

1

3,792,086

PROCESS FOR THE PREPARATION OF ACRYLIC AND METHACRYLIC ACIDS

Charles E. Frank and Jawad H. Murib, Cincinnati, Ohio, assignors to National Distillers and Chemicals Corporation, New York, N.Y.

No Drawing. Continuation-in-part of abandoned application Ser. No. 99,283, Dec. 17, 1970. This application Nov. 10, 1971, Ser. No. 197,495

Int. Cl. C07c 51/32, 57/04

U.S. Cl. 260—533 N

8 Claims

ABSTRACT OF THE DISCLOSURE

Process for the preparation of acrylic or methacrylic acids, involving the vapor phase oxidation of propylene or isobutylene, respectively, at temperatures of up to 300° C. and in the presence of a catalyst composition containing phosphoric acid and a catalytically effective amount of palladium metal. The acrylic or methacrylic acids are selectively produced in the single step vapor phase process.

RELATED APPLICATION

This application is a continuation-in-part of U.S. application Ser. No. 99,283, filed Dec. 17, 1970, and now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a process for the preparation of acrylic or methacrylic acids by the catalytic oxidation of propylene or isobutylene, respectively, in the vapor phase.

A number of processes have recently been proposed for the vapor phase oxidation of propylene or isobutylene to form, inter alia, acrylic acid or methacrylic acid. Such processes are described, for example in U.S. Pats. Nos. 3,065,264; 3,293,290; 3,392,196; 3,401,198; 3,428,674; and 3,475,488.

One such process which has been developed and utilized for the preparation of acrylic acid, for example, involves a multi-step procedure for the vapor phase oxidation of propylene into acrolein and acrylic acid. The prescribed multi-step operations present obvious processing problems. Moreover, the acrylic acid formed in the successive reaction zones is subject to autoxidation, resulting in relatively low product yields.

It is among the objects of the present invention to provide a new and improved process for the selective preparation of acrylic and methacrylic acids in substantial conversions. Other objects and advantages of the invention will be apparent from consideration of the following detailed description of preferred forms thereof.

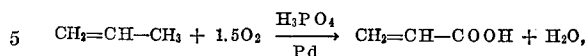
SUMMARY OF THE INVENTION

In accordance with the present invention, propylene or isobutylene is oxidized in the vapor phase with molecular oxygen at temperatures of up to 300° C. and in the presence of a catalyst composition containing phosphoric acid and a catalytically effective amount of palladium metal, to selectively form the desired acid. The process is carried out at elevated temperatures, employing a heterogeneous catalyst contact system, e.g., a system utilizing a fixed, moving or fluidized catalyst bed. The reactions thus

2

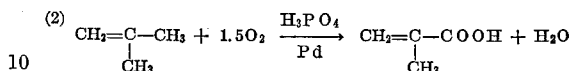
carried out, employing the process of this invention, may be illustrated by the following equations:

(1)



or

(2)



It has been found that use of the indicated procedure facilitates the selective formation of the respective acids in markedly improved conversions. Moreover, the direct vapor phase process may be utilized commercially. Carrying out the reaction in gas phase is a relatively simple and efficient operation since no moving parts are required in the processing equipment. Product separation is also simplified since the reaction product can be separated from the reaction mixture by azeotropic or extractive distillation or by solvent extraction. Further, gas phase reactions generally permit continuous operation and do not necessitate the use of expensive, volatile solvents.

The following description of preferred forms of the invention relates principally to the oxidation of propylene to acrylic acid. It will, however, be understood that the process described herein is similarly applicable to the vapor phase oxidation of isobutylene to methacrylic acid, as set forth hereinabove, and that such latter embodiment is, therefore, also embraced within the scope of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The propylene or isobutylene reacted in the present process may be fed in pure form or, alternatively, may be impure in the sense that it may contain minor amounts, e.g., up to about 50 mole percent thereof, of a saturated hydrocarbon vapor such as methane, ethane or propane gas. The oxygen feed may similarly be pure oxygen gas or, alternatively, an oxygen-containing gas mixture such as air or air enriched with oxygen. In addition to these materials the gaseous feed mixture reacted in the process may contain other inert diluents such as carbon dioxide, nitrogen, acetic acid or acrylic acid, as well as other reactive diluents such as acrolein. The gaseous mixture of such reactants is contacted with a catalyst composition comprising phosphoric acid and a catalytically effective amount of palladium metal, suitably supported on a conventional catalyst carrier such as, for example, silica, alumina, titania, carborundum, carbon, an ion exchange resin, or the like. Silica is preferably utilized as the catalyst carrier in the process hereof, it having been found that catalysts deposited on such a support exhibit superior stability characteristics.

