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PROCESS FOR OXIDIZING OLEFINS TO ALDEHYDES AND KETONES

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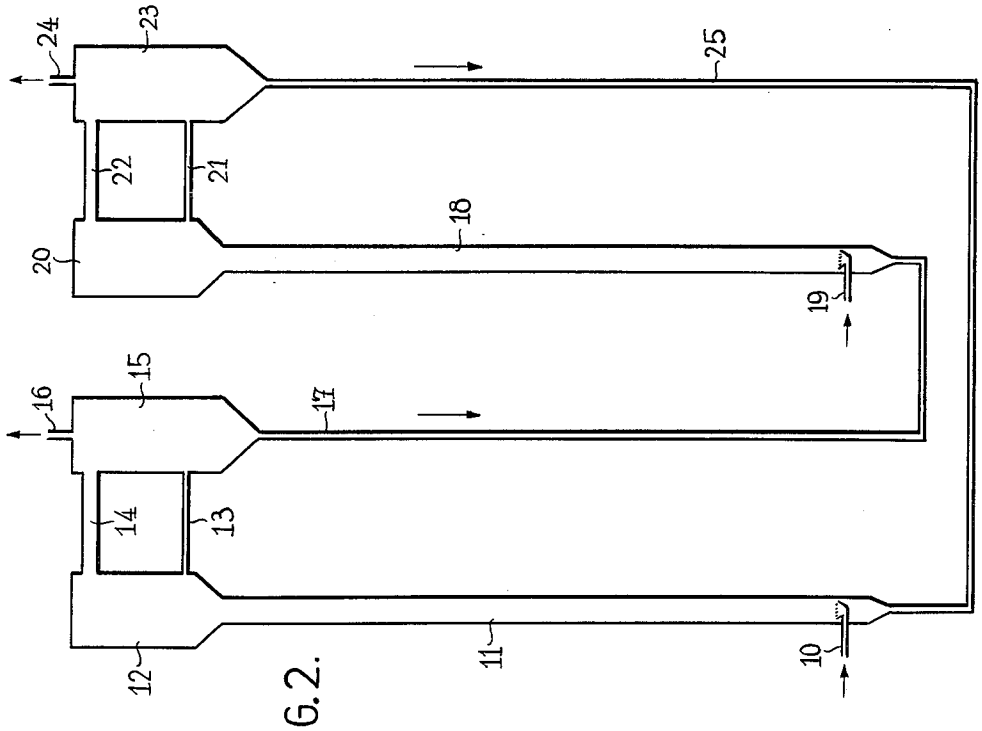


FIG. 2.

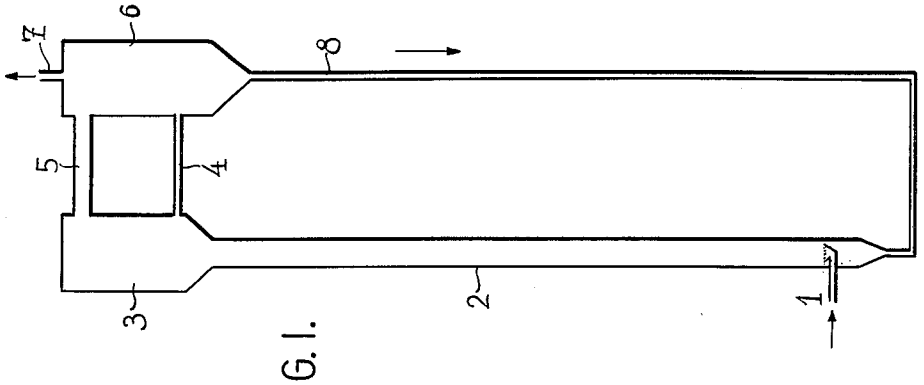


FIG. 1.

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PROCESS FOR OXIDIZING OLEFINS TO ALDEHYDES AND KETONES

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15 Claims. (Cl. 260—604)

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 described 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 Ser. No. 747,116 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 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.

It is furthermore described in application Ser. No. 750,150 to contact the olefin and the oxidizing agent separately with the liquid catalyst. According to said application the reaction may be performed by contacting the liquid catalyst with the olefin and the oxidizing agent in several reaction vessels. Instead of pure olefin a mixture of oxygen and olefin may be used in which the oxygen content is outside the range of exposivity, i.e. for example between 1 and 10%, calculated upon the amount of olefin used.

In application Ser. No. 763,691, filed September 6, 1958, now abandoned, it has been disclosed that the olefins may even be diluted by carbon monoxide and/or hydrogen and that the course of the reaction is not affected by the presence of these gases.

Moreover, it has been disclosed in application Ser.

No. 765,272, filed October 6, 1958, to obtain acetaldehyde and/or acetic acid by oxidation of ethylene by means of an oxidizing agent, preferably molecular oxygen, if desired in admixture with inert gases at an elevated temperature and under an elevated pressure in the presence of water and an inorganic redox system, in which the metal component is at least monovalent in its reduced stage of valence. For example redox systems may be used which contain compounds of Cu, Fe, Co, Ni, Mn, Hg, Ce, Ti, U, Bi, Tl, Sn, Pb, Cr, Mo, V, Sb or mixtures of such compounds.

As is described in application Ser. No. 768,624, filed October 21, 1958, in the presence of copper containing catalysts the conversion is dependent on the molar ratio of copper to halogen and that it is therefore very favorable to keep the molar ratio of copper to halogen and more especially of copper to chlorine within the limits of 1:1 and 1:2, preferably within the limits of 1:1.4 and 1:1.8. Advantageously halogen ions are supplied during the reaction in very accurate dosages to the liquid catalyst.

The above ratio of copper to halogen should be understood to include the amount of halogen added in the form of iron halide or another halide of cations which do not form neutral reacting salts with hydrohalic acids. The amount of halogen which is present in the form of a neutral salt, for example sodium chloride or potassium chloride, or is capable of being bound to form a neutral salt, need not be considered. For example, if the catalyst contains 3 gram equivalents of alkali metal salts or alkaline earth metal salts of acids other than hydrohalic acids, 5 gram equivalents (mols) of chlorine ions added in the form of iron chloride, and 1 mol of copper ions added in the form of copper acetate, the copper to chlorine ratio is 1:2 according to the definition given above.

Furthermore it is described in application Ser. No. 770,007, filed October 28, 1958, now U.S. Patent No. 3,076,032, that the reaction velocity and olefin conversion are increased if it is operated in the presence of a redox system and a quinone, which may be substituted by sulfonic acid and/or carboxylic acid groups.

In the aforesaid applications 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 applications the reaction is carried out in a homogenous liquid 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 occupied, since only part of the contact solution is in foam form in the reactor, while the remainder of the foam flows off and accordingly does not longer participate in the reaction.

We have now found that this disadvantage which increased, when using larger amounts of gases, can be avoided by allowing the contact liquid, which has been conveyed by the gaseous reactants to the head of the reactor, to stay in a quiescent zone, and reintroducing it at the foot of the reactor. Removing the liquid at the head of the reactor and reintroducing it at the foot may

be achieved, for example, by means of a system of pumps or simply by the force of gravity, the gases introduced being charged with the transport of the material from the foot to the head of the reactor.

It has surprisingly been ascertained that the yields of aldehydes or ketones obtained in this cyclic process, while the same amount of noble metal is used in the solution, are superior to those obtained in a process, wherein the catalyst is not circulated. Corresponding tests are described in Example 1 below.

In addition thereto all processing difficulties which are due to foaming do not occur.

A further advantage of this cyclic process consists in the fact that part or even the entire contact liquid flowing back from the head of the reactor may be introduced into an expelling column (stripping column) in order to remove dissolved or liquid reaction products, partially or completely. In this case the formation of by-products may be reduced, for example by keeping the content of acetic acid at a low degree. The reaction products may be expelled by either heating the liquid to a higher temperature, or by means of an inert gas, such as steam or nitrogen. By expelling the entire or part of the reaction product, it is prevented from being further modified by the action of the oxidizing agent. The expelling column, for example, may have the same design as the reactor itself. In this case, too, the contact solution may be circulated by means of the gas or steam used in stripping the reaction products. In a separate reaction of olefins and oxygen as described below, the contact liquid may be introduced, if desired after having been passed through the expelling column, into a regenerator from the quiescent zone of which it flows back into the reactor. In this case, too, regeneration and stripping may be effected simultaneously with the use of the same gas or gas mixture, for example a mixture of oxygen with nitrogen and/or with steam. If use is made of the force of gravity and of the conveying action of the gases passed through, pumps can be dispensed with.

In the accompanying FIGURES 1 and 2 some embodiments of the present invention are described. In FIGURE 1 oxygen and olefin are introduced through one or more inlets 1 into reactor 2 which is filled with a liquid catalyst and which is provided with an enlarged head zone 3 in which the foam partly separates into gas and liquid. This enlarged head zone is connected by pipes 4 and 5 with a second quiescent zone 6. The liquid which has been separated in the enlarged head zone 3 does not fall through the reactor 2 since the force of gravity is compensated by the streaming gases. Accordingly this liquid is conducted by pipe 4 into the second quiescent zone 6 while the gaseous reaction products and gaseous unconverted components and the residual foam are conducted through pipe 5 into the second quiescent zone 6. Said gaseous products are discharged from this quiescent zone 6 by discharge pipe 7 while the liquid constituents are reconducted through pipe 8 into the reactor 2. Pipe 8 has suitably a relatively small diameter in order to reduce the amount of contact liquid as much as possible.

