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(54) PROCEDE D'HYDROGENATION SELECTIVE DE MELANGES D'HYDROFORMYLATION

(54) PROCESS FOR SELECTIVE HYDROGENATION OF HYDRO-FORMYLATION MIXTURES

(57) The invention relates to a process for the selective hydrogenation of reaction mixtures from the hydroformylation of C5 to C24 olefins using hydrogen at solid catalysts at elevated temperature and at elevated pressure, in which process use is made of a supported catalyst which, as active components, comprises copper, nickel and chromium.

O.Z. 5356

Abstract:

The invention relates to a process for the selective hydrogenation of reaction mixtures from the hydroformylation of C_5 to C_{24} olefins using hydrogen at solid catalysts at elevated temperature and at elevated pressure, in which process use is made of a supported catalyst which, as active components, comprises copper, nickel and chromium.

Process for the selective hydrogenation of hydro-formylation mixtures

The invention relates to a process for the selective hydrogenation of hydroformylation mixtures which are produced in the preparation of higher oxo alcohols by hydroformylation of the corresponding olefins. The hydrogenation is selective to the extent that the aldehydes and certain byproducts of the hydroformylation are hydrogenated to give the desired alcohols, whereas the unreacted starting olefins are retained virtually completely.

Higher alcohols, in particular those having from 6 to 25 carbon atoms, are known to be able to be prepared by catalytic hydroformylation (or oxo reaction) of the olefins having one carbon atom less and subsequent catalytic hydrogenation of the aldehyde- and alcohol-containing reaction mixtures. They are predominantly used as starting materials for the preparation of plasticizers or detergents.

It is known that in the catalytic hydroformylation of olefins, reaction mixtures are formed which, apart from the desired products, i.e. aldehydes and the corresponding alcohols, depending on the catalyst and the reaction conditions, can contain, in addition to unreacted olefins, byproducts and secondary products of the hydroformylation, such as saturated hydrocarbons resulting from the olefins by hydrogenation, water, esters of the desired alcohols (e.g. formates), acetals of the target products aldehyde and alcohol, enol ethers and other byproducts or secondary products. The substances can be subdivided into low-boilers having a boiling point below the boiling point of the aldehyde and high-boilers having a boiling point above the boiling point of the alcohol. During the hydrogenation of the reaction mixtures, the desired alcohols are formed from some of the byproducts, such as esters and acetals, which improves the yield. On the other hand, it is desirable that the unreacted olefins remain in the hydrogenation so that they can be recirculated to the hydroformylation reaction, after separating them off from the hydrogenation mixture. Obviously, the olefins could already be separated off prior to the hydrogenation of the hydroformylation mixture by distillation of the aldehydes and the alcohols. However, this would mean an additional process step, since the hydroformylation mixture must be distilled in any case after the hydrogenation of the aldehydes.

The catalytic hydrogenation of reaction mixtures which were prepared by cobalt-catalyzed hydroformylation of olefins having from 2 to 24 carbon atoms is described in DE 35 42 595. The hydrogenation is carried out in two stages. In the first stage, the hydroformylation mixture is hydrogenated at 150-230°C and a hydrogen pressure of 10-350 bar with 80-95% conversion on a supported SiO_2 catalyst which comprises 5-15% by weight of nickel and 2-20% by weight of molybdenum in the form of molybdenum oxide. In the second stage, the hydrogenation is completed at 150-230°C and 10-350 bar hydrogen pressure on a catalyst whose active mass consists of 55-60% by weight of cobalt, 15-20% by weight of copper, 4-10% by weight of manganese and 2-5% by weight of molybdenum in the form of molybdenum oxide and, if appropriate, up to 10% by weight of activating additives. In the process, the formates and acetals present in the mixture are converted to the corresponding alcohols. The process is obviously not aimed at a selective hydrogenation with retention of the olefins, since these are not mentioned at all. Furthermore, a disadvantage in the process is that the hydrogenation is carried out in two stages and at high pressures, according to the example at 250 or 245 bar.

