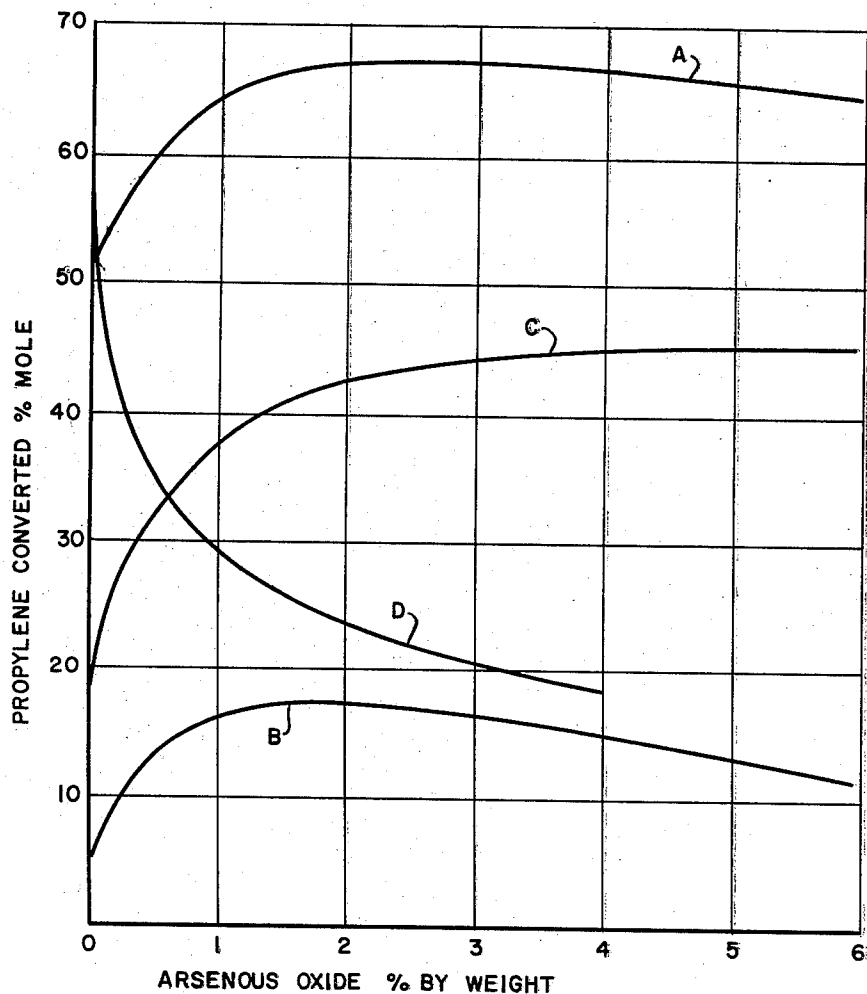


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VAPOR PHASE OXIDATION OF PROPYLENE AND BUTYLENE IN
THE PRESENCE OF AN ARSENIC
PHOSPHOMOLYBDATE CATALYST
Filed April 24, 1961

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A = TOTAL PROPYLENE CONVERSION

B = PROPYLENE CONVERTED TO ACRYLIC ACID

C = PROPYLENE CONVERTED TO ACRYLIC ACID PLUS ACROLEIN

D = PROPYLENE CONVERTED TO CO + CO₂

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VAPOR PHASE OXIDATION OF PROPYLENE AND BUTYLENE IN THE PRESENCE OF AN ARSENIC PHOSPHOMOLYBDATE CATALYST

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5 Claims. (Cl. 260—533)

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 production of unsaturated acids from alpha,beta-unsaturated aldehydes. This procedure, however, necessitates the separation and recovery, generally by relatively costly, complex operative procedures, of the initially produced unsaturated aldehydes before their subsequent conversion to the unsaturated acids. 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 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.

One 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.

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 admixture with molecular oxygen, with a catalyst consisting essentially of phosphomolybdic acid in combination with arsenic.

The hydrocarbon charge to the process of the invention comprises olefinically unsaturated hydrocarbons. The invention is applied with particular advantage to normally gaseous hydrocarbons comprising propylene and/or isobutylene. Propylene is converted to 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 respective reaction zones.

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. Oxygen and/or olefinic charge may be introduced 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 arsenic or a suitable compound of arsenic. The arsenic component of the catalyst combination is preferably present in combination with oxygen, for example, as an oxide and/or form and/or salt of the acid form. The arsenic-modified phosphomolybdic acid catalysts employed in the process of the invention may be prepared by physical admixture of the phosphomolybdic acid with one or more arsenic compounds. The 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 arsenic 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 arsenic or a compound thereof under conditions resulting in the decomposition of the arsenic component and/or the oxidation of arsenic etc., to result in a final mixture comprising phosphomolybdic acid in combination with an oxide of arsenic.

The arsenic content is maintained within the range of from about 0.1 to about 10%, and preferably from about 0.1 to about 5% by weight (calculated as elementary arsenic) of the catalyst. Particularly preferred are catalysts containing arsenic in the amount of from about 0.5 to about 2% by weight of the catalyst, which range, it has been found, is definitely critical with respect to the obtaining of optimum and unexpected results. Thus, by reference to Example III hereinafter and to the attached drawing showing a correlation between arsenic content of the catalyst and results obtained therewith, it is seen that little if any acrylic acid is produced with an arsenic content in the catalyst below about 0.1% (curve B) and that the greater part of the reaction products obtained consists of oxides of carbon (curve D). It has now been found that the by-product reactions leading to the formation of oxides of carbon are suppressed to a surprising degree by incorporating arsenic in the catalyst in an amount above about 0.1% w., and that suppression of the oxides of carbon forming-reaction becomes progressively more marked with increase in arsenic content until in the very critical range of from about 0.5% to about 5% w. of arsenic in the catalyst there is obtained a maximum production of desired acrylic acid (curve B) with substantially reduced oxides of carbon production (curve D). In general, it is found that the arsenic content of about 5% need not be exceeded. Above this amount there is a definite trend toward a decrease in acrylic acid production with a simultaneous increase in acrolein formation, which, however, does not become very marked until the arsenic content is permitted to exceed about 10% w. of the catalyst. It is furthermore apparent from the attached drawing that the remainder of the products in a once through operation will consist predominantly of acrolein (curve C) which valuable product is, upon recycling to extinction in a continuous operation, readily converted to addition acrylic acid.

A particularly preferred catalyst combination consists essentially of phosphomolybdic acid in admixture with arsenous oxide. The catalyst may be employed as such,

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

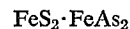
Example I

To 134.5 grams of phosphomolybdic acid dissolved in 100 cc. of water there is added at 50° C. 320 grams of dry arsenous oxide (As_2O_3) in powder form. To the resulting mixture there is added 42 g. of stabilized silica sol (Ludox). A stream of hot air is then passed through the resulting mixture to evaporated 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 500° C. The calcined product was screened to obtain a 10/20 mesh size. The resulting catalyst consisted essentially of arsenous oxide-modified phosphomolybdic acid containing 1.5% by weight of arsenic acid, 8.4% by weight of silica.

Other methods of preparing suitable arsenic-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 arsenic; the addition of aqueous ammoniacal As_2O_3 to hot aqueous phosphomolybdic acid followed by drying and calcining of the resulting mixture, etc.

The phosphomolybdic acid component of the suitable catalysts may comprise the commercially available phosphomolybdic acids. Suitable phosphomolybdic acids include phospho-12-molybdic acid and the phospho-18-molybdic acid. The phosphomolybdic 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 arsenous oxide-modified phosphomolybdic acid in combination with silica has been chosen in the foregoing illustrative example it is to be understood that the invention is in no wise limited to the use of only those arsenic-modified phosphomolybdic acid catalysts containing arsenic in the arsenous oxide form. The arsenic may be employed, for example in the form of an oxide of trivalent or pentavalent arsenic. Other specific examples of suitable arsenic components comprise arsenous acid, metallic arsenides such as, for example, Cu_3As , $FeAs_2$, $CoAs_2$, etc., compounds of arsenic with halogen such as $AsCl_3$, $AsCl_5$, $AsBr_3$, AsI_2 , AsI_3 , AsI_5 , compounds of arsenic with sulfur such as, for example, As_2S_3 , As_2S_5 ,



(arsenopyrite), etc.

Since the arsenic component may possess appreciable volatility under the conditions employed, depending upon the specific form in which arsenic is used, it is at times prepared to employ arsenic in combination with an agent reducing its volatility without adversely affecting to any substantial degree its effectiveness. Such agent may be present in physical or chemical combination with the arsenic. Thus, a part or all of the arsenic component may be present as a metal salt of a metal, for example, lead arsenate, tin arsenate, and other combinations of arsenic with metals having little if any volatility under the conditions used.

The suitable catalysts employed in the process of the invention may comprise the arsenic in more than one form. Thus, the arsenic may be present in the form of

one or more oxides or one or more other compounds of arsenic. A part or all of the arsenic compound may be present in chemical combination with molybdenum, for example, as arsenomolybdic acid. It is to be stressed, however, that the requisite proportion of phosphomolybdic acid is present as such, regardless of the form in which the arsenic 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 catalyst comprising this specific supported material. Thus, a part or all of the catalyst support employed may consist of one or more of such materials, for example, as the known aluminous supports, at the adsorptive 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 comprise phosphomolybdic acid and arsenic, 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, Cu, 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 the acrylic acid production in the presence of the arsenic-modified phosphomolybdic acid catalysts.

The addition of arsenic, or a compound of arsenic, during the course of the process is contemplated within the scope of the invention. Such addition of arsenic is made in controlled amounts to assure the maintenance of the arsenic within the above-prescribed permissible amount within the system. The addition of the arsenic, or compound thereof, during the course of the oxidation process may be carried out by introducing the arsenic 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 arsenic into the reaction zone may furthermore be effected by dissolving, or suspending, the arsenic 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 as a fluid bed, make-up arsenic as required may be added to the catalyst recycled within the system.

When, after prolonged use, the catalysts used in the process of the invention have lost to some extent their desired activity, they 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 arsenic, or an arsenic compound to assure the presence of the arsenic 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 450° to about 600° C. and preferably in the range of from about 475° to about 550° C. The use of a temperature in the range of from about 495° to about 525° 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 phosphomolybdic acid-arsenous oxide-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, absorption, adsorption, 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 34% and higher. The following examples are illustrative of the presently claimed invention:

Example II

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 arsenic-modified phosphomolybdic acid catalyst consisting essentially of 90.4% phosphomolybdic acid, 1.1% arsenous oxide (As_2O_3) and 8.5% silica (all percentages by weight), at a temperature of 506° C. and a pressure of slightly above atmospheric. The contact time was 0.5 second. The reactor effluence was recovered and analyzed. Results obtained were as follows:

	Mol percent
Total propylene conversion -----	65.7
Propylene converted to:	
Acrolein -----	24.1
Acrylic acid -----	15.7
Acetic acid -----	2.9
Acetaldehyde -----	0.6
Maleic acid -----	1.0
Acetone -----	0.7
Oxides of carbon -----	20.4

This represents a selectivity to acrolein of 36.7% and to acrylic acid of 23.9% 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 37.8%. This represents a selectivity to acrylic acid of 42% 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 arsenic-modified phosphomolybdic acid consisting of phosphomolybdic acid-arsenous oxide-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 8-9% by weight of silica. The rest of the catalyst consisted of phosphomolybdic oxide and arsenous oxide in the relative proportions indicated by the arsenic 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 arsenic content of the catalyst was varied. One run was made with a phosphomolybdic acid-silica catalyst containing 11% w. silica but no arsenic component, under otherwise 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 the attached drawing wherein are plotted versus arsenous oxide content of the catalyst (abscissae): (1) total propylene conversion—Curve "A," (2) propylene converted to acrylic acid—Curve "B," (3) propylene converted to acrolein and acrylic acid—Curve "C," and (4) propylene converted to carbon monoxide and carbon dioxide—Curve "D."

Example IV

An arsenic-modified phosphomolybdic acid catalyst containing arsenic as lead arsenate was prepared by mixing 152 grams of phosphomolybdic acid with 3 grams of lead arsenate and adding the resulting admixture to 50 grams of colloidal silica sol (circa 30% w. SiO_2). The resulting mixture was dried and calcined for 4 hours at 500° C. The calcined mixture was broken and screened to 10/20 mesh size. The catalyst thus obtained consisted essentially of 88% w. of phosphomolybdic acid, 9% w. silica and contained 0.31% w. arsenic in the form of lead arsenate.

A mixture containing propylene, air and water vapor, containing a mol ratio of $C_3H_6:O_2:H_2O$ of 1:1.5:6, respectively, was passed over the catalyst thus prepared at a temperature of 501° C., at a pressure of 3-4 p.s.i.g., and a contact time of 0.5 second. A propylene conversion of 64.6 was obtained with a selectivity to acrylic acid of 21.2% and to acrolein of 33.4%.

Similarly propylene was oxidized to oxidation products comprising substantial amounts of acrylic acid with the use of a catalyst consisting essentially of phosphomolybdic acid, silica and tin arsenate.

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

We claim as our invention:

1. The process for the conversion of an olefin selected from the group consisting of propylene and isobutylene to a reaction mixture containing the alpha,beta-unsaturated aliphatic aldehyde and alpha,beta-unsaturated carboxylic acid corresponding to said olefin, which consists essentially of reacting said olefin with uncombined molecular oxygen, in vapor phase, at a temperature of from about 450 to about 600° C. in the presence of a catalyst consisting essentially of arsenic-containing phosphomolybdic acid having an arsenic content of from about 0.1 to about 10% by weight calculated as elementary arsenic.

2. The process in accordance with claim 1 wherein said arsenic-containing phosphomolybdic acid consists essentially of phosphomolybdic acid in combination with an oxide of arsenic, said combination containing from about 0.5% to about 5% by weight of arsenic calculated as elementary arsenic.

3. The process in accordance with claim 2 wherein said catalyst has an arsenic content of from about 0.5 to about 2% by weight calculated as elementary arsenic.

4. The process in accordance with claim 1 wherein said arsenic is present in said catalyst as arsenous oxide, and said catalyst is used in combination with an amount of silica in the range of from about 5 to about 75% by weight of said catalyst.

5. The process for the production of acrylic acid which consists essentially of reacting propylene with uncombined

molecular oxygen in the presence of added steam and a catalyst consisting essentially of phosphomolybdic acid in combination with from about 0.1 to about 10% by weight of arsenic, calculated as elementary arsenic, at a temperature of from about 450 to 600° C., thereby reacting propylene with uncombined molecular oxygen with the formation of reaction products comprising acrolein and acrylic acid, subjecting said reaction products to partial condensation, thereby separating a vapor phase comprising acrolein from a liquid phase comprising aqueous acrylic acid, and recycling at least a part of said vapor phase to said reaction.

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