

1

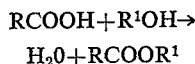
3,384,656

VAPOR PHASE ESTERIFICATION OF ALIPHATIC ALCOHOLS WITH LOWER ALIPHATIC ACIDS IN THE PRESENCE OF NIOBIUM OXIDE

Joseph F. McMahon, Clinton, N.J., assignor to Commercial Solvents Corporation, New York, N.Y., a corporation of Maryland
No Drawing. Filed Dec. 29, 1965, Ser. No. 517,447
5 Claims. (Cl. 260-488)

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

A conventional process for the manufacture of aliphatic esters consists of catalytically reacting an aliphatic alcohol and an aliphatic carboxylic acid in the vapor-phase. The reaction whereby the aliphatic esters are obtained may be written as follows:



wherein R represents hydrogen or an alkyl radical and wherein R¹ represents an alkyl radical.

Considerable work has been done in the field to which this invention relates and as a consequence there are a number of publications outstanding which describe the vapor-phase reaction of an aliphatic alcohol and an aliphatic carboxylic acid in the presence of various catalysts. Among the materials which are known to catalyze this reaction are zirconium dioxide, titanium dioxide, activated carbon and potassium hydrogen sulfate.

It is an object of this invention to provide a process for the production of aliphatic esters by the vapor-phase reaction of an aliphatic alcohol and an aliphatic carboxylic acid.

Another object of this invention is to provide a process for the production of aliphatic esters in high yields by the vapor-phase reaction of an aliphatic alcohol and an aliphatic carboxylic acid in the presence of catalytic amounts of niobium oxide.

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

It has been discovered in accordance with the present invention that high yields of aliphatic esters are obtained by reacting in the vapor-phase an aliphatic alcohol and an aliphatic carboxylic acid in the presence of a niobium oxide catalyst.

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



wherein R 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 acid, 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 inven-

2

tion 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 R¹ 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 results in the process, methanol is the preferred alcohol.

Since the reaction of 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 from about 100 to about 400° 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 200 to about 350° C.

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

The mole ratio of aliphatic carboxylic acid to aliphatic alcohol may vary over a wide range. The mole ratios may be quantitative, that is to say 1 mole of aliphatic carboxylic acid for each mole of aliphatic alcohol. Typically suitable mole ratios of aliphatic carboxylic acid to aliphatic alcohol are in the range of from 0.1 mole of aliphatic carboxylic acid to 1 mole of aliphatic alcohol to 10 moles of aliphatic carboxylic acid to 1 mole of aliphatic alcohol.

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 the catalyst is comprised of niobium oxide and a support, the respective materials may be present in any suitable proportions. It has been found that a suitable catalyst, because of the efficiency of the process conducted therewith, comprises approximately 10 parts by weight of niobium oxide and correspondingly approximately 90 parts by weight of support material.

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 coprecipitation 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 may be utilized with the niobium oxide to assist in obtaining the aliphatic esters. Representative promoters include the alkali metal oxides, for example lithium oxide

3

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 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 the reaction the catalyst may show loss of 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 from about 500 to about 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 aliphatic alcohol and aliphatic carboxylic acid through the catalyst bed may 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 aliphatic 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 aliphatic 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 and aliphatic alcohol downward through an electrically heated glass tube, the lower portion of which contained the catalyst material. Vapors issuing from the reaction

4

through a reactor tube containing niobium oxide impregnated on alumina at a temperature of 250° C. at atmospheric pressure and at a flow rate of 1.3. The catalyst contained 10% by weight of niobium oxide. The condensed effluent from the reactor was found to contain methyl acetate in a yield of 90% based on acetic acid.

EXAMPLE 3

A gaseous mixture of methanol and acetic acid in a mole ratio of methanol to acetic acid of 3.3:1 was passed through a reactor tube containing niobium oxide impregnated on alumina at a temperature of 350° C. at atmospheric pressure and at a flow rate of 1.1. The catalyst contained 10% by weight of niobium oxide. The condensed effluent from the reactor was found to contain methyl acetate in a yield of 96% based on acetic acid.

EXAMPLE 4

A gaseous mixture of methanol and propionic acid in a mole ratio of methanol to propionic acid of 4.6:1 was passed through a reactor tube containing niobium oxide impregnated on alumina at a temperature of 250° C. at atmospheric pressure and at a flow rate of 1.3. The catalyst contained 10% by weight of niobium oxide. The condensed effluent from the reactor was found to contain methyl propionate in a yield of 95% based on propionic acid.

EXAMPLE 5

A gaseous mixture of methanol and propionic acid in a mole ratio of methanol to propionic acid of 5.1:1 was passed through a reactor tube containing niobium oxide impregnated on alumina at a temperature of 200° C. at atmospheric pressure and at a flow rate of 1.4. The catalyst contained 10% by weight of niobium oxide. The condensed effluent from the reactor was found to contain methyl propionate in a yield of 50% based on propionic acid.

EXAMPLES 6-11

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

TABLE

Example No.	Acid	Alcohol	Catalyst	Product
6.....	Acetic	Ethanol	Niobium oxide impregnated on silica gel	Ethyl acetate.
7.....	Butyric	Methanol	Niobium oxide impregnated on silicon carbide	Methyl butyrate.
8.....	Caproic	do	Niobium oxide impregnated on alumina	Methyl caproate.
9.....	Acetic	Propanol	Niobium oxide coprecipitated with alumina	Propyl acetate.
10.....	do	Butanol	Niobium oxide impregnated on alumina	Butyl acetate.
11.....	Propionic	Hexanol	do	Hexyl propionate.

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 methanol and acetic acid in a mole ratio of methanol to acetic acid of 3.3:1 was passed through a reactor tube containing niobium oxide impregnated on alumina at a temperature of 300° C. at atmospheric pressure and at a flow rate of 1.1. The catalyst contained 10% by weight of niobium oxide. The condensed effluent from the reactor was found to contain methyl acetate in a yield of 100% based on acetic acid.

EXAMPLE 2

A gaseous mixture of methanol and acetic acid in a mole ratio of methanol to acetic acid of 3.3:1 was passed

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.

I claim:

1. A process for the preparation of aliphatic esters which comprises contacting a gaseous mixture consisting essentially of an aliphatic carboxylic acid of the formula RCOOH wherein R is hydrogen or a lower alkyl radical and an aliphatic alcohol of the formula R'OH wherein R' is a lower alkyl radical with a niobium oxide catalyst at a temperature of from about 100 to about 400° C.

2. The process of claim 1 wherein the reaction is conducted at a pressure in the range of from about 10 to about 1000 pounds per square inch.

3. The process of claim 1 wherein the aliphatic alcohol

is methanol and the aliphatic carboxylic is acetic acid or propionic acid.

4. The process of claim 3 wherein the temperature is in the range of from about 200 to about 350° C.

5. The process of claim 4 wherein the reaction is conducted at a pressure in the range of from about 10 to about 1000 pounds per square inch.

References Cited**UNITED STATES PATENTS**

3,127,375 3/1964 Keck ----- 260—475

5 LORRAINE A. WEINBERGER, *Primary Examiner*.
V. GARNER, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,384,656

May 21, 1968

Joseph F. McMahon

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 75, "3.3:1" should read -- 2.3:1 --.
Column 4, line 69, "nobium" should read -- niobium --.

Signed and sealed this 25th day of November 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents