United States Patent Office 3,535,371 Patented Oct. 20, 1970

3,535,371

PROCESS FOR THE PREPARATION OF ACRYLIC ESTERS

Calvin N. Wolf, Princeton, and Joseph F. McMahon, Clinton, N.J., assignors to Commercial Solvents Corporation, New York, N.Y., a corporation of Maryland

No Drawing. Filed Dec. 29, 1965, Ser. No. 517,436
The portion of the term of the patent subsequent to Apr. 22, 1986, has been disclaimed
Int. Cl. C07c 69/54
U.S. Cl. 260—486 6 Claims

ABSTRACT OF THE DISCLOSURE

A process for preparing acrylic esters by contacting a gaseous mixture of formaldehyde, an aliphatic carboxylic acid, for example acetic acid, and an aliphatic alcohol, for example methanol, with a niobium oxide catalyst.

This invention generally relates to a process for the production of acrylic esters by the vapor phase reaction of formaldehyde, an aliphatic alcohol and an aliphatic carboxylic acid. In a particular aspect this invention relates to the production of acrylic esters by the vapor-phase reaction of formaldehyde, an aliphatic alcohol and an aliphatic carboxylic acid in the presence of a niobium oxide catalyst. In a further aspect this invention relates to the production of acrylic esters by the vapor-phase reaction of formaldehyde, an aliphatic alcohol and an aliphatic carboxylic acid in the presence of a niobium oxide catalyst supported on alumina.

Acrylic esters, especially methyl acrylate, methyl methacrylate and ethyl acrylate, are used extensively in the manufacture of a wide group of polymeric materials. From the standopint of simplicity of reaction, one of the more satisfactory methods for the preparation of acrylic esters is the catalytic vapor-phase reaction of an alkyl ester and formaldehyde. Materials which have been found to catalyze this reaction include the zeolites, for example magnesium alumino silicate and sodium alumino silicate, zinc chromate, rubidium hydroxide, the alkali metal oxides and the alkaline earth metal oxides. This process has not been entirely satisfactory, however, due to the necessity to first form the alkyl ester in a separate reaction from its corresponding acid and alcohol.

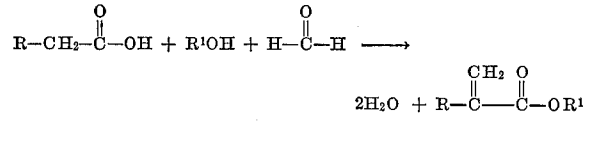
It is an object of this invention to provide a process for the production of acrylic esters.

Another object of this invention is the provision of a process for the production of acrylic esters by the vapor-phase reaction of formaldehyde, an aliphatic alcohol and an aliphatic carboxylic acid in the presence of catalytic amounts of niobium oxide.

A further object of this invention is the provision of a process for the production of acrylic esters by the vapor-phase reaction of formaldehyde, an aliphatic alcohol and an aliphatic carboxylic acid in the presence of catalytic amounts of niobium oxide supported on alumina.

Still further objects and advantages of the present invention will be apparent from the specification and appended claims.

In its broadest embodiment this invention is directed to a process for the production of acrylic esters by the vapor-phase reaction of formaldehyde, an aliphatic alcohol and an aliphatic carboxylic acid at temperatures at which acrylic esters are formed. This reaction may be represented by the following formula:

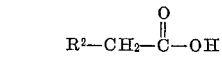


in which R represents hydrogen or an alkyl radical and in which R^1 represents an alkyl radical.

A second embodiment of this invention is directed to a process for the production of acrylic esters by contacting a gaseous mixture of formaldehyde, an aliphatic alcohol and an aliphatic carboxylic acid with catalytic amounts of niobium oxide at temperatures at which acrylic esters are formed.

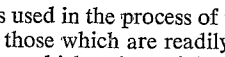
A third and preferred embodiment of this invention is directed to a process for the production of acrylic esters by contacting a gaseous mixture of formaldehyde, an aliphatic alcohol and an aliphatic carboxylic acid with catalytic amounts of niobium oxide supported on alumina at temperatures at which acrylic esters are formed.

The aliphatic carboxylic acids employed in the process of this invention are converted by reaction with formaldehyde and aliphatic alcohol to acrylic ester. Suitable aliphatic carboxylic acids are represented by the formula



wherein R^2 represents hydrogen or a lower alkyl radical. For the purpose of this invention the term "lower alkyl radical" is taken to mean an alkyl radical containing a sufficiently low number of carbon atoms such that the aliphatic carboxylic acid or aliphatic alcohol of which it is a substituent will be readily vaporizable without substantial decomposition. Representative aliphatic carboxylic acids suitable for use in this invention include acetic acid, propionic acid, butyric acid, valeric, caproic acid and the like. It is preferred to use acetic acid or propionic acid in the process because they are readily available and give good results.

The alcohols used in the process of the present invention should also be those which are readily vaporizable at temperatures below which substantial decomposition of the particular alcohol occurs. Typically suitable alcohols are represented by the formula



wherein R^3 represents a lower alkyl radical. Representative alcohols include methanol, ethanol, propanol, butanol, pentanol, hexanol and the like. Because it is low in cost and gives good results in the process, methanol is the preferred alcohol.

The formaldehyde used in this invention can be of any suitable form. The formladehyde can be anhydrous paraformaldehyde or if desired it can be in the form of a solution such as aqueous formaldehyde.

Since the reaction of formaldehyde, aliphatic alcohol and aliphatic carboxylic acid is carried out in the vapor phase, the temperatures employed must be sufficient to maintain the reactants in the vapor phase but should not exceed temperatures at which substantial decomposition of the particular reactants and reaction products occur. In general the temperature that is used will be in the range of about 200° C. to about 500° C. The preferred temperature naturally will principally depend on the reactants utilized. As for example when methanol and acetic acid are utilized as reactants in the process the reaction proceeds best at temperatures in the range of from about 250 to about 400° C.

It is an advantage of the present invention that it may be conveniently practiced at atmospheric pressure. However, if it is desired, sub-atmospheric pressures or superatmospheric pressures may be utilized. Generally suitable pressures are in the range of from about 10 to about 1000 lbs. per square inch.

The mole ratios of formaldehyde to aliphatic carboxylic acid and aliphatic alcohol to aliphatic carboxylic acid may vary over a wide range. The mole ratios may be quantitative, that is to say 1 mole of aliphatic car-

boxylic acid for each mole of formaldehyde and each mole of aliphatic alcohol. Typically suitable mole ratios of formaldehyde to aliphatic carboxylic acid are in the range of from about 0.1 mole of formaldehyde to 1 mole of aliphatic carboxylic acid to 10 moles of formaldehyde to 1 mole of aliphatic carboxylic acid. Similar mole ratios of aliphatic alcohol to aliphatic carboxylic acid are also employed.

The present invention is characterized by the catalytic action of niobium oxide. The niobium oxide catalyst is usually employed with a suitable catalyst support. Such supports include silicon carbide, silica gel and alumina.

When alumina is used as the support it appears to contribute in promoting the reaction. In this respect alumina has been found to be more advantageous than other supports and is therefore preferred as the supporting material for niobium oxide in the present invention.

When the catalyst is comprised of niobium oxide supported on alumina the respective materials may be present in any suitable proportions. It has been found that a particularly valuable catalyst because of the efficiency of the process conducted therewith comprises approximately 10 parts by weight of niobium oxide and approximately 90 parts by weight of alumina.