According to US-A 5 399 793, for the hydrogenation of decobalted reaction mixtures, as arise in the hydroformylation of C_5-C_{12} olefins, use is made of Ni/Mo catalysts on Al_2O_3 or $Al_2O_3 \cdot SiO_2$ as support materials. The total process comprises the following individual steps:

(a) cobalt-catalyzed hydroformylation
(b) decobalting of the reaction mixture

(c) hydrogenation of the crude reaction mixture at elevated temperature and at elevated pressure
(d) production of alcohols having very low amounts of aldehydes by distillation and
(e) finish-hydrogenation of the alcohols.

The hydrogenation of stages (c) and/or (e) can be carried out using a bimetallic, phosphorus-free Ni/Mo hydrogenation catalyst. This hydrogenation catalyst produces fewer high-boiling byproducts than a corresponding phosphorus-containing catalyst. Although, in the examples, the presence of low-boilers, that is to say olefins and paraffins, is mentioned, no information is given on the weight ratio of these substances before and after the hydrogenation. It is a disadvantage in any case that to prepare an on-specification alcohol which is suitable for preparing plasticizers, two hydrogenation stages are necessary and that at least in the hydrogenation stage (b) a relatively high pressure of 1000 psig (about 70 bar) is necessary.

In addition, processes have become known in which a compound which contains a carbonyl function and an olefinic double bond is hydrogenated catalytically to the corresponding alcohol selectively retaining the olefinic double bond. Thus, according to Japanese Patent Publication SHYO 57-110354, 7-octenal is selectively hydrogenated to 7-octen-1-ol at from 70 to 150°C, use being made of a chromium oxide catalyst or a catalyst which consists of at least two of the metals chromium, copper and tin. However, this process has the disadvantage that a solvent is used which must be separated off again. In addition, the achievable space-time yields in the temperature range of from 70 to 130°C are too low for an industrial application. At higher temperatures at which the hydrogenation rate is higher, the hydrogenation selectivity decreases rapidly owing to the unwanted hydrogenation to the saturated alcohol. At 140°C, the hydrogenation selectivity to the unsaturated alcohol is already below 95%.

In addition, citronellal may be hydrogenated to citronellol, retaining the olefinic double bond. For this purpose, according to Applied Catalysis, 25 (1986), 181-189, use is made of ruthenium catalysts and a yield of up to 90% is achieved. Using Cu/Cr catalysts, according to Iv. Akad. Nauk. Gruz. SSR. Ser. Khim. 16 (4) (1990), 287-292, a yield of 92% was achieved.

On the other hand, it is known that 2-ethylhex-2-enal, when use is made of a Cu/Cr/Ni catalyst which contains an alkali metal component, can be hydrogenated to 2-ethylhexanol (EP 0 326 674 A2). In this case, not only the carbonyl function but also the olefinic double bond are hydrogenated.

In the present invention, it is attempted to hydrogenate reaction mixtures of the hydroformylation of C_5 to C_{24} olefins under comparatively mild conditions and, in particular low pressures, selectively in such a manner that the aldehydes and certain accompanying substances present in addition to alcohols and aldehydes, in particular formates, are converted as substantially as possible into the desired alcohols and the unreacted olefins remain unhydrogenated as much as possible.

The present invention provides a process for the selective hydrogenation of reaction mixtures which originate from the hydroformylation of C_5 to C_{24} olefins using hydrogen as solid catalysts at elevated temperature and at elevated pressure, in which process, as catalyst, use is made of a supported catalyst which, as active components, comprises copper, nickel and chromium.

Preferably, use is made of the supported catalyst disclosed in EP 0 326 674 A2, which contains, as active components, copper and nickel at concentrations of in each case from 0.3 to 15% by weight, chromium at a concentration of from 0.05 to 3.5% by weight and an alkali metal component at a concentration of from 0.01 to 1.6% by weight, in each case based on the supported catalyst. Another preferred supported catalyst contains copper, nickel and chromium in the amounts specified above, but no alkali metal component.

The process according to the invention offers a number of advantages. The aldehydes in the hydroformylation mixtures are hydrogenated to the corresponding alcohols in only one hydrogenation stage typically at a conversion rate greater than 98% at a selectivity of greater than 99%. The esters and, in particular, the formates and also the acetals are likewise converted into the desired alcohols. The starting olefins present in the mixture surprisingly remain very substantially unchanged, although the same catalysts under comparable conditions virtually quantitatively hydrogenate the olefinic double bond in 2-ethylhex-2-enal. In contrast, in the process according to the invention, typically less than 5% (based on the olefins) of the olefins of the starting material are hydrogenated to hydrocarbons. The hydrogenation can be carried out in the low-pressure region of below 25 bar and at high space-time yields.

The starting materials for the hydroformylation are monoolefins having from 5 to 24 carbon atoms and a terminal or middle-position C-C double bond or their mixtures, such as 1- or 2-pentene, 2-methyl-1-butene, 1-, 2- or 3-hexene, the isomeric C_6 olefin mixture (dipropene) produced in the dimerization of propene, 3-methyl-1-hexene, 1-octene, the isomeric C_8 olefin mixture (dibutene) produced in the dimerization of butenes, 1-nonene, 2-, 3- or 4-methyl-1-octene, the isomeric C_9 olefin mixture (tripropene) produced in the trimerization of propene, 1-, 2- or 3-decene, 2-ethyl-1-octene, 1-dodecene, the isomeric C_{12} olefin mixture (tetrapropene or tributene) produced in the tetramerization of propene or the trimerization of butenes, 1-tetradecene, 1- or 2-hexadecene, C_{16} olefin mixtures (tetrabutene) produced in the tetramerization of butenes, and olefin mixtures prepared by cooligomerization of olefins having different carbon numbers (preferably 2 to 4), if appropriate after separating off by distillation into fractions of identical or similar carbon number. Preferably, mixtures are hydrogenated which are produced in the hydroformylation of C_8, C_9, C_{12} or C_{16} olefin mixtures.

The olefins are hydroformylated in a conventional manner and then give the starting materials for the hydrogenation process according to the invention. Rhodium catalysts, or preferably cobalt catalysts, are therefore employed, with or without complex-stabilizing additives, such as organic phosphines or phosphites. The temperatures and the pressures can vary, depending on catalyst and olefin, in broad ranges. A description of the hydroformylation of olefins is found, for example, in J. Falbe, New Syntheses with Carbon Monoxide, Springer-Verlag, Heidelberg-New York, 1980, pages 99ff., and in Kirk-Othmer, Encyclopedia of Chemical Technology, volume 17, 4th edition, John Wiley & Sons, pages 902-919 (1996).

The hydroformylation reaction mixtures are preferably firstly freed from the catalyst. If a cobalt catalyst is used, this can be achieved by pressure relief, separating off the aqueous catalyst phase, oxidation of the cobalt carbonyl compounds remaining in the hydroformylation mixture with air or oxygen and scrubbing out the resulting cobalt compounds with water or aqueous acid. Decobalting processes are well known, see, for example, J. Falbe, loc. cit., Kirk-Othmer, loc. cit., 164, 175, BASF process; and EP-0 850 905 A1.

If a rhodium compound is used as hydroformylation catalyst, it can be separated off from the hydroformylation mixture as distillation residue by means of thin-film evaporation.

The hydroformylation reaction mixtures preferably freed from the hydroformylation catalyst generally comprise 3-40% by weight, at most 5-30% by weight, of low-boilers, principally olefins, in addition the corresponding saturated hydrocarbons and water, 30-90% by weight of aldehydes, 5-60% by weight of alcohols, up to 10% by weight of formates of these alcohols and from 5 to 15% by weight of high-boilers. It may be emphasized, however, that the process according to the invention can also be carried out using hydroformylation mixtures whose composition does not correspond to these specifications in this or that relationship.

