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MANUFACTURE OF UNSATURATED ALIPHATIC CARBOXYLIC ACIDS

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ABSTRACT OF THE DISCLOSURE

A process for the manufacture of an unsaturated aliphatic carboxylic acid, comprising reacting in the vapor phase at a temperature ranging from 200° to 500° C. and α-olefin selected from the group consisting of propylene and isobutylene with molecular oxygen in the presence of a catalyst of the following formula:

$$Co_vSn_wMo_xTe_yO_z$$

wherein v is from 1 to 16, w from 1 to 5, x is 12, y from 0.1 to 6, and z from 20 to 82.

This is a continuation-in-part of U.S. application Ser. No. 413,290, filed Nov. 23, 1964, now abandoned.

This invention relates to the manufacture of unsaturated aliphatic carboxylic acids. More particularly, the invention pertains to the oxidation of propylene or isobutylene in the vapor phase with molecular oxygen to produce acrylic acid or methacrylic acid in a single step process.

There have been proposed in the prior art various processes for the conversion of α-olefins to the corresponding unsaturated carboxylic acids, which processes may be broadly classified into two categories, namely, the double step processing comprising oxidizing α-olefins and then oxidizing the resultant unsaturated aldehydes into the desired unsaturated carboxylic acids; and the single step processing comprising manufacturing the desired unsaturated carboxylic acids directly from the starting α-olefins without intermediate steps. From the commercial and industrial points of view, the latter process is manifestly desirable.

The aforesaid single step process, however, is not necessarily satisfactory. The order of conversion of the starting α-olefins into the corresponding unsaturated carboxylic acids is generally poor, and a considerable amount of unsaturated aldehydes is produced in admixture with the desired unsaturated carboxylic acids, so that the unreacted starting α-olefins and the intermediate aldehydes should be recyclied if a good yield of the desired unsaturated carboxylic acids is to be secured. For instance, in Japanese patent publication Nos. 4,209 (1962), 14,562 (1963) and 19,260 (1963), British Patent 878,802 and Belgium Patent 602,472, there are disclosed varied processes for the manufacture of the desired unsaturated aliphatic carboxylic acids in a single step process. These processes, however, not only are poor in conversion of the starting α-olefins but also produce a considerable amount of unsaturated aldehydes as a byproduct, so that the resultant unsaturated aldehydes and unreacted olefins should be recycled for further conversion if the yield of the desired unsaturated carboxylic acids is to be improved. From the economic and industrial points of view, said recycling of the unreacted α-olefins and unsaturated aldehydes is manifestly undesirable.

The major object of this invention is accordingly to provide a process for the manufacture of acrylic acid or methacrylic acid in a single step processing from propylene or isobutylene in a considerably high order of yield, namely, in a high order of conversion and selectivity, substantially necessitating no recycling of the unreacted olefins and the intermediate aldehydes.

Other objects and specific features of this invention will become apparent in view of the following:

The process of this invention for the manufacture of unsaturated aliphatic carboxylic acids comprises contacting in the vapor phase propylene or isobutylene with molecular oxygen in the presence of a catalyst of the formula:

$$Co_vSn_wMo_xTe_yO_z$$

wherein v is from 1 to 16, w from 1 to 5, x is 12, y from 0.1 to 6, and z from 20 to 82.

The present invention is based upon the discovery that the catalyst of the above formula enables the starting propylene or isobutylene to convert selectively in a single step to the corresponding unsaturated aliphatic carboxylic acids, acrylic acid or methacrylic acid, in a high order of selective conversion without recycling the unreacted α-olefins and the unsaturated aldehydes. The amount of the resultant unsaturated aldehydes and other byproducts is negligible, and the per pass yield of the desired unsaturated carboxylic acids is markedly improved.