Since the foam and gases have a larger volume and the foam is less fluid than the liquid, pipe 5 generally has a larger diameter than pipe 4. If desired, pipes 4 and 5 may, however, be omitted and replaced by a single overflow. In a further embodiment the second quiescent zone 6 may be omitted and the gaseous reaction products and unconverted gases may be discharged in the upper portion of enlarged head zone 3 which in this case advantageously is constructed higher and/or broader in order to allow the foam to separate into the liquid and gaseous constituents. In another embodiment tube 4 may, of course, be arranged somewhat lower or higher than shown in FIGURE 1.

In FIGURE 1 the second quiescent zone 6 has been shown to be in a height corresponding to that of the top of the reactor. By this arrangement it is possible to reconduct the liquid into the reactor by the force of gravity. Of course, it is not necessary to arrange the second quiescent zone 6 in such a height. In may well be arranged lower. If in this case the force of gravity is not large enough to cause a circulating of the catalyst liquid through the reactor system, then pumps may be used in order to produce such circulation.

In FIGURE 2 an apparatus is shown which is suitable if the process is carried out in two stages as it is described below. An olefin, such as ethylene, is introduced through one or more inlets 10 into reactor 11 which is provided with an enlarged head zone 12. This head zone is connected by pipes 13 and 14 with a second quiescent zone 15 from which the gases are discharged by discharge pipe 16. The liquid which has separated in quiescent zone 15 is conducted by pipe 17 into regenerator 18 into which oxygen or an oxygen containing gas is introduced by inlet 19. Regenerator 18 may likewise be provided with an enlarged head zone 20 which is connected by pipes 21 and 22 with a further quiescent zone 23 from which unconverted gases are discharged by pipe 24 while the regenerated catalyst liquid is reconducted by pipe 25 into reactor 11.

It is in the scope of the invention that the embodiments described above in the one-stage-process may likewise be made in the two-stages-process. Furthermore it is not necessary in the two-stages-process that the regenerator likewise contains enlarged head zones or quiescent zones though such an arrangement is preferred. If the contact liquid is stripped before the regeneration step the stripping device may likewise be provided with enlarged head zones or other quiescent zones of the type described above.

The present invention may be carried out with the catalysts and under the conditions broadly described in the above-mentioned applications, for preparing carbonyl compounds from the corresponding olefins, i.e. olefins having the same number of carbon atoms as the carbonyl compounds. These catalysts contain one or more redox systems and preferably a compound of a noble metal of group VIII of the periodic table, particularly palladium.

As redox systems which may be present there are, for example, mentioned 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 inorganic redox systems other than the latter preferably in admixture with compounds of other of the aforesaid metals, 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 in the process according to the present invention, for example, compounds of palladium, iridium, ruthenium, rhodium or platinum, i.e. of the metals the stable valence of which is at most 4. Compounds of this series of metals are believed to be capable of forming addition compounds or complex compounds with ethylene. The reaction may likewise be carried out in the presence of a noble metal.

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 or in the form of air enriched with oxygen. 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 ethylent and, for example, saturated hydrocarbons.

The reaction may be supported or carried out by addi-

tion 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. 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 prolonged.

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

If the present process is carried out in the presence of noble metals of group VIII of the periodic system and of redox systems, it can be carried out with special advantage at temperatures within the range between 50 and 160° C., preferably 50 and 100° C.; if it 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. to 120° C. Furthermore atmospheric pressure, a raised pressure or reduced pressure may be applied, that is, 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. It is furthermore of importance to carry out the process in an acid to neutral medium. The preferred pH-values are within the range between 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.

If the present process is carried out in the absence of noble metals and in the presence of inorganic redox systems, as disclosed in application Ser. No. 765,272, mentioned above, generally a temperature between 50 and 250° C., more suitably between 100 and 250° C. and preferably between 130 and 200° C. and pressures above atmospheric pressure and below 400 atmospheres (gauge pressure), more suitable between 20 and 200 atmospheres (gauge pressure) and preferably between 80 and 120 atmospheres (gauge pressure) are applied. Of course the reaction may be carried out at lower or higher temperatures, for example above room temperature, or under a higher pressure, for example at 450 atmospheres. In this embodiment of the present invention operating at pH-values between 1 and 5 is most preferred, though operating at higher or lower pH-values, for example at pH 0 is likewise possible.

