of 15% of O_2 and 85% of ethylene. 40 grams of acetaldehyde are obtained per hour.

Example 21

3 grams of palladium nitrate, 50 grams of

$$Cu(NO_3)_2 \cdot 3H_2O$$

and 500 cc. of water are introduced in the apparatus used in the preceding example, and gassed with 30 liters per hour of a mixture consisting of 65% of ethylene and 35% of oxygen. The reaction temperature is at 90° C. The gas escaping from the reactor contains 20% by volume of acetaldehyde.

Example 22

A catalyst solution containing, per liter of water, 1.0 gram of $PdCl_2$ and 50 grams of $CuCl_2 \cdot 2H_2O$ is adjusted to a pH of 1.5 by addition of perchloric acid. The solution so treated is introduced into a vertically arranged glass tube provided with a gas inlet frit and gassed at a temperature of 80° C. with a mixture of 20 liters of ethylene and 10 liters of oxygen per hour. The conversion of ethylene to acetaldehyde raised rapidly to 20–25%, decreased somewhat after 30 hours, and could readily be brought to the initial degree by addition of 5 cc. of 70% perchloric acid. The conversion could be maintained constant by occasional addition of a further amount of perchloric acid.

Only slight amounts of by-products are obtained. The same results can be obtained by substituting sodium perchlorate and sometimes hydrochloric acid for perchloric acid.

Example 23

A solution containing, per liter of water, 1.0 gram of $PdCl_2$, 50 grams of $CuCl_2 \cdot 2H_2O$ and 5 grams of potassium chlorate is introduced into a tube provided with a frit and gassed, per hour at 80° C., with 20 liters of ethylene and 10 liters of oxygen. The conversion of ethylene to acetaldehyde increases within 2 hours to 40% and remains then at 20–25% over a period of more than 100 hours by incidental addition of a small amount of potassium chlorate and hydrochloric acid. CO_2 and CH_3Cl are obtained as by-products in a proportion of up to 1% each.

Example 24

A solution containing, per liter of water, 3 grams of $PdCl_2$ and 63 grams of $CuBr_2$ is introduced into a vertically arranged tube and gassed at 90–95° C. with a mixture of 20 liters of isobutylene and 5 liters of oxygen. The escaping gases are conducted through cooling traps in which isobutyraldehyde and tertiary butanol can be obtained as reaction products.

Example 25

A reactor is charged with 500 cc. of a catalyst containing 50 grams of $CuCl_2 \cdot 2H_2O$, 0.5 gram of $PdCl_2$ and 2.5 cc. of concentrated hydrochloric acid; the solution has a pH of 1.25. A mixture of about 8 liters of ethylene and about 4 liters of oxygen is introduced into the reaction solution at a temperature of 80° C. The reaction solution is kept at a pH of about 0.8–1.8. Acetalydehyde is obtained in a yield of more than 50%, calculated upon the amount of ethylene used.

Example 26

A tower provided with a frit or another device suitable to ensure a fine gas distribution is charged with a solution consisting of 100 parts by weight of $CuCl_2 \cdot 2H_2O$ in ten times the amount of water, to which has been added 1 part by weight of $PdCl_2$ and 1.1–1.2 part by weight of 10 N-hydrochloric acid. The solution has a pH of between 1 and 2.

A mixture of 75% of ethylene and 25% of oxygen is passed through the solution in finely distributed form at 85° C., and acetaldehyde is separated from the reaction gas by washing it in known manner.

The conversion is dependent on the amount of gas reacted, the gas distribution and the height of the liquid column. For a long period it is for example at 30–35%, calculated upon the amount of ethylene used; the conversion may be considerably increased by varying the conditions and by the application of pressure.

Example 27

10 liters of ethylene per hour and 5 liters of oxygen per hour are introduced at a bath temperature of 80° C. into a pressure apparatus containing 250 cc. of a contact solution consisting of 0.25 grams of palladium chloride, 25 grams of $CuCl_2 \cdot 2H_2O$ and 1 cc. of concentrated hydrochloric acid. The interior temperature is between 80° C. and 90° C. A yield of more than 30% is obtained, calculated upon the ethylene used.

Example 28

A reaction tube is kept at 84° C. by boiling 1.2-dichlorethane and charged with 50 parts by volume of a contact solution containing, per liter, 500 grams of crystalline $CuCl_2 \cdot 2H_2O$, 2 grams of $PdCl_2$ and 20 cc. of normal hydrochloric acid. 2000 parts by volume of a reaction gas of oxygen and ethylene (ratio by volume: 1:2) are introduced by means of a frit extending to the bottom of the reaction tube. 25% of the ethylene used are converted in one passage to acetaldehyde. In the course of 50 hours, the conversion increases to more than 35%; after that time, the conversion remains at a constant degree of about 30%.