The catalyst employed in this invention consists of cobalt, tin, molybdenum, tellurium and oxygen in the order as disclosed in the aforesaid formula. Lack of any one element as specified in the formula results in a reduction in conversion and selectivity, so that the objects of this invention cannot be attained. The known catalyst consisting of cobalt, molybdenum, tellurim and oxygen, for instance, invites a deterioration in conversion if selectivity is to be enhanced and vice versa, so that it is impracticable for said catalyst to improve the yield of the resultant unsaturated carboxylic acids in a single step. When the catalyst of this invention is employed, on the other hand, conversion and selectivity are both raised to a high order, producing in a single step the desired unsaturated carboxylic acids in high yields. The term conversion and selectivity as herein employed are defined as follows:

$$\text{Percent conversion}=\frac{\begin{array}{c}\text{Number of moles of}\\\text{starting olefin fed}-\text{Number}\\\text{of moles of unreacted olefin}\end{array}}{\begin{array}{c}\text{Number of moles of}\\\text{starting olefin fed}\end{array}}\times 100$$

$$\text{Percent selectivity}=\frac{\dfrac{\begin{array}{c}\text{Number of moles of each final}\\\text{product}\times\text{Number of carbon}\\\text{atoms of each final product}\end{array}}{\begin{array}{c}\text{Number of carbon atoms of}\\\text{starting olefin fed}\end{array}}}{\begin{array}{c}\text{Number of moles of reacted}\\\text{olefin}\end{array}}\times 100$$

The catalyst employed in this invention essentially consists of Co, Sn, Mo, Te and O in the atomic ratio of 1–16:1–5:12:0.1–6:20–82. Preferable effects are obtained in the atomic ratio of 3–11:1.2–4:12:0.5–3:25–67, the most desirable ratio being 7:1.7:12:2:54 or thereabout.

The catalyst employed in this invention is prepared by any of the conventional processes, such as precipitation and evaporation to dryness or mixing oxides of each component metal. The procedures for preparing the catalyst of this invention will be described in more detail in the appended examples.

The catalyst employed in this invention may be regarded as a mixture of oxides of each component metal or a mixture of a heteropoly acid salt and a metal oxide, such as a mixture of cobalt-tin-molybdate and tellurium oxide.

But the exact chemical structure of the catalyst is yet unknown. Whether the exact structure is known or not, however, it has been made clear for the first time in the art by the present inventors that the aforesaid catalyst has a property to produce the desired unsaturated aliphatic carboxylic acids in a markedly high order of per pass yield.

The aforesaid catalyst of this invention may be employed singly or in conjunction with a suitable support, such as silica, diatomaceous earth, alumina, silicon carbide, titanium oxide or zirconium oxide.

The starting olefins employed in this invention are propylene and isobutylene.

In the mechanism of the reaction involved in this invention, the starting α-olefins are oxidized into the corresponding aldehydes and the resultant aldehydes are subsequently converted to the desired corresponding unsaturated carboxylic acids. The catalyst of this invention can therefore be successfully applied to the oxidation of unsaturated aldehydes to produce the corresponding unsaturated carboxylic acids in high yields. Even if there are present in the feed stock α-olefins and the corresponding α,β-unsaturated aldehydes in mixture, said olefins and aldehydes are respectively converted into the corresponding unsaturated aliphatic carboxylic acids, so that there can also be employed as a feed stock α-olefins containing the corresponding unsaturated aldehydes in various proportions. In this case a gas mixture of propylene and acrolein or a mixture of isobutylene and methacrolein is preferably employed to produce the corresponding acrylic acid or methacrylic acid in a yield as high as is the case with the single application of propylene or isobutylene.

The range of amount of oxygen to be fed to the reactor varies widely, but good results are obtained when oxygen is employed in the order of from 0.1 to 20 moles, preferably from 3 to 12 moles, per mole of the starting α-olefin or the starting mixture of an α-olefin and the corresponding aldehyde. The reaction gas of the starting organic compound and oxygen may be diluted, where desirable, with an inert gas, such as carbon dioxide, nitrogen, saturated hydrocarbon or steam, so that air is advantageously used as an oxygen source from the economic point of view. The most desirable diluent is steam as conversion and selectivity are still more increased when the reaction gas is diluted with steam. The range of amount of steam to be applied is very wide. To secure the desirable effects, however, steam is employed in the order of from 1 to 60 moles, preferably from 5 to 30 moles, per mole of the starting α-olefin or the starting mixture of an α-olefin and the corresponding aldehyde.

The reaction temperature employed in this invention ranges from 200° to 500° C., preferably from 250° to 400° C. There is no appreciable effect of pressure on reaction. Hence the reaction may be carried out under normal, increased or reduced pressure, but normal atmospheric pressure is preferred.

