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CONTACT AGENTS FOR CONVERTING ETHYLENICALLY UNSATURATED HYDROCARBONS TO CARBONYLIC COMPOUNDS

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ABSTRACT OF THE DISCLOSURE

Process for converting ethylenically unsaturated hydrocarbons to carbonylic compounds in the presence of a novel catalyst composition comprising a titania or zirconia supported mixture of at least one of molybdenum trioxide, molybdenum heteropolyacid and a salt of molybdenum heteropolyacid together with a second component of platinum or palladium or compounds thereof. The process is useful for preparing products which are useable both for solvent extraction purposes and for the preparation of war gasses, resins, glycerin, polyurethane, polyester resins and the like.

This application is a continuation-in-part of our copending application Ser. No. 163,079, filed Dec. 29, 1961 and now abandoned.

This invention relates to the preparation of carbonylic compounds. More particularly, this invention relates to the conversion of ethylenically unsaturated hydrocarbons to carbonylic compounds at relatively mild conditions of temperature and pressure. In a specific aspect, this invention relates to the preparation of carbonylic compounds at relatively mild reaction conditions in the presence of contact agents containing platinum or palladium metals or compounds of these metals.

It is known that carbonylic compounds can be prepared by oxidizing ethylenically unsaturated hydrocarbons, for example, ethylene, propylene or butene, in the presence of noble metals. However, such processes suffer from a number of disadvantages and are not, therefore, wholly desirable oxidation processes for the preparation of carbonylic compounds. For example, the use of noble metals as major active components in such processes places a heavy cost burden on these processes making them economically unattractive. Furthermore, in liquid phase operation particularly, these systems tend to suffer a reduction in oxidation state with consequent plating out or precipitation of insolubles which give rise to processing complications, for example, complications in stirring, conveying and reconstitution of noble metal components. Moreover, prior art processes for converting ethylenically unsaturated hydrocarbons to carbonylic compounds have, for the most part, employed rather severe reaction conditions. It is obvious, therefore, that the state of the art will be greatly enhanced by providing a process for the conversion of ethylenically unsaturated hydrocarbons to carbonylic compounds which process employs noble metal components but is not subject to the aforementioned disadvantages.

Accordingly, it is an object of this invention to provide a novel process for the preparation of carbonylic compounds from ethylenically unsaturated hydrocarbons.

Another object of this invention is to provide a process for the selective conversion of ethylenically unsaturated hydrocarbons to carbonylic compounds in the presence of contact agents that are extremely effective at relatively mild reaction conditions.

Another object of this invention is to provide a process

for the conversion of ethylenically unsaturated hydrocarbons to carbonylic compounds at relatively mild reaction conditions in the presence of highly active contact agents containing very small amounts of noble metal components and thus obtaining a substantial economy in operation over prior art carbonylation processes employing substantial amounts of noble metal components.

Another object of this invention is to provide a novel process for the conversion of ethylenically unsaturated hydrocarbons to carbonylic compounds at mild reaction conditions employing a contact agent comprising two components which are ineffective when used separately at these same mild reaction conditions.

Another object of this invention is to provide a liquid phase oxidation process for ethylenically unsaturated hydrocarbons using contact agents containing only very small amounts of noble metal components resulting in the avoidance of troublesome precipitation of insolubles which is often associated with prior art liquid phase oxidation processes employing noble metal components.

Still another object of this invention is to provide contact agents comprising noble metal components and molybdenum trioxide or heteropolyacid components which contact agents enable the simple, economical, selective and direct conversion of ethylenically unsaturated hydrocarbons to carbonylic compounds at relatively mild reaction conditions.

In accordance with this invention it has been found that ethylenically unsaturated hydrocarbons can be oxidized to carbonylic compounds by exposing them to a supported or unsupported contact agent comprising (1) at least about 1%, by weight, of molybdenum trioxide or a heteropolyacid or salt thereof and (2) very small amounts, i.e. 1×10^{-5} to about 3%, by weight, of platinum or palladium metals or inorganic compounds of these metals, in the presence or absence of a gaseous oxidizing agent at temperature and pressure conditions more fully discussed hereinafter. In the absence of a gaseous oxidizing agent, the apparent action of the contact agents disclosed herein is that of oxidant while, in the presence of a gaseous oxidizing agent it appears that their action is of a catalytic nature or a combination catalytic-oxidant nature. However, it should be understood that the invention is not limited to any particular explanation for the action of the agent and the term "contact agent" is used to designate the particular reagents employed in the process of this invention regardless of whether they act as catalysts or oxidants or as both or in some other capacity, as is obvious to one skilled in the art.

The novel process of this invention is extremely effective for carbonylation of ethylenically unsaturated hydrocarbons alone or in admixture, and particularly the monoethylenically unsaturated hydrocarbons containing 2–10 carbon atoms. These ethylenically unsaturated hydrocarbons are converted to the corresponding carbonylic compound containing the same number of carbon atoms in a simple, economic and direct manner. For example, ethylene is easily converted to acetaldehyde while styrene is easily converted to acetophenone. The composition of the gaseous feed employed in the practice of this invention can be varied over a wide range. Thus, when operating in a continuous manner using oxygen in the feed, the amount of such oxygen can be varied over a wide range depending, for example, upon the design of equipment in use, the temperature, contact time, partial pressure of other reactants, as is obvious to one skilled in the art. The ethylenically unsaturated hydrocarbons which can be employed in the practice of this invention include, for example, ethylene, propylene, butene, hexene, heptene, octene, decene, dodecene, butadiene, pentadiene, cyclopen-

tene, cyclohexene, styrene and the like. Total conversion of such ethylenically unsaturated hydrocarbons can be increased by recycling gaseous reaction product as a whole, or even further, by separation and recycling of unreacted ethylenically unsaturated hydrocarbon.

As already indicated, the contact agents employed in the practice of this invention comprise at least two components, one of which is molybdenum trioxide or a heteropolyacid or salt thereof, while the other component of the contact agent contains platinum or palladium. It was quite surprising that these two components could be combined to form contact agents which can be used in liquid or solid form to oxidize ethylenically unsaturated hydrocarbons since either component of the contact agent alone is ineffective under conditions where the total contact agent is extremely effective, as illustrated by working examples which follow.

The molybdenum trioxide which can be used as one component of the contact agent can be readily prepared from ammonium molybdate, for example, by calcining this compound before or after inclusion into the contact agent. In addition to, or as an alternative for, the molybdenum trioxide, a heteropolyacid or salt of a heteropolyacid can also be employed as one component of the contact agent. The structures of the heteropolyacids are difficult to determine owing to the very large size of their molecules. However, the heteropolyacids may best be described as complex inorganic substances of relatively high molecular weight in which two or more different acid cations or oxides of metals or metaloids are associated with varying, frequently indeterminate amounts of combined water as water of hydration. The typical acid atom of the heteropolyacid, that is, the phosphorus atom in phosphoheteropolyacids, the silica atom in silicoheteropolyacids, etc., is regarded as the central atom of a nucleus. This central atom is hydrated and attached to 6 oxygen atoms, thus H_7PO_6, H_8SiO_6, etc. The oxygen appears to be linked to the nuclear atom of phosphorus, silica, boron, arsenic or the like in the same way that molecules of ammonia are bound to the metal atom in the metallic amines. The oxygen atoms can be wholly or partially substituted by radicals such as MoO_4, Mo_2O_7, WO_4, W_2O_7, VO_3 and V_2O_6. Thus, phosphomolybdic acid, phosphotungstic acid, phosphovanadic acid and the like can be formed. The heteropolyacids or salts thereof form a well-known class of compounds and include, for example, phosphomolybdic acid, silicomolybdovanadic acid, titanomolybdotungstic acid, silicomolybdic acid, germanomolybdic acid, chromimolybdic acid, stannotungstic acid, phosphotungstic acid, cobalt phosphomolybdate, cadmium borotungstate, cadmium silicomolybdate, ferric silicomolybdate, ammonium vanadomolybdate, zinc phosphomolybdate, nickel stannotungstate, nickel silicotungstate, nickel borotungstate and the like.