Example 29

8 liters of propylene and 4 liters of oxygen are passed per hour through 800 cc. of an aqueous catalyst solution containing per liter, 100 grams of copper chloride and 1.0 gram of palladous chloride. 5.0 grams of acetone are obtained per hour and a small amount of propionaldehyde. The conversion is 26%, calculated upon the amount of propylene used. The residual gas consists of unreacted propylene and oxygen; it may be reused.

Example 30

The catalyst used is prepared as follows:

16.5 grams of iron turnings and 51.7 grams of copper turnings are dissolved in nitric acid in a large dish and under a vent. The solution is evaporated to dryness, concentrated hydrochloric acid is poured over the dry substance (three times) and the whole is again evaporated to dryness (three times). 2 grams of palladium chloride are added, the salts are taken up in 80 cc. of concentrated hydrochloric acid, 50 cc. of glacial acetic acid are added and the whole is diluted with water to obtain 1000 cc. of solution. The solution is introduced into a vertically arranged glass tube provided with a gas inlet frit and a heating jacket, heated to 80° C., and 40 liters of ethylene and 10 liters of oxygen are passed through per hour.

The acetaldehyde contained in the escaping gas corresponds to a 35% conversion of the ethylene used.

Example 31

A reactor is charged with 500 cc. of a catalyst solution containing 50 grams of $CuCl_2 \cdot 2H_2O$, 0.5 grams of $PdCl_2$ and 2.5 cc. of concentrated hydrochloric acid and having a pH of 1.25. A mixture of about 8 liters of ethylene and about 4 liters of oxygen is then introduced into the reaction solution at a temperature of 80° C. The reactor used is provided with a high temperature resisting glass electrode of high ohmic resistance, and a calomel electrode, and connected to a measuring device. The pH is adjusted to 0.8–1.8 by regulation of the amount of ethylene and oxygen introduced. The reaction is undisturbed and acetaldehyde is obtained in a yield of 50%, calculated upon the ethylene used.

Example 32

A catalyst solution containing, per liter of water, 1 gram of $PdCl_2$ and 100 grams of $CuCl_2.2H_2O$ which has been used over a prolonged period for the oxidation of ethylene to acetaldehyde, is almost neturalized by addition of sodium hydroxide solution. The whole is filtered and carbon monoxide is passed through the filtered solution at room temperature with exclusion of substantial amounts of oxygen. White CuCl precipitates first, and then black Pd. The supply of gas is interrupted as soon as the supernatant liquid has become practically colorless. The whole is suction-filtered and washed with water. The liquid filtered off is free from detectable amounts of palladium. The CuCl-Pd mixture is suspended with water, the necessary amount of hydrochloric acid is added, the lost amount of $CuCl_2$ is replaced, and the whole is returned into the reactor. The catalyst is used under the standard conditions set forth in the preceding examples and the usual yields are obtained after oxygen is introduced for a short time.

Example 33

Ethylene is substituted for carbon monoxide and introduced under the conditions described in Example 32. During the ethylene introduction care is taken by cautious addition of sodium hydroxide solution that the pH of the liquid does not fall below 3. The acetaldehyde formed in this reaction may be recovered from the ethylene in the usual manner.

Example 34

A catalyst containing, per liter of water, 1 gram of $PdCl_2$ and 100 grams of $CuCl_2.2H_2O$ is gassed per hour at 75° C. with 20 liters of ethylene and 10 liters of oxygen. Acetaldehyde is obtained in a yield of about 30% for a period of more than 1000 hours if care is taken that the acetic acid formed during the reaction is continuously removed from the reactor together with the distilling water. In this manner the content of acetic acid in the catalyst solution is constantly kept at 12–14%. The water distilling off is replaced by fresh water. The chlorine entrained must be replaced by continuous addition of hydrochloric acid.

Example 35

700 parts by volume (the relationship of parts by volume to parts by weight is the same as that of the liter to the kilogram) of a catalyst containing, per liter, 1 gram of palladium, 0.2 mol of iron, 0.8 mol of copper, 1.0 mol of chlorine and 1 mol of acetic acid are contacted in a contact furnace per hour at 105–115° C. under a pressure of 2 atmospheres gauge with 200,000 parts by volume of an ethylene-oxygen mixture (measured at 0° C. under atmospheric pressure). The yield of acetaldehyde is initially 80 parts by weight per hour, and 100 parts by weight per hour after 2 days. The yield of acetaldehyde decreases after 8 days in spite of hydrochloric acid being added. The catalyst is then practically free from dissolved iron. The precipitated iron hydroxide is then isolated, dissolved with the necessary amount of concentrated hydrochloric acid, and again added to the catalyst. Acetaldehyde is again obtained in the initial yield of 80 parts by weight per hour.