The support is impregnated or loaded with the phosphoric acid, and the palladium metal, whether alone or admixed, alloyed, or in solid solution with a minor amount of a further metal e.g., another Group VIII metal, or a Group I-B metal such as silver or gold, is deposited thereon. As indicated below, the catalytically effective palladium metal and the phosphoric acid may be deposited on or impregnated in the catalyst carrier in any desired sequence, the combined supported catalyst composition, however formed, being active in the present

vapor phase process. The phosphoric acid may also be added continuously to the reaction mixture in the form of an aqueous solution to maintain a trickle liquid phase over the catalyst bed. In this case, the phosphoric acid in the effluent mixture may be recovered and recycled.

The palladium metal is incorporated in amounts of from about 0.01 to 5%, preferably from about 0.1 to 2%, by weight of the total catalyst composition. On the other hand, the phosphoric acid is incorporated in amounts of at least about 1% and up to as much as about 50%, preferably from about 5 to 30%, by weight of the total catalyst composition.

It has been found, in accordance with the present invention, that other catalyst compositions, e.g., palladium metal-containing catalyst compositions, which do not incorporate phosphoric acid, or catalyst compositions containing noble metals, other than palladium, either with or without phosphoric acid, e.g., platinum, are not useful in the process. Thus, platinum metal cannot be employed as a catalyst in the vapor phase oxidation of propylene since the use of such material as a catalyst results in extensive combustion of the olefin to carbon dioxide and water. Similarly, when it is attempted to utilize palladium chloride as the catalyst, halogenation of the olefin occurs as well as some dimerization and trimerization thereof. On the other hand, palladium metal-phosphoric acid catalyst compositions provide the highest conversions to, and selectivities of, acrylic or methacrylic acid production.

Palladium metal-phosphoric acid-Group VIII or Group I-B catalyst compositions are similarly active and may exhibit improved stability characteristics as well.

Deposition of the catalytically effective amount of palladium metal utilized in this process may be effected by conventional techniques, such as by contacting the catalyst support with a solution of a suitable palladium salt or complex, e.g., palladium chloride, palladium acetate, palladium nitrate or palladium acetylacetonate, and thereafter reducing the palladium compound to the metal with hydrogen or other appropriate reducing agent. Alternatively, the salt may, if desired, be reacted with alkali to form the corresponding palladium oxide and the latter thereafter reduced to the catalytically active metal.

When the palladium metal is deposited prior to impregnation of the support with phosphoric acid the palladium salt may be applied from either aqueous or organic media, e.g., water or organic solvent such as lower alkanols, e.g., methanol or ethanol, benzene, chloroform, or the like. When, on the other hand, the catalytically active palladium metal is deposited on the catalyst support after impregnation of the phosphoric acid, the palladium salt is usually applied from an organic solvent. Organic media are preferred for deposition of palladium metal in this alternative embodiment inasmuch as the presence of water may tend to remove a portion of the phosphoric acid from the carrier.

The catalyst carrier may be loaded with the phosphoric acid by impregnating the support with syrupy phosphoric acid, e.g., 85% H_3PO_4 , and subsequently drying the carrier as, for example, in a vacuum oven. The impregnated support may thereafter be calcined to improve bonding of the phosphoric acid to the carrier.

Commercially available catalyst materials may be utilized in the preparation of the catalyst compositions hereof. Thus, for example, either a commercial supported palladium metal catalyst may be treated with phosphoric acid, or a commercial supported phosphoric acid catalyst may have palladium metal deposited thereon, to form catalyst compositions useful herein.

