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OXYGEN-CONTAINING COMPOUNDS
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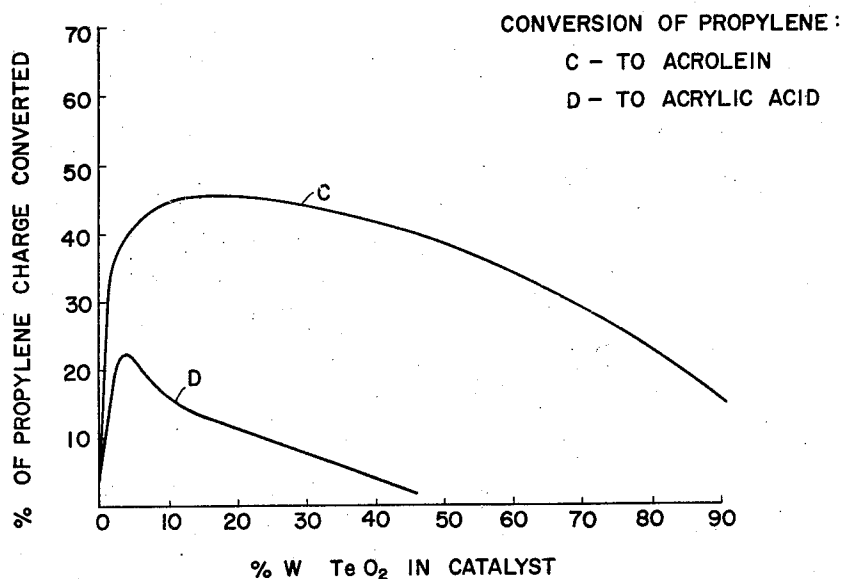


FIG. 2

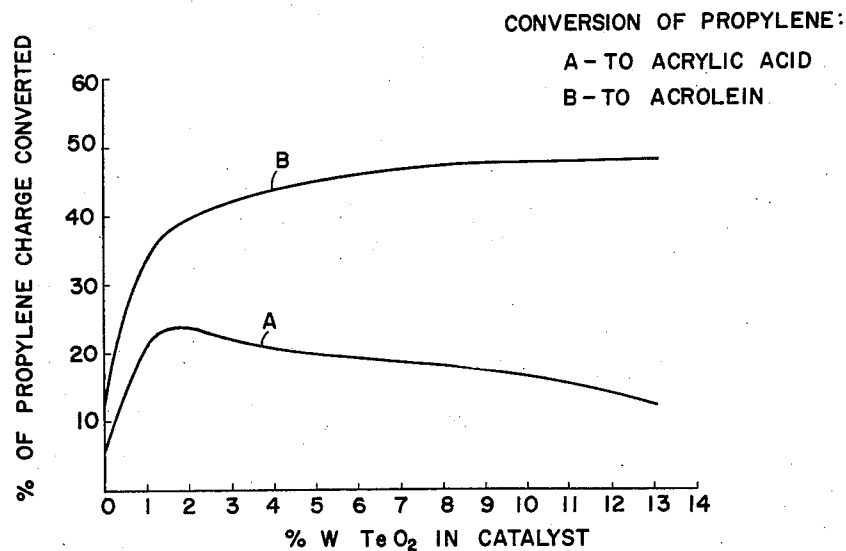


FIG. 1

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PRODUCTION OF ALPHA,BETA-UNSATURATED OXYGEN-CONTAINING COMPOUNDS

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This invention relates to improvements in the production of alpha,beta-unsaturated oxygen-containing compounds comprising aliphatic monocarboxylic acids. The invention relates, more particularly, to an improved process for the direct vapor phase oxidative conversion of propylene and/or isobutylene to acrylic acid and/or methacrylic acid, respectively.

Alpha,beta-unsaturated aliphatic monocarboxylic acids, such as, for example, acrylic acid and methacrylic acid, because of their highly reactive nature, are valuable starting and intermediate materials in a number of important fields of application. However, their very reactive nature also contributes materially to the problems heretofore generally encountered in their large scale production. Processes disclosed heretofore directed to the production of acrylic and/or methacrylic acid are often based upon operational procedures which are not only complex and relatively costly, but which, in addition, do not lend themselves readily to efficient large scale operations. These comprise liquid phase operations which are often difficult to control and generally necessitate the use of relatively costly equipment.

A potential source of these alpha,beta-unsaturated acids is their corresponding olefins. As a consequence of relatively low yields and/or costly operational steps involved in processes available heretofore, large scale production of the acids from such starting materials has not found general acceptance.

Processes have been disclosed heretofore directed to the catalytic vapor phase oxidation of olefins to unsaturated carbonylic compounds. Under the conditions of the processes disclosed heretofore the reaction mixtures however often consist essentially of alpha,beta-unsaturated aldehydes and contain little or no alpha,beta-unsaturated monocarboxylic acids. Efforts directed to the production of the desired unsaturated acids were therefore generally directed heretofore to the utilization of the unsaturated aldehydes as the charge to a separate operative procedure containing no substantial amounts of olefins in the feed. Such procedure, however, necessitates the separation and recovery, generally by relatively costly, complex operative procedure, of the initially produced unsaturated aldehydes in relatively pure state before their subsequent conversion to the unsaturated acids. Even so the yields of acid obtained under the condition disclosed heretofore are generally so low as to render such vapor phase operations commercially unattractive. A further serious handicap in such operations as disclosed heretofore resides in the nature of the catalysts often employed therein. These are often of a complexity rendering difficult and costly their reproducibility and maintenance in a desired state of activity. Because of the extreme reactivity of these unsaturated aldehydes and acids substantial conversion to undesired by-products under conditions generally prevailing in vapor phase operations disclosed heretofore is generally encountered. At elevated temperatures acrylic acid, for example, readily decomposes. In the presence of most oxidation catalysts this tendency is generally increased so that in their presence, at conditions prescribed heretofore, the rate for reactions

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involving decomposition of acrylic acid approaches, and often exceeds, that of its formation.

It is, therefore, an object of the present invention to provide an improved process enabling the more efficient vapor phase, oxidative conversion of normally gaseous olefinic hydrocarbons to alpha,beta-unsaturated oxygen-containing products comprising alpha,beta-unsaturated monocarboxylic acids.

Another object of the present invention is the provision of an improved process enabling the more efficient single stage, vapor phase, oxidative conversion of normally gaseous olefinic hydrocarbons having from three to four carbon atoms to the molecule to alpha,beta-unsaturated oxidation products comprising substantial amounts of alpha,beta-unsaturated aliphatic monocarboxylic acids corresponding to said normally gaseous hydrocarbons.

Still another object of the present invention is the provision of an improved process enabling the more efficient production of acrylic and methacrylic acids by vapor phase, catalytic oxidation of propylene and isobutylene, respectively.

A particular object of the present invention is the provision of an improved process enabling the more efficient single stage, direct, vapor phase, catalytic, oxidative conversion of normally gaseous hydrocarbons comprising propylene to acrylic acid. Other objects and advantages of the present invention will become apparent from the following detailed description thereof, made with reference to the attached drawing wherein FIGURES I and II are graphs showing variation in yield of acrylic acid and acrolein obtained in the catalytic oxidation of propylene by varying the concentration of tellurium component in a tellurium-modified phosphomolybdic acid catalyst.

In accordance with the present invention normally gaseous olefinic hydrocarbons such as, for example, propylene and isobutylene, are oxidatively converted to alpha,beta-unsaturated oxidation products comprising alpha,beta-unsaturated monocarboxylic acids such as, for example, acrylic and methacrylic acid, respectively, by contacting said hydrocarbons, in vapor phase, in admixture with molecular oxygen, with a catalyst consisting essentially of phosphomolybdic acid in combination with a critical amount of tellurium, at a temperature of from about 350° to about 575° C.

It has now been found that whereas the use of phosphomolybdic acid per se as catalyst in the vapor phase oxidation of olefins does not result in any substantial conversion to alpha,beta-unsaturated carbonylic products the incorporation of a well defined, but relatively small amount, of tellurium into this catalyst results in substantial increase in conversion and yield to these desired unsaturated compounds. Quite surprisingly it was found that tellurium-modified phosphomolybdic acid containing a critical, but relatively small, amount of the tellurium component enables the obtaining of unusually high conversions to acrylic acid, whereas the presence of this modifying component in higher amounts results in products containing no appreciable amounts of the unsaturated acid.

The hydrocarbon charge to the process of the invention comprises broadly olefinically unsaturated hydrocarbons. The invention is applied with particular advantage to normally gaseous hydrocarbons comprising propylene and/or isobutylene. Propylene is converted to reaction products comprising substantial amounts of acrylic acid, and isobutylene to methacrylic acid, under the conditions of the presently claimed invention as defined herein. The olefins charged to the process need not necessarily be in a pure state. They may comprise materials which are in the vapor state and which do not undergo any substantial reaction, and which do not adversely affect the desired

olefin oxidation under the conditions of the presently claimed process. A normally gaseous olefinic charge may include, in addition to propylene and/or isobutylene, normally gaseous paraffinic hydrocarbons, such as, for example, methane, ethane, propane, butanes, or other paraffins, which are in the vapor state under the conditions at which the claimed process is executed. Particularly suitable charge materials comprise the commercially available propylene- and isobutylene-containing hydrocarbon fractions. The inclusion of normally gaseous paraffinic hydrocarbons is, at times, advantageous. Such diluent materials function as entraining agents for the reaction mixture and aid in maintaining uniformity of reaction conditions within the reaction zone.

In accordance with the process of the invention, the olefin-containing charge, in admixture with added oxygen or oxygen-containing gas, is passed through a catalyst-containing reaction zone. Oxygen charged as oxygen reactant may consist of concentrated molecular oxygen, such as obtained, for example, by the fractionation of air, or it may consist of a more dilute molecular oxygen-containing gas. A suitable oxygen-containing gas comprises, for example, molecular oxygen in admixture with an inert diluent gas, such as, for example, nitrogen. Air may be used as the source of the molecular oxygen reactant. The oxygen-containing charge may be admixed with the olefinic charge to the system before its introduction into the reaction zone or it may be introduced in part, or in its entirety, directly into the reaction zone at one or a plurality of points thereof.

Within the reaction zone, the reactants are brought into contact with a catalyst consisting essentially of phosphomolybdic acid in combination with a well defined critical, but small proportion of tellurium or a suitable compound of tellurium. The tellurium component of the catalyst combination is preferably present in combination with oxygen, for example, as an oxide such as tellurium dioxide and/or acid form and/or salt of the acid form. The tellurium-modified phosphomolybdic acid catalysts employed in the process of the invention may be prepared by physical admixture of the phosphomolybdic acid with tellurium or with one or more tellurium compounds. The use of an oxide of tellurium is generally preferred. They may be mixed in the dry state and the resulting physical admixture used as such; or use may be made of suitable carrying media in preparing the combination. Thus, the phosphomolybdic acid or the tellurium component, or both, may be dissolved or suspended in a suitable liquid medium and then combined; the carrying medium being thereafter removed by suitable means comprising one or more such steps as, for example, decantation, evaporation, filtering, centrifuging, and the like. One or both components may be combined with a suitable carrying medium such as, for example, water, or any other suitable inert liquid, to form a paste before being admixed with each other. The resulting mixture is then dried and calcined. Comprised within the scope of the invention is the pretreatment of the phosphomolybdic acid with tellurium, or a compound thereof, under conditions resulting in the decomposition of the tellurium component and/or the oxidation of tellurium, etc., to result in a final mixture comprising phosphomolybdic acid in combination with an oxide of tellurium.

The content of the tellurium component in the tellurium-modified phosphomolybdic acid, it has been found, is highly critical and determines the nature of the reaction mixture obtained. Essential to the attainment of alpha,beta-unsaturated acids in yields commensurate with efficient practical scale operation is the maintenance of the tellurium component below about 10% and preferably in the range of from about 0.1 to about 6%, by weight. Highly efficient direct oxidation of olefins to the corresponding alpha,beta-unsaturated acid, as, for example, propylene to acrylic acid, is obtained by maintaining the tellurium component of the catalyst in the

range of from about 1% to about 4% by weight of the combination catalyst. Increasing the concentration of the tellurium component in the catalyst above 10% results in a relatively rapid decrease in alpha,beta-unsaturated acid content of the reaction products. Thus, as seen from the following Examples III and IV, and curves A and D of the graphs in FIGURES I and II, respectively, of the attached drawing showing a correlation between content of tellurium component in the tellurium-modified phosphomolybdic acid and results obtained therewith in the oxidation of propylene, little acrylic acid is obtained with a content of tellurium component below about 0.1% (curve A—FIGURE I). It is furthermore seen therefrom that the range of from about 1 to about 6% by weight of tellurium component in the catalyst marks a remarkably well-defined critical range in which unusually high yields of the acrylic acid are obtained (curves A and D—FIGURES I and II, respectively). Increasing the tellurium component above 10% by weight of the catalyst results in a decided and continuously progressive decrease in acrylic acid yield (curves A and D, FIGURES I and II, respectively).

It is furthermore apparent from the Examples II and III and the graphs of the attached drawing that products of a once-through operation in the presence of the tellurium-modified catalyst also contain substantial amounts of acrolein (curves B and C) which valuable product is, upon recycling to extinction in a continuous operation, readily converted to additional acrylic acid. It is seen that optimum conversions to acrolein necessitate somewhat larger proportions of tellurium component in the catalyst than is needed for acrylic acid. Thus, optimum yields of acrolein are obtained with a tellurium component concentration in the range of from about 10% to about 25% by weight of the tellurium-modified phosphomolybdic acid catalyst.

A particularly preferred catalyst combination consists essentially of phosphomolybdic acid in admixture with an oxide of tellurium, for example, tellurium dioxide. The catalyst may be employed as such, or in further combination with a suitable solid catalyst support material. A preferred catalyst support material, particularly advantageous when employing phosphomolybdic acid in combination with tellurium dioxide is silica. The silica support may be combined with a preformed phosphomolybdic acid-tellurium oxide combination or it may be combined with the catalyst combination during its preparation. The silica may comprise, for example, from about 5% to 75%, and preferably from about 5% to about 10% by weight of the catalyst. One method of preparing a suitable tellurium-modified phosphomolybdic acid catalyst is illustrated by the following example:

Example I

To 152 grams of phosphomolybdic acid dissolved in 100 cc. of water there is added at 50° C. 1.5 grams of dry tellurium dioxide (TeO_2) in powder form. To the resulting mixture there is added 50 grams of stabilized silica sol (Ludox). A stream of hot air is then passed through the resulting mixture to evaporate water and convert the mixture into the form of a paste. The resulting paste is dried in air, calcined 2 hours at 250° C. and another three hours at 400–450° C. The calcined product is screened to obtain a 10/20 mesh size. The resulting catalyst consists essentially of tellurium dioxide-modified phosphomolybdic acid containing 89% by weight of phosphomolybdic acid, 1% tellurium dioxide and 10% by weight of silica.

Other methods of preparing suitable tellurium-modified phosphomolybdic acid catalysts comprise, for example, the treatment of phosphomolybdic acid at an elevated temperature, up to but not substantially above about 450° C. with tellurium, etc.

The phosphomolybdic acid component of the suitable catalysts may comprise the commercially available phos-

phomolybdc acids. Suitable phosphomolybdc acids include phospho-12-molybdc acid and the phospho-18-molybdc acid. The phosphomolybdc acid component may be prepared by conventional means, for example, by reaction of molybdenum trioxide or the sodium molybdenum trioxide with phosphoric acid.

Although a catalyst consisting essentially of tellurium dioxide-modified phosphomolybdc acid in combination with silica has been chosen in the foregoing illustrative example it is to be understood that the invention is not limited to the use of only those tellurium-modified phosphomolybdc acid catalysts containing tellurium in the tellurium oxide form. The tellurium may be employed, for example, in other forms, for example, tellurium sulfate. The suitable catalysts employed in the process of the invention may comprise the tellurium in more than one form. A part of all of the tellurium component may be present in chemical combination with molybdenum, for example, as tellurides of molybdenum (MoTe_2 ; MoTe_3). It is to be stressed, however, that the requisite proportion of phosphomolybdc acid is present as such, regardless of the form in which the tellurium is present in the combination catalyst.

Although silica is indicated herein as a preferred catalyst support material, it is to be understood that the invention is not limited to supported catalysts comprising this specific support. Thus, a part or all of the catalyst support employed may consist of one or more such materials as, for example, the known aluminous supports, the absorptive aluminas, bauxite, Porocel; combinations of silica and alumina; Alundum; aloxite; and other materials such as Carborundum, silicon, silicon carbide, ceramically bonded aluminous and/or silicious materials, clays, fire brick, charcoals, activated carbons, etc.

Although the essential components of the catalysts used in the process of the present invention consist essentially of phosphomolybdc acid in combination with a tellurium component, other components capable of modifying the catalyst may be present in minor amounts. Such modifiers comprise, for example, one or more metals, such as Fe, Cu, Pb, Ni, W, Pb and Sb or oxides thereof. Such modifiers may be present in amounts not substantially exceeding about 1% by weight of the combination catalyst. The metal bismuth and compounds thereof, are avoided since they are found to have an adverse effect upon acrylic acid production in the presence of the tellurium-modified phosphomolybdc acid catalysts.

The addition of tellurium or a compound of tellurium during the course of the process is contemplated within the scope of the invention. Such addition of tellurium is made in controlled amounts to assure the maintenance of the tellurium within the above-prescribed permissible amount within the system. The addition of the tellurium, or compound thereof, during the course of the oxidation process may be carried out by introducing the tellurium in the form of a vapor, mist, dust, smoke, or the like, into the bed of catalyst in the reaction zone. The introduction of the tellurium into the reaction zone may furthermore be effected by dissolving, or suspending, the tellurium in a suitable solvent or carrying medium before introduction into the system. The process of the invention may be carried out with the catalyst in the form of a solid fixed bed, as a suspension, or as a fluid catalyst bed. When using the catalyst in the form of a suspension, or a fluid bed, make-up tellurium as required may be added to the catalyst recycled within the system.

When, after prolonged use, the catalyst has lost to some extent its desired activity, it may be reactivated by heating in an oxygen-containing stream such as, for example, air, which may be diluted with an inert gas, such as flue gas or the like, at elevated temperatures, for example, from about 500° to about 600° C. The time of such heating may vary within the scope of the invention. In general, a period of from about 0.5 to about 2 hours will be found satisfactory. Longer or shorter heating

times may, however, be used within the scope of the invention. After the heating step the catalyst is treated with tellurium, or a tellurium compound at a lower temperature to assure the presence of the tellurium in the regenerated catalyst in an amount within the above-defined range. Regeneration of the catalyst may be carried out in situ.

Reaction of the olefinic charge with oxygen in accordance with the invention is carried out at a temperature of from about 350 to about 575° C. and preferably in the range of from about 450 to about 520° C. The use of a temperature in the range of from about 475° to about 500° C. is generally still more preferred. Somewhat higher or lower temperatures may, however, be employed within the scope of the invention.

Pressures in the range of from about atmospheric to about 50 p.s.i.g. are generally satisfactory although somewhat higher pressures, for example, up to about 150 p.s.i.g. may at times be advantageously employed. In general, it is found that acrylic acid production rate is not improved by increase in pressure, and the use of the lower pressures is in general preferred. The use of atmospheric, subatmospheric or superatmospheric pressures broadly, is, however, comprised within the scope of the invention.

Contact times preferably employed may vary considerably within the scope of the invention in accordance with temperature and specific catalyst used. In general, a contact time in the range of from about 0.1 to about 10 seconds may be employed. Higher or lower contact times may, however, be used within the scope of the invention. Acrylic acid formation in the presence of the catalysts of the invention is generally favored by relatively short contact times. The use of a contact time in the range of from about 0.1 to about 5, and preferably from about 0.5 to about 2 seconds are usually employed.

The rate at which propylene and oxygen are fed to the reaction zone is preferably controlled to maintain a mol ratio of propylene to oxygen in the feed in the range of from about 1:0.15 to about 1:3, and preferably about 1:1 to 1:2. Higher or lower relative ratios of these feed components may, however, be employed within the scope of the invention. In general, it is preferred to maintain a molecular excess of oxygen over propylene in the feed to the process. A particularly preferred ratio comprises a ratio of propylene to oxygen of about 1:1.5 when employing a catalyst consisting essentially of a phosphomolybdc acid-tellurium dioxide-silica combination.

Water vapor is preferably added to the system. Care is, however, taken to assure that no substantial amount of liquid water comes into contact with the catalyst during the operation. The water vapor may be introduced into the reaction zone in a molar proportion of water to propylene of from about 1:1 to about 12:1, and preferably from about 3:1 to about 8:1. Greater or lesser amounts of water vapor may, however, be introduced into the system in accordance with the invention.

Diluents, such as normally gaseous materials or materials which are in vapor state under conditions of execution of the reaction, and which are relatively inert and do not undergo any substantial reaction during the course of the process, may be introduced into the system. Suitable diluents comprise, for example, paraffinic hydrocarbons, flue gas, nitrogen, etc. Such diluent fluids are optionally introduced into the system to aid in maintaining desired conditions of temperature and contact time. Addition of heat to, or withdrawal of heat from such diluents before their introduction into the system may be resorted to within the scope of the invention.

Under the above-defined conditions olefins will react with molecular oxygen with the formation of reaction products comprising substantial amounts of the corresponding alpha,beta-unsaturated monocarboxylic acid. In addition thereto there are obtained substantial amounts of the corresponding alpha,beta-unsaturated aldehyde.

Thus, when charging propylene the reaction products will consist essentially of acrylic acid and acrolein. When charging isobutylene the reaction products will consist essentially of methacrylic acid in admixture with methacrolein. Comprised within the scope of the invention is the introduction of more than one reactive olefin to the process.

Reaction products leaving the reaction zone are sent to suitable product separating means wherein unsaturated alpha,beta-unsaturated monocarboxylic acid and the corresponding aldehyde are separated by conventional means comprising one or more such steps as, for example, distillation, fractionation, extractive distillation, scrubbing, adsorption, absorption, liquid-liquid extraction, etc.

A particular advantage inherent in the process of the invention resides in the fact that the high production rate of alpha,beta-unsaturated monocarboxylic acid, in the presence of water vapor, now makes possible the separation of the reactor effluent by simple indirect cooling, optionally with the aid of liquid quenching, for example, with water, into a normally liquid fraction comprising the greater part of the unsaturated acid product from a vapor fraction comprising the greater part of the unsaturated aldehydes produced. Thus, in the production of acrylic acid from propylene, the reactor effluence is subjected to controlled partial condensation to result in the separation of a liquid phase, comprising water and acrylic acid, from a vapor phase, comprising acrolein and unconverted propylene. The acrolein content may be separated from such gaseous phase and recovered as a final product of the process. In a preferred method of carrying out the process of the invention, however, such vapor phase is recycled, at least in part to the reaction zone to effect the substantially complete conversion of the recycled acrolein to acrylic acid.

Acrylic acid is separated from the liquid phase, separated from the reactor effluence by controlled cooling by conventional means, and recovered as the essential final product of the process of the invention. In this wise propylene is oxidatively converted in continuous recycle operation to acrylic acid efficiently with yields of 50% and higher. The following examples are illustrative of the presently claimed invention:

Example II

A mixture of propylene, air and steam, containing a mole rate ratio of propylene to oxygen to steam of 1:1.5:6, respectively, was passed through a bed of tellurium-modified phosphomolybdic acid catalyst consisting essentially of 89% phosphomolybdic acid, 1% tellurium dioxide (TeO_2) and 10% silica (all percentages by weight), at a temperature of 486°C . and a pressure of 2.5 pounds gauge. The contact time was 0.5 second. The reactor effluence was recovered and analyzed. There was obtained a propylene conversion of 77.6% for an oxygen conversion of 84%, with a selectivity to acrolein of 43.9% and to acrylic acid of 27.5% based on propylene.

The operation was repeated under substantially identical conditions but with the exception that the reactor effluence was subjected to controlled cooling to effect partial condensation of the effluent stream with the formation of a liquid phase containing aqueous acrylic acid and a vapor phase containing unreacted propylene and acrolein. The vapor phase was recycled to the reaction zone with the exception of a small portion which was bled from the system. In this wise there was obtained a conversion of propylene to acrylic acid of 49%. This represents a selectivity to acrylic acid of 59% based on propylene reacted.

Example III

In a plurality of operations a mixture of propylene, air and steam, containing a mole ratio of propylene to oxygen to steam of 1:1.5:6, respectively, was passed through a bed of tellurium-modified phosphomolybdic acid consist-

ing of phosphomolybdic acid-tellurium dioxide-silica, at a temperature of 514°C ., a pressure of about 2 p.s.i.g. and with a contact time of 0.5 second. The catalysts used were prepared as described in the foregoing Example I and contained 10% by weight of silica. The rest of the catalyst consisted of phosphomolybdic oxide and tellurium dioxide in the relative proportions indicated by the tellurium dioxide content shown in the abscissa of the graph of the attached drawing. The plurality of operations were carried out under substantially identical conditions but with the exception that the tellurium dioxide content of the catalysts was varied. One run was made with a phosphomolybdic acid-silica catalyst containing 11% w. silica but no tellurium component, under otherwise substantially identical conditions as the other runs. The products obtained in each of the operations were determined. The results obtained are indicated in the graph of FIGURE I of the attached drawing wherein are plotted versus tellurium dioxide content of the catalyst (abscissae): (1) propylene converted to acrylic acid—curve A and (2) propylene converted to acrolein—curve B.

Example IV

The operation of Example III was repeated under substantially identical conditions used in Example II but with the exception that the series of operations was continued and carried through higher proportions of tellurium dioxide in the phosphomolybdic acid catalysts as shown in the graph of FIGURE II of the attached drawing. In FIGURE II of the drawing the content of tellurium dioxide in the catalyst (abscissae) is plotted against results obtained in terms of propylene converted to acrolein (curve C) and to acrylic acid (curve D).

Similarly methacrylic acid is produced by passing isobutylene in admixture with air and steam over the above-indicated tellurium-modified phosphomolybdic catalysts at the above-defined conditions.

It is seen that the invention thus enables the efficient single stage oxidation of olefins to alpha,beta-unsaturated monocarboxylic acids with unusually high selectivity to the unsaturated acid by maintaining no more than about 10% of the tellurium component in the phosphomolybdic acid catalyst. The invention furthermore enables the oxidation of olefins directly to alpha,beta-unsaturated carbonylic compounds consisting essentially of admixed alpha,beta-unsaturated aldehydes and acids corresponding to the olefins charged, by maintaining the tellurium modifier in the catalyst below a concentration of about 25% by weight of the catalyst.

A suitable charge to the process of the invention comprises a part of or even all of the effluence from an oxidation zone wherein olefins are oxidized to products comprising alpha,beta-unsaturated carbonylic compounds with the aid of any of the catalysts disclosed heretofore as suitable for this reaction. In this wise, a substantial increment in desired alpha,beta-unsaturated compounds, including substantial amounts of monocarboxylic acid over that obtained in the absence of the present invention, is generally obtained.

In one embodiment of the invention olefins are converted to alpha,beta-unsaturated monocarboxylic acids in a plural stage operation comprising the passage of the olefinic charge successively through two beds of catalyst; the first bed of catalyst comprising a tellurium modified phosphomolybdic acid catalyst containing from about 10 to about 25% by weight of the tellurium component, for example, tellurium dioxide, and the second bed comprising a tellurium-modified phosphomolybdic acid catalyst containing from about 0.1 to about 10% by weight of the tellurium component, for example, tellurium dioxide. The two catalyst beds may be positioned in a single reactor or may each be positioned in a separate reactor and the reactors arranged in series flow. The two catalyst beds may also be positioned contiguously in a single reaction zone to provide a single large bed made up of separate

segments of the two catalysts. Thus, propylene is converted to acrylic acid in a two-stage process by contact with a phosphomolybdc acid catalyst containing from about 10 to about 25% tellurium dioxide at a temperature of from about 350 to about 575° C. in a first reaction zone; and the total effluence from the first reaction zone is passed through a second reaction zone at a temperature of from about 450 to about 520° C. containing a phosphomolybdc acid catalyst having a tellurium oxide content of from about 0.1% to about 10% by weight.

By selectivity to acrylic acid and to acrolein, based on propylene charged, as used herein is meant the number of moles of acrylic acid and acrolein, respectively, produced multiplied by 100 divided by the number of moles of propylene in the charge converted.

We claim as our invention:

1. The process for the conversion of an alpha mono-olefinic hydrocarbon having from three to four carbon atoms to the molecule to a reaction mixture comprising a substantial amount of alpha,beta-unsaturated aliphatic mono-carboxylic acid corresponding to said olefinic hydrocarbons, which comprises reacting said olefinic hydrocarbon in the vapor phase with oxygen at a temperature of from about 350 to about 575° C., in a bed of catalyst consisting essentially of phosphomolybdc acid in combination with an oxide of tellurium, said catalyst containing the tellurium component in the range of from about 0.1 to about 10% by weight of said catalyst.

2. The process in accordance with claim 1 wherein said tellurium component is present in said phosphomolybdc acid catalyst in the range of from about 1 to about 6% by weight.

3. The process for the production of acrylic acid which comprises reacting propylene with oxygen in the vapor phase, at a temperature of from about 450 to about 520° C., in a bed of catalyst consisting essentially of phos-

phomolybdc acid in combination with from about 0.1 to about 10% by weight of tellurium dioxide.

4. The process in accordance with claim 3 wherein said catalyst contains from about 1 to about 6% by weight of tellurium dioxide.

5. The process for the conversion of propylene to a reaction mixture consisting essentially of acrylic acid and acrolein which comprises contacting said acrolein in vapor phase in admixture with oxygen at a temperature of from about 350 to about 575° C., in a bed of catalyst consisting essentially of phosphomolybdc acid in combination with from about 0.1 to about 10% by weight of said catalyst of an oxide of tellurium.

6. The process for the production of acrylic acid which comprises passing propylene in vapor phase in admixture with oxygen consecutively through two beds of catalyst consisting essentially of phosphomolybdc acid in combination with tellurium dioxide arranged in series flow and maintained at a temperature of from about 350 to about 575° C., and maintaining the concentration of tellurium dioxide in said catalyst in the range of from about 10 to about 25% by weight in said first bed, and in the range of from about 0.1 to about 10% by weight in said second bed.

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