The niobium oxide catalyst may be prepared by any available procedure known to the art. As one example, the catalyst may be prepared by impregnating the support with an aqueous solution of a water-soluble source of niobium oxide, such as niobium oxalate, filtering the impregnated material to remove water and then calcining the filtered material in an oxygen-containing atmosphere such as air at elevated temperatures on the order of 500–1000° C. When the desired support for the niobium oxide is alumina, the catalyst material may be prepared by co-precipitation of the two materials. In this preparation a precipitating agent, for example ammonium hydroxide, is added to an aqueous solution containing water soluble sources of niobium oxide and alumina. The thus precipitated material is filtered to remove water and then calcined at elevated temperatures to obtain the catalyst. Aluminum nitrate is an example of a suitable water-soluble source of alumina.

The niobium oxide may be used as the sole catalyst in the present invention or if desired small amounts of promoters other than or in addition to alumina may be utilized with the niobium oxide to assist in obtaining the acrylic esters. Representative promoters include the alkali metal oxides, for example lithium oxide and potassium oxide, and the alkaline earth metal oxides, for example calcium oxide and magnesium oxide.

The catalyst including the supporting material if one is used may be of any suitable size or shape. The catalyst may be used in the form of compacted pellets or other shaped pieces of suitable size or it may be used in the form of fragments or other particles of regular or irregular contour. The catalyst may also be used in "fluidized" form such as a fine powder or dust. During the course of most catalytic reactions, the catalyst may lose some of its activity. However, the activity of the catalyst may be readily restored by heating it in an oxygen-containing atmosphere at elevated temperatures on the order of 500 or 1000° C.

The process of the present invention is most conveniently carried out in a continuous manner although batchwise operation may also be used. For continuous operation the feed components are brought into the vapor state in a suitable vaporizer and the reaction is effected by passing the gaseous mixture of the feed components through a reaction zone containing the catalyst. The reaction zone advantageously is defined by an elongated tube or tubes wherein the catalyst is positioned. A separate vaporizing means may be employed or the forepart of the heated reaction zone may serve as the vaporizer for the feed components.

The flow rate of the gaseous mixture of formaldehyde, aliphatic alcohol and aliphatic carboxylic acid through the catalyst bed can be varied over a wide range. Typically the flow rate is within the range of about 0.2 to about 5.0 grams of gaseous feed per hour per cubic centimeter of catalyst material.

The acrylic esters produced by the process of the present invention may be recovered by any suitable procedure. One such procedure involves liquefying the reaction product by cooling and then subjecting the liquefied product to fractional distillation to recover a purer acrylic ester product.

The invention will be understood more fully by reference to the following examples. It is understood that the examples are presented for purposes of illustration only and are not intended as a limitation of the invention.

In the following examples the reactions were carried out by passing gaseous mixtures of aliphatic carboxylic acid, formaldehyde and aliphatic alcohol downward through an electrically heated glass tube the lower portion of which contained a catalyst material. Vapors issuing from the reaction tube were passed through an ice-cooled condensing system and the condensed products were collected for analysis. Before each run the system was flushed with nitrogen and the unit was brought to the desired temperature.

EXAMPLE 1

A gaseous mixture of formaldehyde, methanol and acetic acid in a mole ratio of formaldehyde to acid and a mole ratio of methanol to acid of 2.0 to 1.0 and 1.9 to 1.0 respectively was passed through a reactor tube containing as catalyst niobium oxide impregnated on alumina at a temperature of approximately 300° C. at atmospheric pressure and at a flow rate of 1.2. The catalyst contained 10% by weight of niobium oxide. The condensed effluent from the reactor was found to contain methyl acrylate in a yield of 31% based on acetic acid.

EXAMPLE 2

A gaseous mixture of formaldehyde, methanol and acetic acid in a mole ratio of formaldehyde to acid and a mole ratio of methanol to acid of 2.3 to 1 and 2.2 to 1, respectively, was passed through a reactor tube containing as catalyst niobium oxide on alumina at a temperature of approximaetly 275° C. at atmospheric pressure and at a flow rate of 1.3. The catalyst was prepared by the coprecipitation of niobium oxide and alumina. The catalyst contained 10% by weight of niobium oxide. The condensed effluent was found to contain methyl acrylate in a yield of 21% based on acetic acid.

EXAMPLE 3

A gaseous mixture of formaldehyde, methanol and acetic acid in a mole ratio of formaldehyde to acid and methanol to acid of 2.4 to 1.0 and 2.3 to 1.0, respectively, was passed through a reactor tube containing as catalyst niobium oxide on silicon carbide at a temperature of approximately 275° C. at atmospheric pressure and at a flow rate of 1.4. The catalyst contained 10% by weight of niobium oxide. The condensed effluent was found to contain methyl acrylate in a yield of 12% based on the acetic acid.

EXAMPLE 4

A gaseous mixture of formaldehyde, methanol and acetic acid in a mole ratio of formaldehyde to acid and methanol to acid of 1.9:1 and 1.8:1, respectively, was passed through a reactor tube containing as catalyst niobium oxide on silica gel at a temperature of 275° C. at atmospheric pressure and at a flow rate of 1.2. The catalyst contained 10% by weight of niobium oxide. The condensed effluent was found to contain methyl acrylate in a yield of 3% based on the acetic acid.

EXAMPLE 5

A gaseous mixture of formaldehyde, methanol and propionic acid in a mole ratio of formaldehyde to acid

and methanol to acid of 3.4:1 and 2.0:1, respectively, was passed through a reactor tube containing as catalyst niobium oxide impregnated on alumina at a temperature of approximately 300° C. at atmospheric pressure and a flow rate of 1.5. The catalyst contained 10% by weight of niobium oxide. The condensed effluent was found to contain methyl methacrylate in a yield of 13% based on acetic acid.

EXAMPLES 6–11

Additional examples of the preparation of acrylic esters are given in Table 1. The acrylic esters are prepared following the general procedure utilized in Example 1.

TABLE 1

Example No.	Acid	Alcohol	Product
6	Butyric acid	Methanol	Methyl alpha-ethyl acrylate.
7	Valeric acid	do	Methyl alpha-propyl acrylate.
8	Caproic acid	do	Methyl alpha-butyl acrylate.
9	Acetic acid	Ethanol	Ethyl acrylate.
10	do	Propanol	Propyl acrylate.
11	do	Hexanol	Hexyl acrylate.

Since many embodiments of this invention may be made and since many changes may be made in the embodiments described the foregoing is to be interpreted as illustrative only and the invention is defined by the claims appended hereto.

We claim:

1. A process for the preparation of acrylic esters which comprises contacting a gaseous mixture comprising formaldehyde, an aliphatic carboxylic acid of the formula

$$R^2-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

wherein R^2 is hydrogen or lower alkyl and an aliphatic alcohol of the formula R^3—OH wherein R^3 is lower alkyl, the said mixture having a mole ratio of formaldehyde to acid of in the range of about 0.1:1 to 10:1 and a mole ratio of alcohol to acid of in the range of about 0.1:1 to 10:1 with a niobium oxide catalyst at a temperature in the range of from about 200 to about 500° C.

2. The process of claim **1** wherein the niobium oxide catalyst is supported on alumina.

3. The process of claim **1** wherein the reaction is conducted at pressures in the range of about 10 to about 1000 pounds per square inch.

4. The process of claim **1** wherein the aliphatic alcohol is methanol and the aliphatic carboxylic acid is acetic acid or propionic acid.

5. The process of claim **4** wherein the temperature is in the range of 250 to 400° C.

6. The process of claim **5** wherein the reaction is conducted at a pressure in the range of about 10 to about 1000 pounds per square inch.

References Cited

UNITED STATES PATENTS

2,464,768	3/1949	Redmon et al.	260—486
2,821,543	1/1958	Etherington	260—486
2,947,779	8/1960	Idol et al.	260—486
3,014,958	12/1961	Koch et al.	260—486
3,022,338	2/1962	Enk et al.	260—486
3,100,795	8/1963	Frantz et al.	260—486

LORRAINE A. WEINBERGER, Primary Examiner

P. J. KILLOS, Assistant Examiner