The time of contact of the gas mixture with the catalyst can be varied widely. Satisfactory results, however, are obtained in the range of from 0.1 to 20 seconds, preferably from 1 to 10 seconds. The term contact time as employed herein is defined as follows:

$$\text{Contact time in second} = \frac{\text{Apparent volume of the catalyst in the reactor}}{\text{Standardized volume of gas fed to the reactor per unit time}}$$

The catalyst bed employed in this invention may be fixed or fluidized, of which the fluidized bed is preferable because of its ability to prevent the reaction system from the occurrence of hot spots due to the exothermic reaction.

Besides the desired unsaturated aliphatic carboxylic acids, the gaseous product from the reactor contains a small amount of unreacted starting gases, unsaturated aldehydes, saturated carboxylic acids, carbon monoxide and carbon dioxide. The desired unsaturated aliphatic carboxylic acids are separated from said product in accordance with the known processes, such as condensation or extraction with water or other suitable solvents.

In order to afford a fuller understanding of the principles of this invention, there are provided the following examples which are illustrative only and not limiting the invention:

EXAMPLE 1

In 1,800 cc. of hot water were dissolved with stirring 494 grams of ammonium paramolybdate of a formula $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and heated to boil the solution. To the resultant boiling mixture were added 107 grams of ammonium chloride dissolved in a small amount of warm water. There were then added dropwise 126 grams of stannic chloride of a formula $SnCl_4 \cdot 3H_2O$ dissolved in 100 cc. of water. The mixture was heated with stirring for further 10 minutes, and the precipitate was filtered, washed with water and dried.

Whole amount of the resultant precipitate was heated with stirring in 500 cc. of water, to the resultant boiling mixture were added dropwise 475 grams of cobalt nitrate of a formula $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 400 cc. of water, and further added 59.5 grams of metal tellurium dissolved in 150 cc. of nitric acid in 310 cc. of water. The mixture was heated and evaporated with stirring, and the dried mixture was pelleted and dried in air stream at 400° C. for 4 hours. The resultant catalyst was confirmed to have an atomic ratio of Co:Sn:Mo:Te:0=7:1.7:12:2:54.

80 cc. of the catalyst were filled in a U-shaped stainless steel reactor, 25 mm. in internal diameter, and the reactor was dipped in a nitrate bath heated to 375° C. Into this reactor was introduced a gas mixture of 1.9 percent by volume of propylene, 58.9 percent by volume of air and 39.2 percent by volume of steam, and reacted by contact for 7.8 seconds. The resultant reaction products were scrubbed with water and analyzed. Results obtained were as follows:

Conversion of propylene: 100%,

Selectivity=Acrylic acid: 65.3%, acetic acid: 2.1%, acrolein: 6.9%, carbon dioxide: 12.3%, carbon monoxide: 10.8%, others: 2.6%.

EXAMPLE 2

The pellet catalyst of Example 1 was employed under the reaction conditions identical to those employed in Example 1, except the contact time was reduced to 6 seconds. Results obtained were as follows:

Conversion of propylene: 96.4%,

Selectivity=acrylic acid: 70.3%, acetic acid: 1.4%, acrolein: 9.8%, carbon monoxide: 6.1%, others: 0.8%.

EXAMPLE 3

40 cc. of the pellet catalyst of Example 1 were placed in a U-shaped stainless reactor, 25 mm. in internal diameter, and the reactor was dipped in a nitrate bath heated to 305° C. Into this reactor was introduced a gas mixture of 1.1 percent by volume of isobutylene, 60.9 percent by volume of air, and 38 percent by volume of steam, and reacted by contact for 2.7 seconds. Results obtained were as follows:

Conversion of isobutylene: 67.7%,

Selectivity=methacrylic acid: 42.1%, mechacrolein: 1.2%, acetic acid: 10.3%, carbon dioxide: 29.8%, carbon monoxide: 11.3%, others: 5.3%.

EXAMPLE 4

60 cc. of the pellet catalyst of Example 1 were placed in a U-shaped stainless steel reactor, 25 mm. in internal diameter, and the reactor was dipped in a nitrate bath heated to 360° C. Into this reactor was introduced a gas mixture of 1.2 percent by volume of propylene, 40 percent by volume of air, and 58.8 percent by volume of nitrogen, and reacted by contact for 4.8 seconds. Results obtained were as follows:

Conversion of propylene: 94.8%,

Selectivity=acrylic acid: 50.3%, acetic acid: 3.6%, acrolein: 6.1%, carbon dioxide: 26.7%, carbon monoxide: 12.1%, others: 1.2%.