Difficulties which may appear 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 the 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, these salts—like hydrochloric acid itself or other alkali metal or alkaline earth metal halides such as LiCl, $CaCl_2$, $MgCl_2$ or other salts such as $FeCl_3$, $FeCl_2$, $ZnCl_2$ or $CuCl_2$—improve 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.).

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, methylethyleketone or other ketones, mono- or polyhydric alcohols, acyclic ethers or 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 in known manner to acetic acid, for example in the presence of manganese compounds.

Under the conditions specified above under which

ethylene yields acetaldehyde, propylene yields preponderantly acetone and propionaldehyde, α and β-butylene yield perponderantly 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 occuring.

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.

As stated above 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 olefins may however not only be diluted by one or more of the aforementioned gases, but likewise with carbon monoxide and/or hydrogen, if desired in addition to the aforementioned gases. If such gas mixture contains CO, oxygen should be present at least in an amount as is necessary to convert the olefin to aldehyde and carbon monoxide to carbon dioxide.

It is believed that olefin-noble-metal complex compounds are formed as intermediary products which then react with water to yield carbonyl compounds. It is however known from the literature that carbon monoxide expels from these coordination compounds all olefins, including ethylene. For these reasons a mixture of olefins with carbon monoxide was expected to bring about none or only a very small conversion of the olefin to carbonyl compounds. It is therefore surprising that a mixture of carbon monoxide and olefin, if desired in admixture with one or more other gases inert towards the reaction such as those mentioned above, practically yields the same amounts of carbonyl compounds as if no carbon monoxide were present. In this reaction the carbon monoxide is partially converted to carbon dioxide.

It is also known from the pertinent literature that hydrogen reacts in a manner very similar to that of carbon monoxide, and it is therefore just as well surprising that the olefin oxidation takes an absolutely smooth course in the presence of hydrogen. The major amount of hydrogen remains unaltered, whereas a small portion thereof reacts with formation of water and another small portion with hydrogenation of the olefins.

The carbonyl compounds can be obtained in the same manner without a reduction in conversion occuring by using a mixture of carbon monoxide and hydrogen with an olefin or a gas containing an olefin; in this case, it is sometimes favorable for the conversion to work with the application of pressure.

The fact that neither hydrogen nor carbon monoxide affect the process of the invention is of special advantage since accordingly industrial gases, for example refined gases or gases obtained in cracking processes may be used as starting materials. All expensive gas separations can therefore be dispensed with, although a prepurification or concentration of the olefin may prove advantageous, so that a considerably cheaper crude material can be used. Carbon monoxide and/or hydrogen may appear in the gas mixture, for example in double the amount of the olefin, and yet the olefin oxidation is not substantially impaired. This statement is however not intended to indicate a limit. If these gases are present, it is especially suitable to use the multiple stage process described in application Ser. No. 750,150, in which the olefin, if desired in admixture with a small amount of oxygen, is contacted with the catalyst in one stage, while the oxidizing agent is contacted with the catalyst in a second stage or apparatus. This modification of the present process is broadly described below; as a result of these measures it is possible to practically avoid a mixing of the gases used with oxygen, so that the former can be used for further purposes after having left the reactor.

For stoichiometric reasons the molar ratio of olefin 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 which consists substantially of non-converted olefin, if desired in admixture with other inert gases, such as nitrogen and/or with hydrogen and/or carbon monoxide, and which may furthermore contain some oxygen. To this gas oxygen and the olefin such as ethylene are added as they are consumed.

The present process may be carried out for example by contacting the olefin and oxygen or air simultaneously with the catalytic substances. However, it is often very advantageous to contact the olefin and the oxidizing agent separately with the liquid catalyst used. This mode of operating has the advantage that the compositions of the gas mixture need not be controlled carefully and that even in recirculating the olefin, such as ethylene, air may be used as oxidizing medium without disadvantages being involved. This variant may be performed by contacting olefin and oxidizing agent in periodic alternation with the circulating catalyst liquid, preferably however the catalyst liquid is circulated through several reaction units and there reacted separately with the olefin and the oxidizing gas. In this variant, pure olefin or an olefin containing gas may still contain oxygen, the oxygen content being outside the range of explosivity, i.e. for example, calculated, between 1% and 10%, preferably between 3% and 10% of oxygen, calculated upon the amount of olefin used. For example, the explosive limit of an ethylene-oxygen gas mixture is at atmospheric pressure at 20.1% of oxygen. In this modified variant the reaction is preferably carried out in such a manner that the oxygen is almost or completely consumed in the reaction unit and the catalyst is then regenerated in the regeneration unit, where the contact medium is contacted with the oxidizing medium, for example oxygen or air in an amount sufficient to bring about regeneration. Regeneration is brought about under known conditions, for example at 50–150° C., and may be carried out under pressures and at temperatures being different from those of the first stage in which the catalyst is contacted with the olefin.