The second component of the contact agent is platinum or palladium metal or compounds of these metals. The platinum or palladium compounds employed are preferably inorganic compounds of platinum or palladium. However, complex palladium or platinum compounds containing an organic moiety can be employed as long as such compounds are capable of furnishing a platinum or palladium atom to the contact agent in the amounts required. Thus, preferred classes of platinum or palladium compounds include the halides, oxides, nitrates or sulfates of these metals. Suitable second components of the contact agent are exemplified by platinum metal, platinic chloride, platinic acid, chloroplatinic acid, platinic bromide, platinic hydride, platinic iodide, platinic oxide, platinic sulfate, platinic sulfide, platinous bromide, platinous chloride, platinous cyanide, platinous iodide, platinous oxide, palladium, palladous bromide, palladous chloride, palladous cyanide, palladic oxide, palladic sulfide, palladous hydroxide, palladous iodide, palladium monoxide, palladous sulfide, palladous nitrate, sodium palladous chloride, sodium, palladous sulfate and the organo-metal palladium or platinum complexes formed with olefins, for example, ethylene as exemplified by $PdCl_2$—C_2H_4 complex or $K(PtCl_3 \cdot C_2H_4)$. The components of the contact agents can be combined in any suitable manner as is obvious to those skilled in the art, for example, where they are both water soluble, the components are placed in distilled water and stirred and heated. A support can then be stirred into the solution and the water evaporated.

The process of the invention can be carried out in either a liquid or vapor phase and the amounts of the components in the contact agents can be varied over a wide range. For example, the content of the palladium or platinum metal or compound of these metals can range from trace amounts, for example, as little as 1×10^{-5}%, to as much as 3%, by weight, calculated as platinum or palladium, of the total dry weight of the contact agent. In liquid phase particularly, satisfactory results can be obtained with as little as 1×10^{-5}%, by weight, of palladium or platinum component while, in vapor phase, it is generally preferred to employ at least .01%, by weight, of this component. Though the contact agents can be used in unsupported form in vapor phase reaction, it is preferred to use them in supported form, i.e., on a carrier. When used in supported form, the contact agents contain at least 1% and generally no more than about 90%, by weight, of molybdenum trioxide, heteropolyacid or salt thereof, based on the total weight of the contact agent. It is particularly advantageous to employ contact agents containing from about 20% to about 60%, by weight, of the molybdenum trioxide, heteropolyacid or salt thereof. Since the solubility of many of the heteropolyacids or their salts in aqueous medium is very high, a wide range in the concentration of these materials in solutions is available for operation in the liquid phase. However, it is preferred to use concentrations of heteropolyacids or their salts, and particularly phosphomolybdic acid or silicomolybdic acid, from about .005 molar to saturated solutions in water when operating the process of this invention in liquid phase. Molybdenum trioxide can be used as a slurry in any practical proportion with the liquid when operating in liquid phase and in this case, higher temperatures and superatmospheric pressure may be used to increase the rate of reaction. It is also possible to improve the action of the contact agent by the incorporation of small amounts of hydrochloric acid or ferric chloride. Where hydrochloric acid is employed, it is used in concentrations in the range of about .01 to about 3%, by weight, based on the total weight of the contact agent, and ferric chloride can be used in mole ratios of iron to noble metals, i.e., platinum or palladium, of up to about 10:1.

As already indicated, the contact agent can be employed in the process of this invention without being supported on a carrier. However, the use of a carrier has been found to be advantageous in the practice of the invention, and it is preferred that such be used. Carriers that can be used to support the contact agent include any one or mixtures of the conventional carriers known in the art. All carriers, however, do not give equivalent results and it is preferred therefore, that titania or silica, for example, be used rather than alumina, for example. When a support is employed it will generally be used with a surface area of about 8 to 200 sq. m./g. Suitable supports which can be employed in the process of this invention include, for example, silica, pumice, kieselguhr, titania, alumina, silica alumina, zirconia, thoria, clays and silica gel.

Especially preferred among the contact agents of our invention are the solid contact agents which contain (1) about 1% to about 90%, by weight, of a first component which is typically molybdenum trioxide, a heteropolyacid containing molybdenum, or a salt of a heteropolyacid containing molybdenum; (2) about 0.01% to about 3%, by weight, of a second component which is platinum, palladium, or an inorganic compound of platinum or palladium; supported on about 7% to about 99%,

by weight, of a support which contains at least a major amount, i.e., more than 50%, by weight, of titania or zirconia.

Examples of the molybdenum-containing heteropolyacids of these preferred contact agents include phosphomolybdic acid, silicomolybdic acid, chromimolybdic acid, germanamolybdic acid, cerimolybdic acid and others mentioned hereinbefore.

