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A PROCESS FOR THE PREPARATION OF VINYLESTERS

The present invention relates to a process for the catalytic conversion of carboxylic acids with acetylene to vinylesters.

Such a process is known from DE-A-3,030,044,
5 describing the catalytic reaction of acetylene with
carboxylic acids in the gas phase. The catalyst
preferably contains zinc deposited on a solid inert
carrier. The acids are primary carboxylic acids, such as
acetic acid, propionic acid, butyric acid and formic
10 acid.

It has now been found that secondary and tertiary
carboxylic acids can be catalytically converted with
acetylene to vinylesters. The invention therefore relates
to a process for the catalytic conversion of carboxylic
15 acids with acetylene to vinylesters, characterized in
that at least one secondary carboxylic acid and/or at
least one tertiary carboxylic acid is (are) passed in the
gas phase together with acetylene at an elevated
temperature over a catalyst comprising zinc and a solid
20 inert oxidic carrier.

The vinylesters of the secondary and tertiary
carboxylic acids have a good chemical stability and are
particularly useful in polymeric and copolymeric
compounds, such as emulsion paints and as modifiers in
25 alkyd and epoxy resins.

The present invention provides an efficient means to
convert these branched carboxylic acids to vinylesters.
Such branched vinylesters are expected to be prepared

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more difficultly than the vinyl esters of the low boiling primary acids according to DE-A-3,030,044.

5 While the present process has been found to be adaptable to a variety of starting materials in the secondary and/or tertiary carboxylic acids group, it is important to note that the operation of the process requires the carboxylic acids to be vaporized.

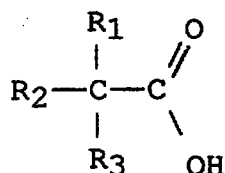
10 At temperatures above 400 °C all carboxylic acids experience decomposition and therefore the acids which can be vaporized at or under 400 °C are the most suitable starting materials for the preparations of the vinyl esters by the present process, and the temperature of the process does preferably not exceed 400 °C.

15 Generally, carboxylic acids having in excess of 20 carbon atoms are prone to thermally decompose prior to vaporization and therefore are not suitable starting materials for the process.

20 A very important group of carboxylic acids, which are suitable starting materials, is the group of carboxylic acids containing a tertiary or quaternary carbon atom in the alpha or beta position with respect to the carboxyl group, i.e. the saturated aliphatic monocarboxylic acids in which the carboxyl group is directly linked to the tertiary or quaternary carbon atom. Since these acids
25 have branched chains their boiling points are generally lower than the isomeric unbranched acids of the series containing 20 or less carbon atoms per molecule. Therefore these alpha-branched acids are the preferred starting materials in the present process.

30 The preferred starting materials are saturated secondary and/or tertiary carboxylic acids having the following formula:

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wherein R₁ is hydrogen or an alkyl group having from 1 to 6 carbon atoms and R₂ and R₃ are alkyl groups, each having from 1 to 6 carbon atoms, the total number of C-atoms of R₁ + R₂ + R₃ being within the range of from 3 to 13. Suitable examples are 2-ethyl-hexanoic acid or VERSATIC 9 or VERSATIC 10 acids (VERSATIC is a trademark). The acids can be prepared by the reaction of a C₃-18 olefinic hydrocarbon fraction with formic acid or alternatively with carbon monoxide and water in an acid catalyzed reaction.

Pivalic acid (trimethylacetic acid) is the acid to be converted in the present process when the total number of C-atoms of R₁ + R₂ + R₃ is 3, the lowest number of the preferred range.

Since this acid generally has a boiling point above 150 °C, dependent on its partial pressure in the gaseous reaction mixture, the minimum temperature of the present process is preferably 150 °C.

While the molar ratio of the acetylene to the vaporized carboxylic acid(s) in the gaseous mixture to be converted to vinylesters can vary within broad limits, the preferred range is from 0.5 to 10, more preferably from 1 to 5.

Ratios outside the preferred limits can be used but with a sacrifice in the yield.

Good conversion of the vaporized carboxylic acids with acetylene to the vinylesters are obtained if the reaction is performed at atmospheric pressure, although

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lower and higher pressures are possible. The reaction is preferably carried out at a pressure in the range of from 0.1 to 5.0 bar.

5 Advantageously the pressure does not exceed 2.4 bar, because the application of pressures substantially above this value necessitates the use of special apparatus with safety measures to eliminate any risk of explosion.

10 The present reaction is suitably carried out in a continuous way. In order to warrant a sufficiently long residence time of the reactants in the reactor the weight hourly space velocity (WHSV) of the acid(s) is preferably in the range of from 0.2 to 10 grams acid(s) per gram catalyst per hour, more preferably 0.5 to 5 g/g/h, if the molar ratio between acetylene and acid(s) is maintained
15 within the range which has been mentioned hereinbefore.

The catalyst comprises zinc and any solid inert oxidic carrier. Suitable carriers are silica, alumina, silica/alumina, titania, zirconia, magnesia, chromia, niobia, manganese oxide, vanadium oxide, the oxides of
20 the lanthanides and the zeolites, and mixtures of these oxides.

Preferred catalyst carriers are formed by alumina embodiments and in particular gamma-alumina because the best results were obtained with these supports.

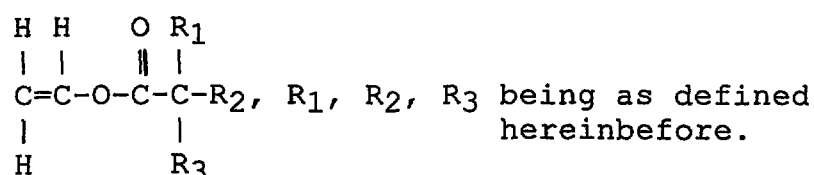
25 The catalyst is advantageously prepared by impregnating the solid inert oxidic carrier with a solution of at least one zinc salt, preferably zinc nitrate and/or zinc acetate, and by drying the impregnated carrier. If a zinc salt of an inorganic acid
30 or of acetic acid is used, an aqueous solution of the zinc salt is applied for the impregnation. If alternatively an organic zinc salt is used, the carrier is suitably soaked with a solution of the zinc salt in an

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alcohol of an ether, followed by the evaporation of the solvent. The concentration of the zinc on the carrier may vary between wide limits, but zinc contents of the catalyst in the range of from 0.1 to 30 %wt are preferred. In most cases zinc contents in the range of from 1 to 20 %wt can advantageously be used.

The catalyst can be in any form, dependent on the way in which the present process is carried out, e.g. in a fixed bed, a fluid bed or a moving bed. For a fixed bed or a moving bed catalyst spheres, pellets or extrudates, having dimensions of 0.3 to 5 mm, are suitable. For a fluid bed, the catalyst is in the form of a powder.

Though we do not want to be bound by theory, it is assumed that the zinc is present on the carrier in the form of a zinc salt of the secondary or tertiary carboxylic acid that is to be converted with the acetylene to a vinylester of the general formula:



The invention will now be illustrated by the following non-limiting examples.

20 Example 1

A catalyst was prepared by impregnating an gamma alumina support with a solution of zinc nitrate. After drying the finished catalyst contained 10 %wt Zn.

A mixture of saturated tertiary carboxylic acids with 10 C-atoms per molecule and acetylene were passed over a fixed bed of this catalyst under the following conditions:

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Temperature : 252 °C
WHSV : 0.714 g acid/g catalyst/h
: 0.497 g acetylene/g catalyst/h
Pressure : 1 bar
5 Molar ratio
acetylene/acids : 4.6
The conversion on
acid basis was : 94.7 mol%
The selectivity to
10 vinylester was : 99.1 %wt

Example 2

The experiment of Example 1 was repeated, using the same conditions with the exception of the temperature which was now: 300 °C.

15 The conversion on acid basis was : 98.0 mol%
The selectivity to vinylester was : 99.2 %wt

Example 3

20 The experiment of Example 1 was repeated, using the same conditions with the exceptions of the temperature which was now 249 °C, and the WHSV which was now 0,815 and 0,565 g/g/h for the acid and the acetylene, respectively. Moreover the zinc content of the catalyst was 20 %wt.

The conversion on acid basis was : 96.6 mol%.
25 The selectivity to vinylester was : 99.0 %wt.

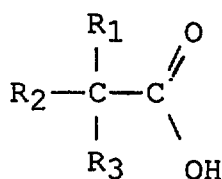
Example 4

The experiment of Example 3 was repeated, using the same conditions with the exception of the temperature which was now: 300 °C.

30 The conversion on acid basis was : 98.4 mol%.
The selectivity to vinylester was : 99.0 %wt.

C L A I M S

1. A process for the catalytic conversion of carboxylic acids with acetylene to vinylesters, characterized in that at least one secondary carboxylic acid and/or at least one tertiary carboxylic acid is (are) passed in the gas phase together with acetylene at an elevated temperature over a catalyst comprising zinc and a solid inert oxidic carrier.
2. A process as claimed in claim 1, characterized in that the secondary and/or tertiary carboxylic acid(s) has (have) the following formula:



- in which R_1 is H or an alkyl group and R_2 and R_3 are alkyl groups, the total number of C-atoms of $\text{R}_1 + \text{R}_2 + \text{R}_3$ being in the range of from 3 to 18.
3. A process as claimed in claim 1 or 2, characterized in that the molar ratio between acetylene and the acid(s) is in the range of from 0.5 to 10, preferably 1 to 5.
4. A process as claimed in any one of the preceding claims, characterized in that the temperature is in the range of from 150 to 400 °c.
5. A process as claimed in any one of the preceding claims, characterized in that the pressure is in the range of from 0.1 to 5 bar, preferably less than 2.4 bar.
6. A process as claimed in any one of the preceding claims, characterized in that the weight hourly space

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velocity of the acid(s) (WHSV) is in the range of from 0.2 to 10 g/g/h, preferably 0.5 to 5 g/g/h.

5 7. A process as claimed in any one of the preceding claims, characterized in that the zinc content of the catalyst is in the range of from 0.1 to 30 %wt, preferably 1 to 20 %wt.

8. A process as claimed in any one of the preceding claims, characterized in that the solid inert oxidic carrier comprises gamma alumina.

10 9. A process as claimed in any one of the preceding claims, characterized in that the catalyst has been prepared by impregnating the solid inert oxidic carrier with a solution of at least one zinc salt, preferably zinc nitrate and/or zinc acetate, and drying the
15 impregnated carrier.