Depending on the conditions applied in this case the olefin dissolved in the catalyst medium is also oxidized and the dissolved reaction product is removed by stripping. In order to produce a good stripping effect, regeneration may also be brought about using mixtures of oxygen or air with steam.

Contacting olefin and oxidizing agent separately with the contact medium involves the advantage that the process can always be carried out under atmospheric pressure and, more especially, under superatmospheric pressure with gas mixtures which are outside the inflammability limit and absoluetly harmless.

As compared with the variant to contact the olefin per se and the oxidizing agent per se with the contact me-

dium, the use of a mixture of olefin with a small amount of oxidizing agent in one stage and of additional oxidizing agent in the second stage offers the further advantage that an occasional separation of undesired solid products is avoided at the place where an olefin-oxygen mixture enters into the reactor, which contains oxygen in an amount smaller than corresponds to the stoichiometric composition as regards the conversion to the carbonyl compound, and the composition of which gas mixture is outside the inflammability limit. A separation of solid substances would cause reduction of the catalytically active substance in the contact liquid and accordingly a reduction of the contact activity; on the other hand, such separation would involve cloggings in conduits, cocks or nozzles. Such separation of solid substances does not appear if a minor amount of oxygen or air is admixed with the olefin and such mixture is contacted in the first stage with the contact solution, and if the contact solution is regenerated in a second stage by addition of a further amount of oxidizing agent. If the olefin and the oxidizing agent, or an olefin containing a small amount of oxygen and the oxidizing medium, for example oxygen, are contacted separately in the manner described above with the catalyst, it may be advantageous to free the olefin-treated contact solution before it is being contacted in a second phase with the oxidizing gases, from residual unreacted olefin and residual reaction product, for example by stronger heating or stripping with an inert gas, such as nitrogen or steam. By connecting the head of the reactor of one phase with the lower liquid inlet of the regenerator and vice versa, it is possible to produce a closed liquid cycle, so that pumps can be dispensed with. The ascending gas currents circulate the liquid vigorously; this circulation can be measured by flow meters or another suitable device.

If it is feared that the mixture comprising residual oxygen or residual air and aldehyde, for example acetaldehyde, could rise slightly above the lower explosive limit, the head of the regenerator may readily be provided with a safety device of known type to prevent explosion, such as bursting disks, a flametrap such as pots filled with steel grains or the like. The danger of explosion is however extremely low in view of the acetaldehyde-oxygen-mixture being saturated with water vapor and in view of the relatively low content of oxygen, which is smaller than the oxygen content of the air.

The aforesaid two-stage embodiments have the mutual advantage, that explosive gas mixtures are not liable to occur even when operating under a raised pressure, and that each gas current can be circulated separately and replenished by fresh gas to the necessary extent. It is also possible to use air as oxidizing agent in view of the fact that a concentration of nitrogen has here no detrimental effect.

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 may still contain inert gas and/or hydrogen and/or carbon monoxide and may be free from oxygen, but may likewise contain oxygen, is reintroduced into the reactor, suitably into its lower part and an amount of olefin and, if desired, 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 recirculated gas. For example, the ethylene or ethylene-containing gas is admixed with the residual gas in an amount corresponding to that consumed. The resulting gas mixture which may be free from oxygen or in which the ratio of olefin and oxygen is, for example, 95 to 99 percent or 90 to 95 percent of olefin (for example ethylene) to 5 to 1 percent or 10 to 5 percent, resp. of oxygen, is then introduced into the reactor. For the sake of security the oxidizing agent, i.e. preferably oxygen, if desired in admixture with inert gases, such as present in air, is preferably introduced through separate inlets especially when about stoichiometric amounts of the reactants are applied and no diluting gas is present.

The oxidizing agent is preferably introduced 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 reactor 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 be 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 noly 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.

The reaction of the present invention is favorably 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 formaton 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 advanagteous 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 a mixture of the said reactants, 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 the present process, in which the catalyst is circulated, it is advantageous to arrange the source of radiation at the lower end of the contact line or, if the reaction is carried out in several stages, at the lower end of the regeneration vessel, immediately above the oxygen inlet. Activation may also be brought about by adding a compound of a radio-active element to the catalyst solution.