Platinum chloride, platinum nitrate, palladium chloride, and palladium nitrate are among the inorganic compounds of platinum or palladium which are especially useful in these solid contact agents.

Typical of the supports which are especially useful in these solid contact agents are titania or zirconia or mixtures containing a major amount, i.e., more than 50%, of titania or zirconia and a minor amount, i.e., less than 50%, of silica.

The amount of the first component of these solid contact agents generally exceeds the amount of the second component of the solid contact agent by at least 15:1 and preferably by at least 30:1.

These solid contact agents preferably contain about 20% to about 90%, by weight, of the first component and about 0.01% to about 3%, by weight, of the second component and, therefore, contain about 7% to about 80% of the support.

Especially preferred among these solid contact agents are those in which the first component is phosphomolybdic acid; the second component is palladium chloride and the support is titania or titania with a minor amount of silica.

A factor having a significant influence on the course of the reaction forming the process of this invention is the use of a diluent or solvent. Thus, the use of steam or liquid water as a diluent, either alone or in admixture with diluents such as nitrogen or other inert gases is particularly advantageous since, in their absence, the yield of carbonylic compound is reduced. In gas-phase reactions it is, of course, possible to use substances which are capable of producing water, for example, hydrogen, rather than employing water directly.

The temperature at which the process of this invention is carried out can be varied over a wide range. However, generally satisfactory results are obtained at temperatures in the range of about 100° to about 300° C. and preferably at temperatures from about 100° to about 225° C. in the vapor phase and from 25° to about 170° C. in liquid phase. As is obvious to one skilled in the art, in order to obtain most selective reaction at highest yields of carbonylic compounds, care should be exercised to avoid temperatures above which substantial decomposition of reactant or product occurs. The pressures employed in the operation of this invention are also subject to wide variation, with pressures in the range of about 1 to about 100 atmospheres being generally satisfactory and pressures in the range of about 1 atmosphere to about 5 atmospheres being preferred.

Any suitable reactor can be employed in carrying out the process of this invention and, for example, can be any one of several conventional types usually employed in oxidation reactions for ethylenically unsaturated hydrocarbons. Thus, the reactor can be a tubular type, fluidized-fixed bed, moving bed or other conventional type of reactor. It will be found particularly advantageous, however, to use apparatus permitting rapid dissipation of heat from the reaction zone when the reaction is carried out in the presence of oxygen or oxygen-containing gas in vapor phase. With continued use of the contact agent in such a reactor, the activity may decrease. It has been found advantageous, therefore, to stop the flow of feed periodically and subject the contact agent to treatment with air or other oxidizing substance. This periodic regeneration can be carried out at the temperature of reaction or at a higher or lower temperature, although elevated temperatures are preferred. The carbonylic compounds prepared according to the process of this invention can be easily collected, for example, by condensation or washing out. The contact time, or the time in seconds a unit volume of the gaseous feed mixture is in contact with a unit volume of contact agent at reaction temperature and pressure, can be varied within wide limits of from about 0.1 second to about 100 seconds and preferably is in the range of about 1 second to about 50 seconds depending upon the level of conversion desired, operating temperature, feed composition, equipment design, etc. Since reaction temperatures can vary considerably, the contact time reported herein is at 100° C. and 735 mm. mercury pressure, unless otherwise indicated.

The excellent results obtained by the improved process of this invention are readily appreciated from an examination of the examples that follow. The tubular Vycor reactor referred to in the following examples is constructed of Vycor Glass and is cylindrical. The outer diameter of the cylindrical tube is 25 mm. and the length is 33 inches. The fluidized-bed reactor referred to is also constructed of Vycor Glass and is cylindrical but with a conical bottom. The internal diameter of the lower portion is 40 mm. for 25 cm. of height and the upper portion of the reactor is 55 mm. in diameter. The feed gases are directed into the bottom of the reactor serving to "fluidize" the catalyst and the reactor is heated electrically. In the following examples, the compositions of the contact agents set forth are those that are calculated from the amounts of components used in their preparation. They are not necessarily intended to represent the actual operating concentrations or even the actual compounds present after use of the contact agents has begun.

This invention can be further illustrated by the following examples of preferred embodiments thereof although it will be understood that these examples are included merely for purposes of illustration and are not wise specifically indicated.

Example 1

As already indicated, carbonylic compounds can be prepared from the corresponding ethylenically unsaturated hydrocarbons using contact agents containing a platinum or palladium component and a molybdenum trioxide, heteropolyacid or heteropolyacid salt component. To illustrate, a granular contact agent of 30%, by weight phosphomolybdic acid and .06% by weight, of palladium chloride on titanium dioxide is heated to 155° C. in the tubular Vycor reactor described hereinbefore. The titanium dioxide support has a surface area of about 8.6 sq. m./g. A gas feed containing 21% ethylene, 9% oxygen, and 70% steam, by volume, is passed through the reaction zone at a contact time of 7 seconds for a period of 30 minutes. The aqueous reaction product is condensed in receivers coiled to 10° C. and −80° C., respectively. Analysis of the product shows that 14.5% of the ethylene is converted to acetaldehyde and the space-time yield, expressed as grams of acetaldehyde produced per liter of contact agent per hour, is 22.7. The effluent from the reactor is substantially free of by-products, as shown by gas chromatography, for example.

Repeating the above procedure after heating the contact agent in a stream of air at 355° C., results in a conversion of ethylene to acetaldehyde of 16.8% and a space-time yield of 26.4. Thus, the activity of the contact agent can be increased by treating it in a stream of an oxygen-containing gas at an elevated temperature after it has once been used.

Example 2

The individual components of the contact agents employed in the process of this invention are not effective under mild conditions of reaction when used separately. To illustrate, Example 1 is repeated except that the contact agent contains only 30%, by weight, phosphomolybdic acid on the same titania support with the palladium chloride being omitted. Upon analysis, the aqueous prod-

uct of this run fails to show the presence of any carbonyl compound.

As a further illustration of this phenomena, Example 1 is repeated using a contact agent containing only 0.06%, by weight, palladium chloride on the same titania support, but omitting the phosphomolybdic acid. The aqueous product from this run shows only a trace amount of acetaldehyde when analyzed. Thus, the omission of either component from the contact agent employed in the process of this invention results in a process which is essentially ineffective.

Example 3

Example 1 is repeated except that the phosphomolybdic acid and palladium chloride are supported on titania having a surface area of 158.3 sq. m./g. and it is heated to 100° C. instead of 155° The run is continued for a period of 45 minutes and the conversion of ethylene to acetaldehyde during this time is 13% and the space-time yield is 20.3.

Example 4

The procedure of Example 1 is repeated at a temperature of 120° C. using the contact agent from Example 3 after heating it in air at 350° C. The duration of the run is 30 min. and the conversion of ethylene to acetaldehyde is 16% with a space-time yield of 25.2.

Example 5

A contact agent of 30%, by weight, phosphomolybdic acid and .06%, by weight, palladium chloride supported on titania is placed in the reactor of Example 1 and heated to 147° C. A gas feed containing 30% ethylene and 70% steam, by volume, is passed through the reactor at a contact time of 9.5 seconds. After 30 min. the conversion of ethylene to acetaldehyde amounts to 8.9% and the space-time yield is 14.

Example 6

The process of this invention can be carried out in a fluidized-bed reactor. Thus, a contact agent of 30%, by weight, of phosphomolybdic acid and .06%, by weight, of palladium chloride on titania is heated to 126° C. in the fluidized-bed reactor described hereinabove. A gas feed containing 21% ethylene, 9% oxygen and 70% steam, by volume, is passed through the bed at a contact time of 4 seconds to impart a fluid motion to the particles. During a period of 30 minutes the aqueous product collected shows a conversion of ethylene to acetaldehyde of 8.1% and a space-time yield of 21.3.

Example 7

Granular contact agent of 30%, by weight, phosphomolybdic acid and .06%, by weight, of palladium chloride on titania is packed into the tubular Vycor reactor. While heated to a temperature of 147° C., the contact agent is exposed to a gas feed containing 21% ethylene, 9% oxygen and 70% steam, by volume, at a contact time of 1.3 seconds. The duration of the run is 30 minutes and the conversion to acetaldehyde is 7.6% and the space-time yield is 59.7.

Repeating this run with a contact agent containing .18%, by weight, of palladium chloride rather than .06% palladium chloride, the conversion of ethylene to acetaldehyde is 9.6% and the space-time yield is 73.6.

Example 8

As indicated hereinbefore, inert gases such as nitrogen can be mixed with steam and the mixture used as diluent in the process of this invention. Thus, the procedure of Example 1 is repeated using a gas feed containing 10.2% ethylene, 2.2% oxygen, 70% steam and 17.6% nitrogen, by volume, at a temperature of 123° C. and a contact time of 3.2 seconds. The aqueous reaction product collected during 30 minutes of operation shows that 18.2% of the ethylene is converted to acetaldehyde with a space-time yield of 28.6.

Example 9

As little as .01%, by weight, of palladium or platinum component can be present in the contact agent. To illustrate, a contact agent of 30%, by weight, phosphomolybdic acid and .01%, by weight, of palladium chloride on titania is contacted with a gas feed containing 21% ethylene, 70% steam and 9% oxygen at a contact time of 7 seconds using the procedure of Example 1. During a run lasting for 30 minutes the conversion of ethylene to acetaldehyde is 13.5%, and the space-time yield is 21.2.

Example 10

The procedure of Example 1 is repeated using a gas feed containing 52.6% propylene, 35.1% oxygen, 8.8% steam and 3.5% nitrogen, by volume, at a temperature of 220° C. and a contact time of 5.3 seconds. In a run lasting for 30 minutes the conversion of propylene to acrolein is 4% and the space-time yield is 25.1.

Example 11

Using the procedure of Example 1, a contact agent of 58.5% phosphomolybdic acid, .05%, by weight, palladium chloride on silica is reacted with the gas feed of Example 1 at 123° C. and a contact time of 7 seconds. During 30 minutes of operation the conversion of ethylene to acetaldehyde is 14% and the space-time yield is 22.0.

Example 12

The procedure of Example 1 is repeated except that the support is zirconia and the contact agent is heated to a temperature of 148° C. The conversion of ethylene to acetaldehyde is 8.5% and the space-time yield is 13.3 in a run of 30 minutes duration.

Example 13

Example 1 is repeated except that the support is silica-alumina instead of titania and the contact agent is heated to 120° C. before contacting it with the gas feed. During 30 minutes the conversion of ethylene to acetaldheyde is 4.3% and the space-time yield is 6.7.

Example 14

The procedure of Example 1 is repeated using a contact agent containing 30%, by weight, phosphomolybdic acid and .13%, by weight, of platinic chloride on titania. The contact agent is exposed to the gas feed of Example 1 while heated to 147° C. at a contact time of 7 seconds. The conversion of ethylene to acetaldehyde is 2.8% and the space-time yield is 4.4 in a run of 30 minutes duration.

Example 15

Different types of reactors can be employed in carrying out the process of this invention and such process can be carried out in liquid or vapor phase. When operating in liquid phase, contact agents using very small amounts, e.g. 1×10^{-5}%, by weight, of platinum or palladium components are generally employed. Thus, ethylene is introduced through a fritted thimble at the bottom of a reactor made from a length of 38 mm. outer diameter Pyrex tubing 8 inches in length, which is packed with ¼ inch ceramic saddles. The tube contains an aqueous solution which is .1 molar in phosphomolybdic acid and 1×10^{-6} molar in palladium chloride. The solution is heated to approximately 90° C. and, on initial contact with the ethylene at an input rate of 48 ml. of ethylene per ml. of solution per hour, the contact agent turns green. With continued exposure the contact agent turns deep blue. The aqueous reaction product is collected by passing the effluent from the reactor through traps cooled to 10° and −80° C. respectively. During a run of 45 minutes duration 11.5% of the ethylene is converted to acetaldehyde and the effluent from the reactor is substantially free of by-product. No evidence of the precipitation of solids from the contact agent could be detected following its use.

The contact agents employed in the process of this

invention can be regenerated after use. Thus, the contact agent employed in this example is regenerated by dispersed gaseous perchloroylfluoride through the solution after flushing out residual ethylene and acetaldehyde. When the above procedure is repeated, following such regeneration, essentially the same results in acetaldehyde production are obtained.

As in the vapor phase operation of the process of this invention, the two components of the contact agent must also be present in the liquid phase in order to have a truly effective contact agent. Thus, omission of the palladium chloride in the above procedure results in no aldehyde being prepared and when the phosphomolybdic acid is omitted only trace amounts of carbonyl compound are detected in the initial reaction effluent following which, no reaction is observed.