Preferred catalysts at which the hydroformylation mixtures are hydrogenated comprise in each case 0.3-15% by weight of copper and nickel and, as activators, 0.05-3.5% by weight of chromium and, advantageously, 0.01-1.6% by weight, preferably 0.02-1.2% by weight, of an alkali metal component on a support material, preferably aluminum oxide or silicon dioxide. The amounts specified relate to the catalyst prepared as described below, which is still not reduced. The alkali metal component can, as mentioned, alternatively be absent.

These catalyst components can be homogeneously distributed in the pores of a support material or enriched in its edge zones. In the former case, an aqueous solution is made up which comprises the components in the form of metal salts as catalyst precursor and whose volume preferably roughly corresponds to 0.8 times the pore volume of the support material. As copper salts, nickel salts or chromium salts, use is advantageously made of those which are converted on heating into oxides, such as nitrates and acetates. If the catalyst is to contain an alkali metal component, this can be introduced together with chromium in the form of alkali metal chromate or alkali metal dichromate, in particular as sodium chromate or sodium dichromate. The metal salt concentration in the solution depends on the desired concentration of the respective component in the finished catalyst. The metal salt solution is then sprayed on to the non-preheated support material, situated in a coating drum and penetrates into the pores thereof. The catalyst is then dried.

If a catalyst is desired having components which are enriched in the edge zones of a porous or a more or less pore-free support material, the metal salt solution can be sprayed onto a preheated support material and the support material can be further heated during the spraying, so that the water evaporates and the catalyst components are fixed essentially on the surface of the support material.

After the catalyst components are applied, the catalysts are calcined, i.e. depending on the catalyst precursor used, heated to temperatures of 200-400°C, which convert the catalyst precursors into the oxidic state. The catalyst is then reduced with hydrogen at the hydrogenation temperatures.

The reduction can be performed just after the catalyst is prepared or expediently not until the hydrogenation reactor.

The catalysts are preferably used in a form in which they offer a low resistance to flow, e.g. in the form of granules, pellets or shaped bodies such as tablets, cylinders, rod extrudates or rings. They are preferably activated prior to use by heating in a hydrogen stream, for example at from 150 to 250°C, if they have not been reduced in the reactor.

The hydrogenation according to the invention can be carried out continuously or batchwise and either in the gas phase or in the liquid phase. Hydrogenation in the liquid phase is preferred, since the gas-phase process requires a higher energy consumption, because of the necessary circulation of large gas volumes. In addition evaporation of the aldehydes having an increasing carbon number requires more energy, and, in addition, the starting material loading of the reduction gas decreases, so that the gas-phase process virtually may not be operated economically in the case of aldehydes having a carbon number greater than about 8.

Various process variants can be selected for the liquid-phase hydrogenation. It can be carried out adiabatically or virtually isothermally, i.e. having a temperature rise of <10°C in a single stage or two stages. In the latter case, both reactors, preferably tube reactors, can be operated adiabatically or virtually isothermally or one can be operated adiabatically and the other virtually isothermally. In addition, it is possible to hydrogenate the hydroformylation mixtures in a straight pass or with product recycling. The reactors can be operated as cocurrent flow reactors with a trickle bed (trickle flow) or preferably with high liquid loadings (pulse flow). In the interest of a high space-time yield, the reactors are preferably operated with high liquid loadings of 5-100 m^3, in particular 15-50 m^3 per m^2 of cross section of the reactor (calculated as an empty reactor) and hour. If a reactor is operated isothermally and in a straight pass, the catalyst space velocity (LHSV) values can be between 0.1 and 10 h^{-1}, preferably between 0.5 and 5 h^{-1}.

The liquid-phase hydrogenation is generally carried out at an overall pressure of from 5 to 30 bar, in particular between 15 and 25 bar. The gas-phase hydrogenation can also be carried out at lower pressures, e.g., 2 bar, with correspondingly greater gas volumes. The reaction temperatures, in the case of hydrogenations in the liquid or gaseous phase, are generally between 120 and 220°C, in particular between 140 and 180°C.

After the hydrogenation, the reaction mixtures are worked up by distillation. This is preferably achieved at reduced pressure, e.g. at an absolute pressure of 400-900 mbar. The olefins can be recirculated to the hydroformylation.

The examples below are intended to illustrate the invention further, but not restrict its field of application which is given by the patent claims.

Example 1

Hydrogenation of C_{13} aldehydes in the liquid phase

One liter of a reaction discharge, which has been freed from catalyst by thin-film evaporation, from the Rh-catalyzed hydroformylation of a C_{12} olefin mixture (tributene) was hydrogenated in a recirculation apparatus at 175°C and an overall pressure of 20 bar with hydrogen on 100 g of catalyst. The catalyst, together with aluminum oxide as support material, prior to activation with hydrogen (8 h at 200°C) comprised

12.1% by weight of Cu
3.0% by weight of Ni
and 2.5% by weight of Cr

The catalyst was present in the form of rod extrudates having a bulk density of 0.67 kg/l. The analyses of starting material and product can be taken from Table 1 below.

Table 1

(amounts of substance in % by weight; 1/LHSV in $l_{cat} \cdot h / l_{starting\ material}$)

	1/ LHSV	Olefins	Paraffins	Aldehydes	Alcohols	Esters	High-boilers	Water
Starting material	0	14.8	1.3	76.5	6.4	0	1.0	0
Product	1.75	14.3	1.8	0.5	82.1	0	1.3	0

It can be seen that more than 99% of the aldehydes, but only approximately 3% of the olefins, were hydrogenated.

Example 2

Hydrogenation of C_9 aldehydes in the liquid phase

One liter of a decobalted reaction discharge of the cobalt-catalyzed hydroformylation of a C_8 olefin mixture (dibutene) was hydrogenated with hydrogen at 170°C in a recirculation apparatus, the overall pressure being 20 bar. 100 g of the catalyst of Example 1 was used, the liquid loading was 35 m^3 per m^2 of reactor cross section (superficial tube) and hour.

The starting material and product analyses can be seen in Table 2 below.

Table 2

(Amounts of substance in % by weight, calculated as anhydrous, except for water); 1/LHSV in $l_{cat} \cdot h/l_{starting\ material}$)

	1/LHSV	Olefins	Paraffins	Aldehydes	Alcohols	Esters	Methanol	High-boilers	Water
Starting material	0	7.6	4.4	47.2	32.1	4.5	0	4.2	2
Product	0.65	7.3	4.7	0.3	82.5	0.1	0.8	4.3	2

It can be seen that, again, more than 99% of the aldehydes, but only approximately 4% of the olefins, were hydrogenated.

Example 3

Hydrogenation of C_9 aldehydes in the liquid phase

One liter of a reaction discharge of the Rh-catalyzed hydroformylation of a C_8 olefin mixture (dibutene), which was freed from catalyst by thin-film evaporation, was hydrogenated with hydrogen at 170°C in a recirculation apparatus, the overall pressure being 20 bar. 100 g of the catalyst of Example 1 were used, the liquid loading was again 35 m^3 per m^2 of reactor cross section and hour.

The starting material and product analyses can be seen in Table 3 below.

Table 3

(Amounts of substance in % by weight; 1/LHSV in $l_{cat} \cdot h/l_{starting\ material}$)

	1/LHSV	Olefins	Paraffins	Aldehydes	Alcohols	Esters	High-boilers	Water
Starting material	0	5.4	0.6	87.9	4.1	0	2.0	0
Product	0.55	5.2	0.8	0.3	91.6	0	2.1	0

It can be seen that more than 99% of the aldehydes, but only approximately 4% of the olefins, were hydrogenated.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for selective hydrogenation of a hydroformylation reaction mixture of a C_5 to C_{24} olefin, which comprises contacting the hydroformylation reaction mixture with hydrogen in the presence of a solid supported catalyst at an elevated temperature and at an elevated pressure, wherein the solid supported catalyst contains, as active components, copper, nickel and chromium.

2. The process as claimed in claim 1, wherein the supported catalyst contains copper and nickel at a concentration of in each case from 0.3 to 15% by weight and chromium at a concentration of from 0.05 to 3.5% by weight as active components and also contains an alkali metal component at a concentration of from 0.01 to 1.6% by weight, each based on the supported catalyst.

3. The process as claimed in claim 2, wherein the concentration of the alkali metal component is 0.2-1.2% by weight.

4. The process as claimed in claim 1, wherein the supported catalyst contains copper and nickel at a concentration of in each case from 0.3 to 15% by weight and chromium at a concentration of from 0.05 to 3.5% by weight as active components each based on the supported catalyst.

5. The process as claimed in any one of claims 1 to 4, wherein the supported catalyst contains silicon dioxide or aluminum oxide as a support material.

6. The process as claimed in any one of claims 1 to 5, wherein the catalyst components are homogeneously distributed in pores of a support material.

7. The process as claimed in any one of claims 1 to 5, wherein the catalyst components are homogeneously enriched in edge zones of a support material.

8. The process as claimed in any one of claims 1 to 7, wherein the hydroformylation reaction mixture is derived from a C_8, C_9, C_{12} or C_{16} olefin.

9. The process as claimed in any one of claims 1 to 8, wherein the hydrogenation is carried out continuously or batchwise in a liquid phase.

10. The process as claimed in any one of claims 1 to 9, wherein the hydrogenation is carried out in a liquid phase at an overall pressure of from 5 to 30 bar.

11. The process as claimed in claim 10, wherein the overall pressure is from 15 to 25 bar.

12. The process as claimed in any one of claims 1 to 11, wherein the hydrogenation is carried out at a temperature from 120 to 200°C.

13. The process as claimed in claim 12, wherein the temperature is from 140 to 180°C.

14. The process as claimed in any one of claims 1 to 13, wherein the hydrogenation is carried out in a liquid phase and at a liquid loading of 5-100 m^3 per m^2 of cross section of a reactor and hour.

15. The process as claimed in claim 14, wherein the liquid loading is 15-50 m^3 per m^3 of cross section of a reactor and hour.

16. The process as claimed in any one of claims 1 to 15, wherein hydrogenation mixture obtained by the selective hydrogenation is separated by distillation and the olefin is recirculated to the hydroformylation.

17. A process for producing oxo alcohols from a reaction mixture of a hydroformylation of a C_5-C_{24} olefin, the reaction mixture containing unreacted C_5-C_{24} olefin, corresponding C_6-C_{25}-aldehydes, corresponding C_6-C_{25}-oxo alcohols, esters of the alcohols and acetals of the aldehydes and the alcohols, which process comprises:

single-stage selective hydrogenation of the reaction mixture by contacting the reaction mixture with hydrogen in the presence of a solid supported catalyst at a temperature of 120-220°C at an elevated pressure of no more than 30 bar, wherein the solid supported catalyst comprises, as active components, 0.3-15% by weight of copper, 0.3-15% by weight of nickel and 0.05-3.5% by weight of chromium and comprises no or 0.01-1.6% by weight of an alkali metal component, each based on the solid supported catalyst, thereby converting the aldehydes, the esters and the acetals to the desired oxo alcohols while hydrogenating only less than 5% of the unreacted olefin to corresponding saturated hydrocarbon;

distillation of the hydrogenation product to separate the desired oxo alcohols from the unreacted olefin; and

recirculation of the unreacted olefin to the hydroformylation.

18. The process as claimed in claim 17, wherein the single-stage selective hydrogenation is carried out in a liquid phase.

19. The process as claimed in claim 18, wherein the olefin used for the hydroformylation is a C_8, C_9, C_{12} or C_{16} olefin.

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