If copper and halogen are present it has proved to be advisable to keep the molar ratio of copper:halogen and more especially of copper:chlorine within the limits of 1:1 and 1:2, preferably within the limits of 1:1.4 and 1:1.8 as it is described in application Ser. No. 768,624.

If halogen is present in a proportion smaller than corresponds to the ratio of 1:1, the conversion is reduced. In this case the optimum ratio can be readily re-adjusted, for example by addition of hydrogen halide, for example hydrohalic acid. If the catalyst is contacted separately with olefin and oxidizing gas as it has been set forth above free halogen, especially chlorine or chlorine-containing hydrogen chloride, may be allowed to act on the catalyst together with the oxidizing medium, after or prior to the action of the oxidizing medium. It is also possible to allow halogen and olefin to act simultaneously on the catalyst, but in this case side reactions are liable to occur to a certain extent, such as a chlorination. Instead of using halogens or hydrogen halide for regulating the copper to halogen ratio, there may also be employed compounds yielding halogen ions under the reaction conditions, such as halogeno-oxygen compounds or organic substances, for example saturated aliphatic halogen compounds of low molecular weight, such as ethyl chloride. If the catalyst contains more halogen than corresponds to the copper to halogen ratio of 1:2, the reaction is retarded. In this case, part of the halogen ions may be removed, for example in the liquid phase by partial neutralization, precipitation or by means of anion exchangers. Alternatively, it is possible to wait until the volatile halogen-containing by-products formed have entrained so much halogen that the optimum ratio re-appears.

The amount of halogen compound, necessary to adjust the proposed optimum ratio can be readily calculated and controlled by periodic analyses. In the simplest case the term "halogen compound" is here intended to mean hydrochloric acid. The copper analysis need only be made occasionally in view of the fact that the content of copper in the solution practically cannot change. It is therefore sufficient to make periodic chlorine analysis, preferably by the usual rapid method.

In order to immediately adjust the optimum copper to halogen ratio in a fresh catalyst, part of the necessary cupric chloride may be replaced by cuprous chloride or copper acetate; this enables high conversions to be obtained from the very beginning of the reaction.

A constant copper to halogen ratio may be adjusted by adding the components continuously or discontinuously. According to a preferred variant, for example, aqueous hydrochloric acid is pumped into the contact solution by means of a regulable pump; alternatively, if smaller amounts of catalysts are concerned, some drops of hydrochloric acid are added to the catalyst in certain intervals of time.

If mainly aldehydes and ketones are to be prepared it is advantageous to additionally prevent or remove an accumulation of carboxylic acids, for example acetic acid, in the reaction space. It is to be noted, that the liquid catalysts used in the present reaction may become deplete of halogen in the course of time. 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.

Such depletion of halogen is to 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 distil over together with the evaporating water; the water consumed is then replaced by a corresponding amount of fresh water. The amount of carboxylic 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.

Sometimes it is advantageous to add to the catalyst a quinone which may be substituted by sulfonic acid and/or carboxyl groups. By such an addition the reaction velocity and olefin conversion or—if the rate of conversion remains the same—the throughput is considerably increased. It is supposed that by an addition of the aforesaid compounds the slowest reaction which is the velocity determining step for the entire reaction, e.g. the oxidation of intermediately formed cuprous chloride to cupric chloride is accelerated.

As quinones there may be used, for example, ortho- and/or para-quinones, such as benzoquinones, naphthoquinones, anthraquinones, phenanthrenequinones, or alkyl substitution products of such quinones or the substitution products thereof, which have been referred to above. By adding, for example, the potassium salt of 1.2-naphthoquinone-4-sulfonic acid to a dilute copper chloride catalyst activated with palladium chloride, the conversion is more than doubled as compared with a catalyst free from such addition.

As quinones there may, for example, be used benzoquinone-tetrachlorobenzoquinone, 1,2-naphthoquinone-4-sulfonic acid, 1,2-naphthoquinone-4,7-disulfonic acid, 1,4-naphthoquinone-2-carboxylic acid, -2-sulfonic acid, -5-sulfonic acid, -2,6-disulfonic acid, -2,3-dicarboxylic acid, anthraquinone-1-carboxylic acid, -2-carboxylic acid, -1-sulfonic acid, -2-sulfonic acid, 1,5-disulfonic acid, -1,8-disulfonic acid, -2,6-disulfonic acid, -2,7-disulfonic acid, anthraquinone-1-carboxylic-2-sulfonic acid, 2-ethylanthraquinone-sulfonic acid, phenanthrenequinone-1-sulfonic acid of soluble salts thereof, in which the cation is e.g. an alkali salt, such as ammonium, sodium or potassium. Soluble alkaline earth metal salts may likewise be used. Furthermore mixtures of the aforesaid compounds may be applied.