It has been found desirable in accordance with the present invention to additionally incorporate a protonated material, such as water vapor, in the reaction mixture. Whether such material acts as a catalyst promoter or otherwise participates in a complex reaction with the olefin is not presently understood. While such material is, for purposes of convenience, referred to hereinafter as a

catalyst promoter, it will be understood that its use in the vapor phase process is contemplated, irrespective of the actual mechanism by which it may act.

The water vapor may, for example, be added to the gaseous feed mixture by bubbling the gaseous olefin and/or oxygen streams through liquid water. Alternatively, water may be separately vaporized, as by flashing, and metered into the reaction zone. If desired, in lieu of the preferred vapor phase operations of this invention, the water may also be added continuously to the reaction mixture with phosphoric acid to maintain a trickle liquid phase over the catalyst bed.

While stoichiometric proportions of the olefin and oxygen reactants, viz., 1.5 moles of oxygen per mole of propylene or isobutylene, may be utilized in the vapor phase process hereof, such compositions are within the flammability range. On the other hand, it may be preferred to operate outside flammable ratios and to use reaction mixtures in which either the oxygen or the olefin is the limiting reactant. Generally, mixtures are employed in which oxygen is incorporated in amounts of from about 5 to 45 mole percent, in admixture with from about 50 to 95 mole percent of the olefin, and, preferably, up to about 60, and desirably 5 to 40 mole percent of water vapor promoter. Obviously, when inert diluents are present in the reaction mixture, e.g., when the oxygen is added in the form of air, the proportions of the several reactants are correspondingly modified. Thus, propylene may be present in amounts of as low as 5 mole percent when the oxygen is introduced as air. In the case of trickle phase operation, the molar of water to propylene may range between 0.1-10 to 1.0.

The vapor phase reaction is carried out at temperatures markedly lower than those which have, heretofore, been generally regarded as necessary for vapor phase olefin oxidation reactions. It has previously been proposed to conduct such reactions at temperatures of the order of about 350° to 400° C., at which levels substantial combustion of the olefin reactant occurs.

Surprisingly, however, it has been found that selective formation of desired acids may be obtained in accordance with the present invention at substantially lower temperatures. Thus, the acrylic or methacrylic acids may be obtained at temperatures of as low as 50° to 200° C. or higher.

The reaction temperature employed in the process varies inversely with the contact time employed, it being possible to use higher reaction temperatures when employing shorter contact times and, conversely, lower reaction temperatures at longer contact times. It has thus been found possible to carry out the process of the invention at temperatures of as high as 300° C., using relatively short contact times.

The oxidation process is conducted either at atmospheric or elevated pressures, the use of higher pressures somewhat increasing product conversions. The reaction may thus be effected at pressures of up to about 300 p.s.i. It is, however, generally preferred to carry out the vapor phase process under pressures only slightly in excess of atmospheric, e.g., up to about 75 p.s.i., to increase productivity and catalyst efficiency.

After the gaseous reaction mixture contacts the catalyst composition, the exhaust gases are cooled and scrubbed to facilitate recovery of the acrylic or methacrylic acid. The desired material may then be separated by any convenient means such as distillation. Unreacted feed material separated from the recovered effluent mixture may thereafter be recovered and recycled for further reaction.

The following examples are directed to preferred embodiments of the vapor phase process hereof. In the examples, which are intended as illustrative and which should not be construed in a limiting sense, all parts and percentages are given by weight and temperatures in degrees Centigrade unless otherwise specified. As employed

herein, the conversions to acrylic or methacrylic acid, and the selectivities of formation of such products, are defined as follows:

Percent conversion

$$\frac{\text{Number of Moles of Product Actually Formed}}{\text{Number of Moles of Product Theoretically Possible Based on Limiting Reactant}} \times 100$$

$$\text{Percent selectivity} = \frac{\text{Number of Moles of Product}}{\text{Number Moles of Olefin Feed Actually Reacted}} \times 100$$

The proportions of palladium metal and phosphoric acid in the catalyst compositions described above, or identified in the ensuing examples, are given as percentages of the total weight of the catalyst compositions, including both the support and the phosphoric acid and palladium metal components thereof, unless otherwise specified.

