Title: A PROCESS FOR THE PREPARATION OF ALKOCARBOXYLIC ACID ESTERS

Abstract: The present invention relates to a catalytic processes for producing of alkocarboxylic acid esters by reaction of hydroxycarboxylic acid and/or its esters with alcohol on a solid acid catalysts at temperatures ranging 100 - 400 °C and pressures 1-100 bar. The method is characterized by that a solid acid catalysts are phosphoric acid and/or its salts of metals I and II groups of Periodical Table on a solid porous material. According to the process alkocarboxylic acid esters can be produced in a mild condition and a high yield.
Description

A process for the preparation of alkoxycarboxylic acid esters

Technical Field

[0001] The present invention relates to the process of a preparation of alkoxycarboxylic acid esters as useful solvents and plasticizers for photosensitive resins or various polymers.

Background Art

[0002] GB 591710 (CARBIDE & CARBON CHEM CORP) 26.08.1947 report synthesis of ethers of lactic acid esters by heating a diacetal of pyruvic aldehyde and an alcohol at above 100°C in the presence of an acid catalyst such as hydrochloric, sulphuric, phosphoric and sulphonic acids.

[0003] JP 8134017 (MITSUBISHI GAS CHEMICAL CO) 28.05.1996 patented a process for producing of ethers of lactic acid esters by reacting an α-hydroxycarboxylic acid ester with a dialkyl carbonate on a solid acid catalyst. A silica-alumina-based catalyst is preferred as the solid acid catalyst and zeolite at a ratio of Si/Al within the range of 1-5 is especially preferred.

[0004] US 5453534 (BASF AG) 26.09.1995 claims a process for preparing of alkoxycarboxylic acid esters by the reaction of hydroxycarboxylic acid esters with alcohols in the presence of heterogeneous catalysts - zeolites and/or hydrothermally prepared phosphates at temperatures 100-400°C and pressures 0.01-150 bar.

Disclosure of Invention

[0005] The synthesis of alkoxycarboxylic acid esters in prior arts is usually accomplished by using of expensive substances or substantial excess corresponding alcohol. Since the most part of alcohol remains in the final product, use a large number of energy resources for isolation of target product is necessary. Moreover, a yield of alkoxycarboxylic acid esters is at most 77-81%.

[0006] The main object of the present invention is to provide a process of preparation alkoxycarboxylic acid esters with a maximum yield.
The method is characterized by that a solid acid catalysts are phosphoric acid and/or its salts of metals I and II groups of Periodical Table on a solid porous material.

A catalyst was prepared by the impregnation of the porous inert carrier by a water solution of salts and/or phosphoric acid. As salts dihydrophosphate, hydrophosphate and phosphate Na, K, Li was used. As a porous inert carriers silica and alumina may be used.

The following examples illustrate this invention, but not limit the scope of the present invention.

**EXAMPLE 1**

30 g of the catalyst - 5% by weight NaH₂PO₄/SiO₂ - was charged into a stainless steel tubular reactor, having a volume of 50 cm³. The temperature of the catalytic layer was maintained at 260°C.

20 g/h mixture of methyl lactate with a concentration of 50% in methanol was vaporized through a preheating layer and supplied into the catalytic layer. The products of the reaction were condensed and analyzed. A conversion of methyl lactate was 94%, selectivity to methyl 2-methoxypropionate was 98%, the yield of methyl 2-methoxypropionate was 92%. Even in 60 hours after starting the reaction, the yield of methyl 2-methoxypropionate was 91.7%.

**EXAMPLE 2**

30 g of the catalyst – (3% K₂HPO₄ and 0.5% H₃PO₄)/Al₂O₃ - was charged into a stainless steel tubular reactor, having a volume of 50 cm³. The temperature of the catalytic layer was maintained at 240°C and pressures of reactor - 10 bar.

16 g/h mixture of ethyl lactate (20%), lactic acid (10%) and ethanol (60%) was vaporized through a preheating layer and supplied into the catalytic layer. The products of the reaction were condensed and analyzed. A conversion of ethyl lactate - 96%, lactic acid – 98%, selectivity to ethyl 2-ethoxypropionate was 98%, the yield of ethyl 2-ethoxypropionate was 93%. Even in 60 hours after starting the reaction, the yield of ethyl 2-ethoxypropionate was 92.3%.

**EXAMPLE 3**
[0014] 30 g of the catalyst – (0.1% CaHPO₄ and 5% K₂HPO₄)/ SiO₂ - was charged into a stainless steel tubular reactor, having a volume of 50 cm³. The temperature of the catalytic layer was maintained at 300°C.

[0015] 18 g/h mixture of methyl lactate (5%), lactic acid (25%) and methanol (70%) was vaporized through a preheating layer and supplied into the catalytic layer. The products of the reaction were condensed and analyzed. A conversion of methyl lactate - 99%, lactic acid – 97%, selectivity to methyl 2-methoxypropionate was 96%, the yield of methyl 2-methoxypropionate was 91%. Even in 60 hours after starting the reaction, the yield of methyl 2-methoxypropionate was 90%.

EXAMPLE 4

[0016] 30 g of the catalyst – (3% Li₂HPO₄, 0.5% MgHPO₄, and 0.05% H₃PO₄)/Al₂O₃ - was charged into a stainless steel tubular reactor, having a volume of 50 cm³. The temperature of the catalytic layer was maintained at 320°C.

[0017] 22 g/h mixture of methyl lactate (45%) and methanol (55%) was vaporized through a preheating layer and supplied into the catalytic layer. The products of the reaction were condensed and analyzed. A conversion of methyl lactate - 95%, selectivity to methyl 2-methoxypropionate was 94%, the yield of methyl 2-methoxypropionate was 89%. Even in 60 hours after starting the reaction, the yield of methyl 2-methoxypropionate was 88%.

EXAMPLE 5

[0018] 30 g of the catalyst – (4% Na₂HPO₄, 0.5% MgHPO₄, and 0.5% H₃PO₄)/SiO₂ - was charged into a stainless steel tubular reactor, having a volume of 50 cm³. The temperature of the catalytic layer was maintained at 260°C.

[0019] 20 g/h mixture of butyl lactate (40%) and butanol (60%) was vaporized through a preheating layer and supplied into the catalytic layer. The products of the reaction were condensed and analyzed. A conversion of butyl lactate - 98%, selectivity to butyl 2-butoxypropionate was 91%, the yield of butyl 2-butoxypropionate was 89%. Even in 60 hours after starting the reaction, the yield of butyl 2-butoxypropionate was 87%.
Claims

1. A process for the preparation of an alkoxycarboxylic acid esters by the reaction of hydroxycarboxylic acid and/or esters with an alcohol in the presence of solid acid catalysts wherein said solid acid catalysts are phosphoric acid and/or its salts of metals I and II groups of Periodical Table on a solid porous material.

2. A process as claimed in claim 1, wherein salts is dihydrophosphate, hydrophosphate and phosphate Na, K, Li.

3. A process as claimed in claim 1, wherein solid porous material is silica and/or alumina.

4. A process as claimed in claim 1, wherein the reaction is carried out at a temperature of from 100-400°C and at a pressure of from 0.1 to 10 bar.

5. A process as claimed in claim 1, wherein the reaction is carried out under atmospheric pressure.
# INTERNATIONAL SEARCH REPORT

**INVENTION CLASSIFICATION OF SUBJECT MATTER**

INV. C07C67/08 C07C67/31 C07C69/708

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and where practical, search terms used)

EPO-Internal, BEILSTEIN Data, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>A</td>
<td>US 5 453 534 A (ELLER KARSTEN [DE]) 26 September 1995 (1995-09-26) cited in the application column 1, line 4 - line 8 column 2, line 3 - line 64 examples 1,2</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

Special categories of cited documents:

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- **O** document referring to an oral disclosure, use, exhibition or other means
- **P** document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search 24 October 2007

Date of mailing of the international search report 31/10/2007

Name and mailing address of the ISA/

European Patent Office, P. S. 5618 Patentlaan 2 NL - 2280 HV Rijswijk

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