The quinones or their sulfonic of carboxylic acids or the water-soluble salts of quinone sulfonic acids or quinone carboxylic acids are preferably used in a proportion of up to 10 percent by weight, calculated upon the amount of catalyst, and preferably in a proportion of between 0.1 and 3 percent by weight. If the oxidation is carried out in two stages as set forth in application Ser. No. 750,150 it is possible, prior to or during the oxidation of the catalyst, to substitute the corresponding hydroquinones for the quinones or quinone compounds mentioned above, and to oxidize these hydroquinones to quinones.

The use of the aforesaid quinones or their derivatives enables the amount of catalytically active substance in the catalyst, and also the prime cost of the catalyst and the formation of by-products to be reduced.

The process of this invention may be carried out in vertically arranged high reactors, such as tubes provided with frits or oscillatory agitators. These reactors may be

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 vibromixer or a turbomixer. All these variants enable the reaction to be carried out continuously.

The conversion and the space/time/yield depend, for example on the fine distribution of the gas on the residence time in the apparatus and the composition of the catalyst, the temperature and the pressure used. The optimum time of stay can readily be determined by those skilled in the art.

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

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, especially 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 or are worked up to solid bed 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, phosphorous, 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 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 or the catalyst solution is applied to a 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 are then directly used as a catalyst for the olefin oxidation.

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 methods 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 of the lining of the reactor.

The catalysts may be freed from these contaminations and regenerated in a simple manner by precipitating the noble metal compound as elementary metal and—if present—the cupric chloride as cuprous chloride. 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, for instance with water. It is then mixed with water and an acid, suitably hydrogen chloride, if desired in the form of hydrochloric acid, and may then be reused in this state in the reaction, or more suitably after oxidation with oxygen or an oxygen-containing gas, such as air. If a particular 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 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 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 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 carbon monoxide 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 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 liquid catalyst or upon the solution which is obtained by dissolving the active components

from the carrier 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, especially 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 generate 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 from catalysts 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.

The apparatus used in the process of this invention should be made of a material which is not corroded by the catalyst and preferably, especially if solid catalysts are used, 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.

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 poly-olefins, 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

(A) *No Circulation of the Contact Solution*

A vertically arranged reaction tube (diameter: 30 mm., height: 3 meters) is charged at 80° C. with a catalyst solution containing, per liter of water, 1 gram of $PdCl_2$ and 150 grams of $CuCl_2.2H_2O$; the solution is adjusted to a pH of 1.5 by means of hydrochloric acid. 20 liters of ethylene and 10 liters of oxygen are introduced through a frit per hour. The foam formed occupies the entire reaction tube and partially overflows into the quiescent zone arranged at the head of the column. 30% of the ethylene are converted to acetaldehyde which may be removed from the escaping gas by washing.

(B) *Circulation of Contact Solution*

The reaction tube used is the same as that described sub (A) with the exception that it is provided with a contact receiver at the head and an inclined conduit to the foot. The reaction tube is charged as described sub (A) with 3 liters of a catalyst solution containing, per liter of water, 1 gram of $PdCl_2$ and 150 grams of $CuCl_2$, i.e. the same amounts as indicated sub (A). The solution is gassed. Ethylene and oxygen are introduced into the solution at a rate of 20:10 liters per hour at the same temperature as according to (A). The catalyst solution is circulated. About 35–40% of the ethylene used are converted.

EXAMPLE 2

A reaction tube (1 meter long; capacity 500 cc.) is charged with a catalyst solution containing, per liter of water, 1.5 grams of $PdCl_2$, 100 grams of $CuCl_2.2H_2O$ and 2 cc. of 10 N-hydrochloric acid, and ethylene is passed through at a rate of 30 liters per hour. A regeneration tube (1 meter long; capacity: 1000 cc.) is charged with the same solution and 100 liters of air are passed through per hour. Both gases are finely distributed by means of frits. Both tubes are provided with expanded top vessels (quiescent zones) in which the foam decomposes and gas and liquid separate from one another. By connecting the headpiece of the reaction tower with the lower liquid inlet of the regeneration tower and vice versa, a closed liquid cycle is produced, so that pump can be dispensed with. The ascending gas currents circulate the liquid vigorously; in the instant example the circulation rate is above 100 liters per hour; it may be throttled as desired, for example, to 80 liters per hour. The rate of circulation may be measured, for example, by means of a flow meter. The towers are heated to a temperature of about 80–85° C. From the escaping gas currents which are charged with acetaldehyde vapor, acetaldehyde may be isolated in known manner, for example by conducting the gasses separately through wash towers. The ethylene may be reintroduced to participate again in the process, if desired after branching off a small amount of gas. Under these conditions, the conversion is after a certain induction period between 30% and 40% of the ethylene introduced into the reactor. Solid separations do not occur even after a prolonged time of reaction.

In case it is feared that the mixture of residual air and acetaldehyde could slightly rise above the lower explosive limit, it is possible to provide the head of the regeneration tower with security devices to prevent explosions, such as a bursting disk or a flametrap such as pots filled with steel grains or the like. Due to the saturation of the acetaldehyde-air mixture with steam and the relatively low content of oxygen which is smaller than the amount of oxygen contained in the air, the danger of explosion is extremely small.

The yields can be increased by the application of pressure. The gas pressure of the two gases need not be the same, if the difference in pressure is taken into account in calculating the height of the two towers. The towers may also be operated at different temperatures provided that cooling and/or heating devices are installed.

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 comprises contacting an olefinic hydrocarbon having 2 to 8 carbon atoms 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 an inorganic redox system, a salt of a metal showing several valence states under the reaction conditions applied, by introducing said olefinic hydrocarbon and oxygen into said liquid catalyst, streaming said catalyst upwards by the buoyant action of the reactant gases introduced, whereby gaseous reactants and reaction products become admixed with said liquid catalyst, arresting the upward streaming of the liquid catalyst by introducing the catalyst into a quiescent zone wherein gaseous components admixed with the liquid catalyst escape from the liquid catalyst, withdrawing said gaseous components, and recycling the liquid catalyst to the reaction.

2. A process as in claim 1 wherein the liquid catalyst is recycled under the force of gravity.

3. A process as in claim 1 wherein said olefinic hydrocarbon, oxygen, and liquid catalyst are contacted at a temperature of from 50° to 160° C.

4. A process as in claim 1 wherein said olefinic hydrocarbon, oxygen, and liquid catalyst are contacted at a temperature of from 50° to 100° C.

5. A process as in claim 1 wherein said liquid catalyst has a pH of from 0.8 to 3.

6. A process as in claim 1 wherein said olefinic hydrocarbon, oxygen, and liquid catalyst are contacted at a pressure of from about atmospheric pressure to 50 atmospheres gauge pressure.

7. A process as in claim 1 wherein gaseous components withdrawn in said quiescent zone are recycled.

8. A process as in claim 1 wherein said oxygen is present admixed with an inert gas.

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

10. A process as in claim 1 wherein said salt of a noble metal is a salt of palladium, said salt of a metal showing several valence states under the reaction conditions applied is a copper salt, and wherein the amount of copper present in said catalyst, calculated as metallic copper, is 15 to 500 times as great as the amount of palladium present in said catalyst, calculated as metallic palladium.

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

12. 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 comprises contacting an olefinic hydrocarbon having 2 to 8 carbon atoms and oxygen, in a first stage, 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 copper chloride, by introducing said olefinic hydrocarbon and oxygen into said liquid catalyst, streaming said catalyst upwards by the buoyant action of the reactant gases introduced, whereby gaseous reactants and reaction products become admixed with said liquid catalyst, arresting the upward streaming of the liquid catalyst by introducing the catalyst into a quiescent zone wherein gaseous components admixed with the liquid catalyst escape from the liquid catalyst, withdrawing said gaseous components, and then regenerating said liquid catalyst by contacting at least a part of the oxygen necessary for carrying out the reaction with said catalyst in a second stage in the absence of substantial amounts of olefin, and recycling the catalyst to said first stage.

13. A process as in claim 12 wherein chloride ions are present in the catalyst and chloride ions are additionally supplied to the catalyst during the reaction.

14. A process as in claim 12 wherein gaseous compounds are expelled from the liquid catalyst by blowing with a stripping agent inert to reaction products formed.

15. A process as in claim 12 wherein said olefinic hydrocarbon has 2 carbon atoms.

References Cited in the file of this patent

UNITED STATES PATENTS

1,999,620	Van Peski et al.	Apr. 30, 1935
2,468,710	Hull	Apr. 26, 1949
2,523,686	Engel	Sept. 26, 1950
2,690,457	Hackmann	Sept. 28, 1954
2,848,498	Mention	Aug. 19, 1958

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., vol. 16, pages 255–277 (pages 265–72 relied upon) (1894).

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