EXAMPLE 1

Preparation of acrylic acid, employing a 2% palladium-9.1% phosphoric acid catalyst composition

A Pyrex glass reactor 12 x 2.5 cm. (outside diameter), provided with a thermowell (0.8 cm. O.D.), extending the entire length of the reactor is attached to a pre-heating zone (1.2 x 15 cm.) and a capillary exit tube (0.1 x 10 cm.) to permit rapid quenching. The catalyst composition is prepared by treating 25 grams of 2% palladium supported on alumina with 2.5 grams of phosphoric acid dissolved in 10 ml. of water, followed by heating in an open, rotating evaporating dish with a heat gun, delivering hot air at 125° C. to remove unbound water. The catalyst is cooled to room temperature, packed in the reactor and heated at 130° C.

A stream of 35 millimoles/hr. (mmoles/hr.) propylene and 23 mmoles/hr. oxygen is passed through the heated catalyst bed. The exhaust reaction gases are passed through a trap maintained at -40° C. Analysis by gas chromatography after 2 hours operation indicates the formation of 3.2 mmoles/hr. acrylic acid, with the co-production of 0.6 mmoles/hr. acrolein, 0.5 mmoles/hr. isopropanol, 0.2 mmoles/hr. allyl acetate and 1.13 mmoles/hr. of propylene are converted to carbon dioxide. The conversion to acrylic acid is 20.8% and the selectivity of acrylic acid formation is 55%.

CONTROL A

Reaction of propylene and oxygen, employing palladium only as the catalyst composition

For purposes of comparison, the procedure described in the preceding example is repeated employing, however, as the catalyst composition a like quantity of 2% palladium metal on alumina catalyst composition which has not been impregnated with phosphoric acid. After 23 hours operation analysis of the effluent mixture indicates the formation of 0.1 mmole/hr. acrylic acid (a conversion of only 0.63%), and the co-production of trace amounts of acetic and propionic acids, acetone, acrolein allyl acetate and allyl acrylate. The selectivity to acrylic acid is only 5.1%.

EXAMPLE 2

Preparation of acrylic acid, employing a 2% palladium-11% phosphoric acid catalyst composition

The procedure described in Example 1 is repeated employing 28.1 grams of a 2% palladium-11% phosphoric acid on alumina catalyst composition and feeding an identical gaseous feed mixture thereover. Analysis of the effluent mixture indicates the formation of 5.46 mmoles/hr. acrylic acid, and the co-production of 0.55 mmole/hr. acrolein, 0.6 mmole/hr. isopropanol, 0.15 mmole/hr. allyl acetate, 1.2 mmole/hr. acetone and a trace amount

of acetic acid. The conversion to acrylic acid is 35.6% and the selectivity of acrylic acid formation is 63%.

CONTROL B

5 Reaction of propylene and oxygen, employing palladium only as the catalyst composition

For purposes of comparison, the procedure described in Example 2 is repeated employing, however, as the catalyst composition 25 grams of a 2% palladium metal on alumina which has not been impregnated with phosphoric acid. After 24 hours operation, analysis of the effluent mixture indicates the formation of 0.11 mmole/hr. acrylic acid (a conversion of only 0.6%) and the co-production of 5.98 mmoles/hr. carbon dioxide as well as trace amounts of acetone.

EXAMPLE 3

Preparation of acrylic acid, employing a 1.3% palladium 0.55% gold-9.0% phosphoric acid catalyst composition

The procedure described in Example 1 is repeated, employing 27.5 grams of a 1.3% palladium, 0.55% gold and 9.1% phosphoric acid on alumina catalyst composition and feeding a gaseous feed mixture containing 35 mmoles/hr. propylene and 23 mmoles/hr. oxygen thereover. Analysis of the effluent mixture indicates the formation of 5.81 mmoles/hr. acrylic acid and the co-production of 0.2 mmole/hr. acrolein, 0.6 mmole/hr. isopropanol, 0.1 mmole/hr. allyl acetate, 0.8 mmole/hr. acetone, and a trace amount of acetic acid. The conversion to acrylic acid is 38.0% and the selectivity of acrylic acid formation is 67.0%.

EXAMPLE 4

35 Preparation of acrylic acid, employing a 1.3% palladium 0.55% gold-11.09% phosphoric acid catalyst composition

The procedure described in Example 3 is repeated, employing 25 grams of a 1.3% palladium, 0.55% gold and 11% phosphoric acid on alumina catalyst composition and feeding a gaseous feed mixture containing 35 mmoles/hr. propylene and 23 mmoles/hr. oxygen thereover. Analysis of the effluent mixture indicates the formation of 6.31 mmoles/hr. acrylic acid and the co-production of 0.4 mmole/hr. acrolein, 0.6 mmole/hr. isopropanol, 0.1 mmole/hr. allyl acetate, 1.2 mmoles/hr. acetone, and 1.17 mmoles/hr. of propylene are converted to carbon dioxide. The conversion to acrylic acid is 41.2% and the selectivity of acrylic acid formation is 64%.

EXAMPLE 5

Preparation of acrylic acid, employing a 1.3% palladium-0.55% gold-11.0% phosphoric acid catalyst composition and water vapor as a promoter

The procedure described in Example 4 is repeated, employing a like quantity of a 1.3% palladium, 0.55% gold, and 11.0% phosphoric acid on alumina catalyst composition. A gaseous feed of 35 mmoles/hr. propylene and 23 mmoles/hr. oxygen is bubbled through water heated at 70° C. at 1 atmosphere. The mixed vapors are then fed into the heated catalyst composition at 130° C. Analysis of the effluent mixture indicates the formation of 4.21 mmoles/hr. acrylic acid and the co-production of 0.6 mmole/hr. acrolein, 1.0 mmole/hr. isopropanol, a trace amount of acetic acid and no acetone or allyl acetate. The conversion to acrylic acid is 27.5% and the selectivity of acrylic acid formation is 63%.

EXAMPLE 6

70 Preparation of acrylic acid, employing a 2% palladium-9.10% phosphoric acid composition and water vapor as a promoter

The procedure described in Example 5 is repeated employing 27.5 grams of a 2% palladium-9.1% phos-

phoric acid on alumina catalyst and feeding an identical gaseous feed mixture. Analysis of the effluent mixture indicates the formation of 3.67 mmoles/hr. acrylic acid and the co-production of 0.5 mmole/hr. acrolein, 0.4 mmole/hr. isopropanol and traces of allyl acetate and acetic acid. The conversion to acrylic acid is 24.0% and the selectivity of acrylic acid formation is 65%.

CONTROL C

Reaction of propylene and oxygen, employing palladium only as the catalyst composition

For purposes of comparison, the procedure described in Example 6 is repeated employing, however, a like quantity of a 2% palladium metal on alumina catalyst composition which has not been impregnated with phosphoric acid. After six hours operation analysis of the effluent mixture indicates the formation of 1.0 mmole/hr. acrylic acid (a conversion of only 6.5%) and the co-production of 0.2 mmole/hr. acrolein.

EXAMPLE 7

Preparation of acrylic acid, employing a palladium-silver-phosphoric acid catalyst composition

The procedure of Example 1 is repeated employing 26.1 grams of 2.0% palladium, 0.2% silver and 11.2% phosphoric acid as the catalyst.

Analysis of the reaction mixture, after two hours of operating time, discloses the presence therein of 2.4% acrylic acid, 0.4% acrolein, 1.0% acetone, 0.6% isopropyl alcohol and 0.15% allyl acetate. The conversion to acrylic acid is 15.6% based on the oxygen feed per pass, with 51% selectivity based on the propylene converted to volatile products (including carbon dioxide).

EXAMPLE 8

Preparation of methacrylic acid, employing a 1.8% palladium-11.0% phosphoric acid catalyst composition

The procedure of Example 1 is repeated employing 28 grams of a catalyst composition containing 1.8% palladium and 11.0% phosphoric acid supported on alumina and using isobutylene instead of propylene. The gaseous feed stream consists of 34.5 mmoles/hr. of isobutylene and 23 mmoles/hr. of oxygen. The reaction mixture is passed through a trap held at -20°C .

After two hours of operation time, the condensate is analyzed by vapor phase chromatography and mass spectra. The analysis shows formation of methacrylic acid at the rate of 0.5 mmole/hr. corresponding to a conversion of 3.3% based on the oxygen feed per pass.

EXAMPLE 9

Preparation of acrylic acid, employing a 2% palladium-25% phosphoric acid on silica catalyst composition

Example 1 is repeated except the catalyst comprises a 2% palladium-25% phosphoric acid catalyst on a silica gel carrier. The catalyst is packed in the reactor (described in Example 1) and heated at 170°C . A stream of propylene and air containing 67.4 mmoles/hr. oxygen and 95.0 mmoles/hr. propylene is bubbled through water heated at 80°C . The mixed vapors are passed through the heated catalyst.

Analysis of the condensate shows formation of acrylic acid at the rate of 16.2 mmoles/hr. The conversion to acrylic acid is 36.1% based on the oxygen feed with a selectivity of 81.2% based on the propylene converted to volatile products.

EXAMPLE 10

Preparation of acrylic acid, employing a 2% palladium-30% phosphoric acid on alumina catalyst composition

Example 9 is repeated except the catalyst is 2% palladium on an alumina carrier with 30% phosphoric acid heated at 150°C ., and the feed of propylene and air con-

tains 48 mmoles/hr. oxygen and 67 mmoles/hr. propylene. Analysis of the condensate shows formation of acrylic acid at the rate of 15 mmoles/hr. The conversion to acrylic acid is 50.4% based on the oxygen feed with a selectivity of 83.6%, based on the propylene converted to volatile products.

The conversion and selectivity data obtained in the preceding experiments is tabulated below:

TABLE I

[Calculated conversions and selectivities in Examples 1-10 and Controls A-C]

	Catalyst composition ¹	Percent conversion per pass ²	Percent selectivity
15	Example 1.... 2% Pd, 9.1% H ₃ PO ₄	20.8	55
	Control A.... 2% Pd.....	0.63	5.1
	Example 2.... 2% Pd, 11.0% H ₃ PO ₄	35.6	63
	Control B.... 2% Pd.....	0.6	-----
	Example 3.... 1.3% Pd, 0.55% Au, 9.1% H ₃ PO ₄	28.0	67
	Example 4.... 1.3% Pd, 0.55% Au, 11.0% H ₃ PO ₄	41.2	64
	Example 5.... 1.3% Pd, 0.55% Au, 11.0% H ₃ PO ₄	27.5	63
20	Example 6.... 2% Pd, 9.1% H ₃ PO ₄	24.0	65
	Control C.... 2% Pd.....	6.5	-----
	Example 7.... 2% Pd, 0.2% Ag, 11.0% H ₃ PO ₄	15.6	51
	Example 8.... 1.8% Pd, 11% H ₃ PO ₄	3.3	-----
	Example 9.... 2% Pd, 25% H ₃ PO ₄	36.1	81.2
	Example 10.... 2% Pd, 30% H ₃ PO ₄	50.4	83.6

¹ Water vapor is used as a promoter in the experiments of Examples 5 and 6. Alumina is used as the support for each of the catalyst compositions employed, with the exception of the composition utilized in Example 9, for which silica is used as the catalyst carrier.

² In all examples other than Example 8, the conversions and selectivities are given in terms of the production of acrylic acid, based upon the limiting reactant in the respective experiments. In Example 8, the conversion is given with reference to the production of methacrylic acid therein.

EXAMPLES 11-17

Preparation of acrylic acid, employing miscellaneous palladium on silica catalyst compositions

The catalysts identified in Table II below are prepared by simultaneous deposition of the appropriate metal chloride or mixed metal chlorides from aqueous solution on extruded silica, followed by reduction with gaseous hydrogen at 200°C . The catalysts are thereafter loaded with 25% H₃PO₄ (based on total catalyst weight). The volume of each catalyst is equal to 30 ml. The procedure and reaction system described in Example 1 are employed in these examples, the oxidation reactions being conducted at temperatures of about $180-190^{\circ}\text{C}$. at 3.5 seconds contact time. In each instance propylene and oxygen are reacted in the presence of water vapor and nitrogen diluent (the oxygen was fed in the form of air). A feed ratio, C₃H₆:O₂:H₂O:N₂=1:1.7:8.1:6.8, is used. Product samples are collected after 20 hours operation and analyzed.

The conversion and selectivity data obtained in the experiments of these examples are tabulated below:

TABLE II

[Conversions and selectivities in Examples 11-17]

Example	Catalyst composition		Percent conversion per pass	Percent selectivity to acrylic acid ²
	Pd ¹	Co-metal ¹		
11.....	1	None.....	21	72
12.....	1.1	0.5 Au.....	26.4	81
13.....	1.2	0.56 Rh.....	19.8	69.5
14.....	1.2	0.56 Ir.....	31.3	59.2
15.....	1.2	0.56 Ru.....	33.5	71.5
16.....	1.2	0.56 Pt.....	21.0	51.2
17.....	1.2	0.56 Co.....	21.8	74.5

¹ Weight percent of metal based on total catalyst weight.

² The major by-products are acrolein and carbon dioxide with minor amounts of propionic acid, acetic acid and isopropanol.

The present invention thus provides an improved process for the production of acrylic and methacrylic acids by the vapor phase oxidation of propylene and isobutylene, respectively. Since various modifications may be made in the preferred embodiments of the process described hereinabove, the scope of the invention should rather be determined from the claims appended hereto.

We claim:

1. A process for the preparation of acrylic or methacrylic acid, which comprises oxidizing propylene or iso-

9

butylene, respectively, with molecular oxygen in the vapor phase, in the presence of a catalytically effective amount of a catalyst consisting essentially of a palladium metal, and in the presence of a Group VIII or a Group I-B metal, said metals being supported on a carrier impregnated with phosphoric acid, the palladium metal being present in an amount of from 0.01 to 5% by weight of the total catalyst composition, and the phosphoric acid being present in an amount of at least 1% by weight of the total catalyst composition.

2. The process of claim 1, wherein the oxidation is carried out in the presence of gold metal as the Group I-B metal.

3. A process for the preparation of acrylic or methacrylic acid, which comprises oxidizing propylene or isobutylene, respectively, with molecular oxygen in the vapor phase and in the presence of a catalytically effective amount of a catalyst consisting essentially of palladium metal, said palladium metal being supported on a carrier impregnated with phosphoric acid, the palladium metal being present in an amount of from 0.01 to 5% by weight of the total catalyst composition, and the phosphoric acid being present in an amount of at least 1% by weight of the total catalyst composition.

4. The process of claim 3, wherein the reaction is carried out at temperatures of up to 300° C. and under pressures of up to 300 p.s.i.

10

5. The process of claim 3, wherein the respective materials are reacted in proportions of from 5 to 95 mole percent of propylene or isobutylene with from 5 to 45 mole percent oxygen.

6. The process of claim 5, wherein the gaseous reaction mixture further includes water vapor in an amount of up to 45 mole percent thereof.

7. The process of claim 3, in which propylene is oxidized to produce acrylic acid.

8. The process of claim 3, in which isobutylene is oxidized to produce methacrylic acid.

References Cited

UNITED STATES PATENTS

15 3,624,147 11/1971 David et al. ----- 260—533 N

FOREIGN PATENTS

971,666 9/1964 United Kingdom -- 260—533 N

20 LORRAINE A. WEINBERGER, Primary Examiner

R. D. KELLY, Assistant Examiner

U.S. Cl. X.R.

25 252—430, 437; 260—497 A, 597 B, 604 R, 632