When the procedure of this example is repeated using butene-1, or a mixture of cis and trans butene-2 rather than ethylene, there is obtained ethyl methyl ketone substantially free of by-products. Furthermore it is possible to substitute silicomolybdic acid for the phosphomolybdic acid or chloroplatinic acid for palladium chloride and obtain similar results.

Example 16

The procedure of Example 15 is repeated except that proylene is introduced into the reactor instead of ethylene. The effluent from the reactor contains acetone substantialy free of by-products. Thus, it can be seen by comparison of this example with Example 10 that different carbonylic compounds can be prepared from the same ethylenically unsaturated hydrocarbon by varying reaction conditions, for example, temperature.

Example 17

The procedure of Example 7 is repeated except that the contact agent is 30%, by weight, phosphomolybdic acid and .13%, by weight, of palladium nitrate on titania. The conversion of ethylene to acetaldehyde is 10.1% and the space-time yield is 79.2 for a run of 30 minutes duration.

Example 18

The procedure of Example 7 is repeated except that the contact agent is 30%, by weight, silicomolybdic acid and .06%, by weight, palladium chloride on titania. In a run of 30 minutes duration, the conversion to acetaldehyde is 7.8% and the space-time yield is 61.

Example 19

As indicated hereinbefore, the contact agent can also contain ferric chloride. To illustrate, the procedure of Example 7 is repeated except that the contact agent is 30%, by weight, of phosphomolybdic acid, .06%, by weight, of pallidum chloride and .18% ferric chloride on titania. The conversion of ethylene to acetaldehyde is 12.6% and the space-time yield is 99.2 for a run of 30 minute duration.

Example 20

As pointed out hereinbefore, certain of the carriers or supports are preferred over others. Particularly advantageous results can be achieved using titania gel made by precipitation of the oxide from aqueous titanium tetrachloride with ammonia. Repeating the procedure of Example 7 using this particular support the conversion of ethylene to acetaldehyde is 11% and the space-time yield is 86.6.

Example 21

Molybdenum trioxide is an effective component in the contact agent employed in the process of this invention. To illustrate, Example 7 is repeated except that the contact agent is 21.9%, by weight, molybdenum trioxide and .06%, by weight, of palladium chloride on titania having a surface area of approximately 200 sq. m./g. In a run of 30 minutes duration the conversion of acteladehyde is 6.1% and the space-time yield is 48.

Example 22

The phosphomolybdic acid can be formed in situ in preparing the contact agent of this invention. Thus, Example 1 is repeated except that the contact agent is 21.9%, by weight, molybdenum trioxide, 1.24%, by weight, phosphoric acid and .06%, by weight, palladous chloride on titania having a surface area of 7.1 sq. m./g. The atomic ratio of molybdenum to phosphorous is 12:1. In a run lasting 30 minutes the conversion to acetaldehyde is 18.8% and the space-time yield is 29.5.

Repeating the above run with a contact agent of 21.9%, by weight, molybdenum oxide, .62%, by weight, phosphoric acid and 0.6%, by weight, of palladous chloride on titania, there is obtained a conversion to acetaldehyde of 16.0% and a space-time yield of 25.0.

When the above run is repeated using a contact agent of 21.9%, by weight, molybdenum oxide, 2.48%, by weight, phosphoric acid and .06%, by weight, of palladous chloride on titania the conversion to acetaldehyde is 15.1% and the space-time yield is 23.8.

Example 23

A contact agent of 30%, by weight, phosphomolybdic acid and 0.1%, by weight, palladous chloride is prepared by dissolving 30 g. of phosphomolybdic acid and 100 mg. of palladous chloride in 50 ml. of distilled water with stirring and heating. The amber-colored solution is stirred into a mixture of 69.9 g. of titania and the paste thickened by evaporation of the water. The preparation is then dried for a period of 15 hours at a temperature of 145° C., cooled in a desiccator and a −4+20 mesh component screened out. 50 ml. of this contact agent is packed into the Vycor reactor described hereinbefore. During 30 minutes at a furnace temperature of 148° C. the contact agent is exposed to a gas feed containing .089 mole of ethylene, 0.038 mole of oxygen and 0.297 mole of steam. Analysis of the aqueous reaction product collected as in Example 1 shows .016 mole of acetaldehyde corresponding to a conversion of 18% and a space-time yield of 28.2.