Example 36

The reaction vessel used in Example 35 is charged under a pressure of 2 atmospheres gauge with the same amount of a catalyst containing, per liter, 0.05 mol of iron, 0.8 mol of copper, 1.7 mols of chlorine and 1 gram of palladium and the catalyst is contacted per hour with 200,000 parts by volume of an olefin-(ethylene-propylene) oxygen mixture; the olefin is first introduced, the remaining gas mixture is circulated and a further amount of olefin and oxygen is introduced in a ratio of 2:1. The yield of acetaldehyde and acetone is initially 70 parts by weight per hour; the yield decreases after 4 days in spite of hydrochloric acid being added. The precipitated sludge containing about 10% of iron and 90% of an organic copper salt and a copper hydroxychloride, is then isolated, and heated for 5 hours at 250° C. until all organic salts have been decomposed. The residue is then dissolved with the necessary amount of concentrated hydrochloric acid and the solution so obtained is again added to the residual catalyst solution; acetaldehyde and acetone are again obtained in the initial yield of 70 parts by weight per hour. If the sludge is removed continuously by centrifugation or filtration and worked up continuously in the manner described, acetaldehyde and acetone can be obtained in a constant yield of 60 parts by weight per hour.

Example 37

700 parts by volume of a catalyst containing, per liter, 1 gram of palladium, 52 grams of copper, 56.8 grams of chlorine and 60 grams of acetic acid are contacted in a contact furnace per hour at 105–115° C. under a pressure of 2 atmospheres gauge with 200,000 parts by volume of ethylene and oxygen (measured at N.T.P.). Acetaldehyde is obtained in a yield of 50 parts by weight per hour. The activity of the catalyst is kept constant in that precipitated copper oxalate is continuously suction-filtered, then muffled at 280° C., taken up in the calculated amount of hydrochloric acid while passing through oxygen or air, and reintroduced into the catalyst. If the precipitated copper oxalate is not removed, it is impossible to prevent a gradual decrease of the yield by addition of hydrochloric acid.

A catalyst which in addition to the components mentioned above contains also 0.2 mol of iron per liter yields 80 parts by weight of acetaldehyde if the procedure is the same as described above. Precipitated copper oxalate and iron hydroxide are continuously suction filtered, muffled at 280° C., dissolved with the calculated amount of hydrochloric acid, and the solution so obtained is again added to the catalyst to keep the yield constant for a long period.

Example 38

A reaction tube 2 meters long is charged with 1 liter of a catalyst containing, per liter of water, 3 grams of $PdCl_2$, 107 grams of $CuCl_2.2H_2O$, 15 grams of

$$Cu(CH_3COO)_2.H_2O$$

and 12 grams of $FeCl_3$; due to the ascending gas current the catalyst is circulated. 10 liters of oxygen are introduced per hour at the lower end of the reaction tube, and 40 liters of ethylene are nozzled in per hour through a frit 30 cm. above the oxygen inlet. The reaction tube is provided with a mercury quartz lamp installed between the oxygen inlet and ethylene inlet. Care is taken that the permeability for the rays is not affected during the reaction or that such permeability is restored. The temperature is 80–85° C. If the amount of hydrochloric acid

consumed is periodically replaced by a fresh quantity of such acid, the catalyst remains active over a long period without operative disturbances occurring. Acetaldehyde is obtained in a yield of 35%, calculated upon the ethylene used, corresponding to 70% calculated upon the oxygen used; if the use of a mercury quartz lamp is dispensed with while the other conditions are the same, acetaldehyde is obtained in a yield of only about 30%. The escaping gas which consists substantially of ethylene and a small amount of oxygen is washed to remove acetaldehyde and ethylene is added in an amount corresponding to the quantity of ethylene consumed; the gas may be then reintroduced into the reaction tube through the upper inlet, while an amount of fresh oxygen corresponding to the quantity of oxygen consumed is introduced through the lower inlet.

We claim:

1. A process for the conversion of an olefinic hydrocarbon to a carbonyl compound selected from the group consisting of aldehydes and ketones by oxidation of an olefinic carbon atom of said olefinic hydrocarbon to a carbonyl group, which process consists essentially of contacting said olefinic hydrocarbon and oxygen with an acid to neutral liquid catalyst of water, a salt of a noble metal selected from the group consisting of palladium, iridium, ruthenium, rhodium, and platinum, and as a redox system, a salt of a metal showing several valence states under the reaction conditions applied.

2. A process as in claim 1 wherein, additionally, ions selected from the group consisting of bromine ions and chlorine ions are supplied to the catalyst during the reaction.

3. A process as in claim 1 wherein said metal showing several valence states is copper.

4. A process as in claim 1 wherein said liquid catalyst has a pH between 0.5 and 6.

5. A process as in claim 1 wherein said noble metal is palladium, said metal showing several valence states is copper, and wherein the ratio by weight of copper to palladium is between 15 and 500.

6. A process as in claim 1 wherein said oxygen is used in admixture with a diluent inert towards the reaction.

7. A process as in claim 1 wherein said olefin is used in admixture with a diluent inert towards the reaction.

8. A process as in claim 1 wherein said contacting takes place at a temperature of from 50° C. to 160° C.

9. A process as in claim 1 wherein said contacting takes place at a pressure of from one atmosphere to fifty atmospheres.

10. A process as in claim 1 wherein said oxygen is present in an amount of from 8 to 20 percent by volume of the gaseous reactants.

11. A process as in claim 1 wherein said noble metal is palladium, and wherein said liquid catalyst is regenerated by contacting it with acetylene to precipitate a palladium-acetylene compound, then contacting said compound with oxygen to form palladium oxide, dissolving this oxide in a mineral acid, and then recycling the resulting solution to the reaction.

12. A process as in claim 1 wherein said metal showing several valence states is copper, and wherein said liquid catalyst is regenerated by contacting it with a compound selected from the group consisting of carbon monoxide, olefins, hydrogen, and mixtures thereof, and then recycling the regenerated liquid catalyst to the reaction.

13. A process as in claim 1 wherein carboxylic acids formed by the reaction are removed by distillation from the liquid catalyst during the reaction.

14. A process as in claim 1 wherein said contacting takes place in a reaction zone, and wherein gaseous compounds from the reaction zone are recycled into the reaction zone.

15. A process as in claim 1 wherein a soluble neutral salt of a strong inorganic acid is additionally present during the reaction.

16. A process as in claim 1 wherein at least a portion of solid precipitates formed in said liquid catalyst during the reaction is separated from said catalyst and dissolved in mineral acid, and the resulting solution is then recycled to the reaction.

17. A process as in claim 1 wherein at least a portion of solid precipitates formed in said liquid catalyst is separated from said catalyst, decomposed by heating, and dissolved in mineral acid, and the resulting solution is then recycled to the reaction.

18. A process for the conversion of an olefinic hydrocarbon having 2 to 4 carbon atoms to a carbonyl compound selected from the group consisting of aldehydes and ketones by oxidation of an olefinic carbon atom of said olefinic hydrocarbon to a carbonyl group, which process consists essentially of contacting said olefinic hydrocarbon and oxygen, at a temperature of from about 50° C. to 160° C. and at a pH of from 0.5 to 6, with a liquid catalyst of water, a palladium salt, and a member of the group consisting of copper chloride and copper bromide, and, additionally, supplying ions selected from the group consisting of bromine ions and chlorine ions to the catalyst during the reaction.

19. A process for the conversion of an olefinic hydrocarbon to a carbonyl compound selected from the group consisting of aldehydes and ketones by oxidation of an olefinic carbon atom of said olefinic hydrocarbon to a carbonyl group, which process consists essentially of contacting said olefinic hydrocarbon and oxygen with an acid to neutral aqueous catalytic solution of an inorganic salt of a noble metal of Group VIII and as a redox system, a salt of a metal selected from the group consisting of iron, copper and manganese, said catalytic solution containing halogen ions selected from the group consisting of chlorine and bromine ions, the quantity of halogen ions present in said catalytic solution being approximately 60 to 75% of the quantity which would be contained in said catalytic solution if all the metal salts present were present as halides in their highest oxidation stage.

References Cited in the file of this patent

UNITED STATES PATENTS

1,945,067	Nozicka	Jan. 30, 1934
1,999,620	Van Peski et al.	Apr. 30, 1935
2,523,686	Engel	Sept. 26, 1950
2,690,457	Hackmann	Sept. 28, 1954

FOREIGN PATENTS

713,791	Germany	Nov. 14, 1941
891,209	France	Nov. 29, 1943
767,409	Great Britain	Feb. 6, 1957

OTHER REFERENCES

Phillips: Amer. Chem. Jour., volume 16, pages 255–77 (1894).

Chatt: Chem. Abstracts, volume 48, page 5067 (1954).