EXAMPLE 5

60 cc. of the pellet catalyst of Example 1 were filled in a U-shaped stainless steel reactor, 25 mm. in internal diameter, and the reactor was dipped in a nitrate bath heated to 360° C. Into this reactor was introduced a gas mixture of 0.4 percent by volume of propylene, 2 percent by volume of acrolein, 60 percent by volume of air, and 37.6 percent by volume of steam, and reacted by contact for 7.8 seconds. Number of moles of each component present in the resultant product on the basis of 100 moles as total of the propylene and acrolein fed were as follows:

Acrylic acid: 77.2 moles, acetic acid: 1.3 moles, acrolein: 2.5 moles, carbon dioxide: 11.0 moles, carbon monoxide: 6.3 moles, others: 1.7 moles.

EXAMPLE 6

40 cc. of the pellet catalyst of Example 1 were filled in a U-shaped stainless steel reactor, 25 mm. in internal diameter, and the reactor was dipped in nitrate bath heated to 360° C. Into this reactor was introduced a gas mixture of 3 percent by volume of acrolein, 60 percent by volume of air, and 37 percent by volume of steam, and reacted by contact for 4.5 seconds. Results obtained were as follows:

Conversion of acrolein: 90.1%,

Selectivity=Acrylic acid: 90.0%, acetic acid: 1.8%, carbon dioxide: 4.4%, carbon monoxide: 2.8%, others: 1.0%.

EXAMPLE 7

Another series of runs were made employing the catalyst of Example 1 in which the amount of metal tellurium was varied as specified in the subsequent table, thus the catalysts of atomic ratio of

$$\text{Co:Sn:Mo:Te:O}=7:1.7:12:y:z$$

in which y and z are specified in the table, were obtained. Reaction conditions were identical to those employed in Example 2. Results obtained were as follows:

	Catalyst No.						
	1	2	3	4	5	6	7
Metal tellurium added in grams	0	3.0	14.9	29.7	59.5	89.2	178.4
y	0	0.1	0.5	1	2	3	6
z	50	50	51	52	54	56	62
Conversion in percent of propylene	100	100	100	99.2	96.4	92.1	83.0
Selectivity in percent:							
Acrylic acid	2.3	30.1	40.0	48.4	70.3	58.4	39.3
Acetic acid	42.1	19.0	9.9	5.3	1.4	1.0	0.4
Acrolein	1.2	2.1	3.0	4.2	9.8	27.3	42.9
Carbon dioxide	26.8	25.2	24.0	22.7	11.6	7.7	6.8
Carbon monoxide	16.3	16.0	16.1	17.0	6.1	5.1	4.1
Others	11.3	7.6	7.0	2.4	0.8	0.5	6.5

EXAMPLE 8

Further series of runs were conducted employing the catalyst of Example 1 in which the amount of cobalt nitrate was varied as specified in the subsequent table, thus the catalysts of atomic ratios of

$$\text{Co:Sn:Mo:Te:O}=v:1.7:12:2:z$$

in which v and z are specified in the table, were obtained. Reaction conditions were identical to those employed in Example 2. Results obtained were as follows:

	Catalyst No.					
	1	2	3	4	5	6
Cobalt nitrate added in grams	0	68	237	475	712	1,085
v	0	1	3.5	7	10.5	16
z	44	45	49	54	59	67
Conversion in percent of propylene	80.4	85.1	92.7	96.4	98.3	94.4
Selectivity in percent:						
Acrylic acid	31.3	40.4	59.1	70.3	51.8	43.1
Acetic acid	1.0	1.2	1.2	1.4	5.2	7.3
Acrolein	50.4	38.0	20.4	9.8	6.3	5.2
Carbon dioxide	10.3	10.5	10.9	11.6	19.9	25.3
Carbon monoxide	5.2	5.0	5.8	6.1	13.1	15.5
Others	1.8	4.9	2.6	0.8	3.7	3.6

EXAMPLE 9

Still further series of runs were performed employing the catalyst of Example 1 in which the amount of stannic chloride was varied as specified in the subsequent table, thus the catalysts of atomic ratio of

$$\text{Co:Sn:Mo:Te:O}=7:w:12:2:z$$

in which w and z are specified in the table were obtained. Reaction conditions were identical to those employed in Example 2. Results were as follows:

	Catalyst No.				
	1	2	3	4	5
Stannic chloride added in grams	74	89	126	252	370
w	1.0	1.2	1.7	3.4	5
z	52	53	54	57	61
Conversion in percent of propylene	83.4	90.1	96.4	94.4	86.3
Selectivity in percent:					
Acrylic acid	39.1	50.1	70.3	59.5	41.4
Acetic acid	1.6	1.5	1.4	3.3	5.8
Acrolein	35.4	25.6	9.8	6.5	5.9
Carbon dioxide	12.4	12.1	11.6	21.0	26.8
Carbon monoxide	6.8	6.4	6.1	8.9	13.2
Others	4.7	4.3	0.8	0.8	6.9

EXAMPLE 10

A still another series of runs were conducted employing the catalyst of Example 1 in which the amount of cobalt nitrate, stannic chloride and metal tellurium was varied as specified in the subsequent table. Thus the catalysts of atomic ratio of Co:Sn:Mo:Te:O=v:w:12:y:z, in which v, w, y and z are specified in the table were obtained.

Reaction condition were identical to those employed in Example 2. Results obtained were as follows:

	Catalyst No.		
	1	2	
Cobalt nitrate added in grams	204	475	747
Stannic chloride added in grams	89	126	296
Metal tellurium added in grams	14.9	59.5	89.2
v	3	7	11
w	1.2	1.7	4
y	0.5	2	3
z	44	54	67
Conversion in percent of propylene	94.1	96.4	94.1
Selectivity in percent:			
Acrylic acid	48.9	70.3	53.6
Acetic acid	4.5	1.4	4.2
Acrolein	15.6	9.8	13.8
Carbon dioxide	15.2	11.6	15.2
Carbon monoxide	9.8	6.1	10.0
Others	6.0	0.8	3.2

In view of the foregoing, it may be apparent that various changes and modifications can be made in the principles of this invention without departing from the scope and spirit of the same. It is accordingly requested that the invention be understood rather broadly except otherwise described.

We claim:

1. A process for the manufacture of an unsaturated aliphatic carboxylic acid, comprising reacting in the vapor phase at a temperature ranging from 200° to 500° C. an α-olefin selected from the group consisting of propylene and isobutylene with molecular oxygen in the presence of a catalyst of the following formula:

$$Co_vSn_wMo_xTe_yO_z$$

wherein v is from 1 to 16, w from 1 to 5, x is 12, y from 0.1 to 6, and z from 20 to 82.

2. The process of claim **1**, wherein said α-olefin is propylene.

3. The process of claim **1**, wherein said α-olefin is isobutylene.

4. The process of claim **1** in which said α-olefin is used in combination with the corresponding α,β-unsaturated aldehyde.

5. The process of claim **4**, wherein said gas mixture consists of propylene and acrolein.

6. The process of claim **4**, wherein said gas mixture consists of isobutylene and methacrolein.

7. The process of claim **1**, wherein the atomic ratio of Co, Sn, Mo, Te and O of said catalyst is

$$3\text{–}11:1.2\text{–}4:12:0.5\text{–}3:25\text{–}67$$

8. The process of claim **7**, wherein the atomic ratio of Co, Sn, Mo, Te and O of said catalyst is 7:1.7:12:2:54.

9. The process of claim **1**, wherein the reaction gas to be fed contains molecular oxygen in the range of from 0.1 to 20 moles per mole of the starting α-olefin.

10. The process of claim **4**, wherein the reaction gas to be fed contains molecular oxygen in the range of from 0.1 to 20 moles per mole of the starting gas mixture of an α-olefin and the corresponding α,β-unsaturated aldehyde.

11. The process of claim **1**, wherein the reaction gas contains steam as diluent in the range of from 1 to 60 moles per mole of the starting α-olefin.

12. The process of claim **4**, wherein the reaction gas contains steam as diluent in the range of from 1 to 60 moles per mole of the starting gas mixture of an α-olefin and the corresponding α,β-unsaturated aldehyde.

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