Example 24

As already indicated, the materials employed as supports for the contact agent of this invention can be used alone or in admixture. A particularly good mixture for this purpose is a mixture of titania and silica. Thus, a contact agent of 30%, by weight, phosphomolybdic acid, .1%, by weight, palladous chloride, 48.9% titania and 21% silica is employed in a fluid-bed reactor, as described above. The gas feed contains 14.6% ethylene, 65.2% steam and 20.2% air, by volume, at a reactor temperature of 115° C. and a contact time of 0.9 second. The run lasts 60 minutes and the conversion to acetaldehyde is 11.8% and the space-time yield is 95.4.

Thus, by the practice of this invention there is provided a simple, economical and direct process for the conversion of ethylenically unsaturated hydrocarbons to carbonylic compounds containing the same number of carbon atoms. The carbonylic compounds prepared by the process of this invention can be used for a wide variety of solvent extraction purposes as well as intermediates in the preparation of many useful organic compounds. For example, acrolein which can be prepared from the oxidation of propylene using the process of this invention is a well-known compound which is extensively used in the preparation of war gases, resins, glycerin, polyurethane, polyester resins, methionine and pharmaceuticals.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A solid contact agent for promoting the oxidation of ethylenically unsaturated hydrocarbons to carbonylic compounds consisting essentially of

(1) about 1% to about 90% by weight, of a first component selected from the group consisting of:
  (a) molybdenum trioxide,
  (b) a molybdenum containing heteropolyacid, and
  (c) a salt of a molybdenum containing heteropolyacid;

(2) about 0.01% to about 3% by weight of a second component selected from the group consisting of:
  (a) metallic platinum,
  (b) metallic palladium, and
  (c) a compound of platinum or palladium;

supported on about 7% to about 99% by weight of a support which contains at least a major amount of a component selected from the group consisting of:
  (a) titania, and
  (b) zirconia;

wherein the amount of said first component is at least 15 times as great as the amount of said second component.

2. A contact agent according to claim 1 in which the first component is selected from the group consisting of:
(a) phosphomolybdic acid,
(b) silicomolybdic acid,
(c) a salt of phosphomolybdic acid, and
(d) a salt of silicomolybdic acid.

3. A contact agent according to claim 1 in which said second component is selected from the group consisting of:
(a) metallic platinum,
(b) metallic palladium,
(c) platinum chloride,
(d) platinum nitrate,
(e) palladium chloride, and
(f) palladium nitrate,

4. A contact agent according to claim 1 in which said support contains a minor amount of silica.

5. A contact agent according to claim 1 consisting essentially of (1) about 20% to about 90% by weight of said first component; (2) about 0.01% to about 3% by weight of said second component; and about 7% to about 80% by weight of said support; wherein the amount of said first component is at least 30 times as great as the amount of said second component.

6. A contact agent according to claim 5 in which the first component is selected from the group consisting of:
(a) phosphomolybdic acid,
(b) silicomolybdic acid,

(c) a salt of phosphomolybdic acid, and
(d) a salt of silicomolybdic acid.

7. A contact agent according to claim 5 in which said second component is selected from the group consisting of:
(a) metallic platinum,
(b) metallic palladium,
(c) platinum chloride,
(d) platinum nitrate,
(e) palladium chloride, and
(f) palladium nitrate.

8. A contact agent according to claim 5 in which said support contains a minor amount of silica.

9. A contact agent according to claim 5 in which said first component is selected from the group consisting of:
(a) phosphomolybdic acid,
(b) silicomolybdic acid,
(c) a salt of phosphomolybdic acid, and
(d) a salt of silicomolybdic acid;

said second component is selected from the group consisting of:
(a) metallic platinum,
(b) metallic palladium,
(c) platinum chloride,
(d) platinum nitrate,
(e) palladium chloride, and
(f) palladium nitrate;

and said support is selected from the group consisting of:
(a) titania,
(b) zirconia,
(c) titania and a minor amount of silica, and
(d) zirconia and a minor amount of silica.

10. A contact agent according to claim 9 in which said first component is phosphomolybdic acid; said second component is palladium chloride and said support is selected from the group consisting of:
(a) titania, and
(b) titania and a minor amount of silica.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,379,651 April 23, 1968

Charles Wesley Hargis et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, line 6, "P. O Box 511, Kingsport, Tenn. 37662" should read -- Kingsport, Tenn., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey --.

Signed and sealed this 23rd day of September 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents