

Process for preparing higher oxo alcohols from olefin mixtures

The invention relates to a process for preparing higher oxo alcohols by hydroformylation of olefin mixtures, which process includes a selective hydrogenation of the hydroformylation mixtures and recycling of the unreacted olefins.

Prior art

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.

The type of catalyst system and the optimum reaction conditions for the hydroformylation are dependent on the reactivity of the olefin used. The dependence of the reactivity of olefins on their structure is described, for example, by J. Falbe, *New Syntheses with Carbon Monoxide*, Springer-Verlag, Berlin, Heidelberg, New York, 1980, pages 95 ff. The varying reactivity, especially of the isomeric octenes, is likewise known (B.L. Haymore, A. van Hasselt, R. Beck, *Annals of the New York Acad. Sci.*, **415** (1983), pages 159-175).

Industrial olefin mixtures which are used as starting materials for the oxo synthesis comprise olefin isomers of the most varied structures having differing degrees of branching, differing position of the double bond in the molecule and, if appropriate, differing carbon numbers also. This applies especially to olefin mixtures which have been produced by dimerization,

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trimerization or further oligomerization of C_2 - C_5 olefins or other easily accessible higher olefins or by cooligomerization of said olefins. As examples of typical isomeric olefin mixtures which can be reacted by rhodium-catalyzed, or preferably by cobalt-catalyzed, hydroformylation to give the corresponding aldehyde mixtures and alcohol mixtures, tripropenes and tetrapropenes and dibutenes, tributenes and tetrabutenes may be mentioned.

The rate of the hydroformylation reaction decreases with increasing carbon number and with the degree of branching. The reaction rate of linear olefins can be greater by a factor of 5 to 10 than that of the branched isomers. The position of the double bond in the olefin molecule also influences the reactivity. Olefins having a terminal double bond react markedly more rapidly than isomers having the double bond in the interior of the molecule. Because of the differing reactivity of the olefin isomers, relatively long reaction times are required if it is desired to achieve the most substantial possible conversion of the olefins. However, as a result, the product yield is decreased due to unwanted side reactions and secondary reactions. The same occurs if attempts are made to shorten the reaction times by higher reaction temperatures. Especially because of the varying reactivity of the isomers, it is difficult to achieve high conversion rates and simultaneously high selectivities in the hydroformylation of olefin mixtures.

Summary of the invention

An object of the invention is to provide a process for preparing higher oxo alcohols from the corresponding olefin mixtures, which process combines high conversion rates with high selectivities and, in addition, is distinguished by high space-time yields.

The invention therefore relates to a process for preparing higher oxo alcohols from mixtures of isomeric olefins having from 5 to 24 carbon atoms

by hydroformylation in the presence of a catalyst at elevated temperature and at elevated pressure, in which the hydroformylation is carried out in one stage, the olefin conversion rate for one pass is restricted to from 40 to 90%, the reaction mixture, expediently after catalyst removal, is selectively hydrogenated, the hydrogenation mixture is separated by distillation and the olefin fraction is recirculated to the hydroformylation.

Description of the invention

The process according to the invention can be carried out batchwise, but a continuous procedure is advantageous. The figure shows the block diagram of a plant in which the process can be carried out continuously. The olefin mixture 2, synthesis gas (carbon monoxide and hydrogen) 3 and catalyst 4 are introduced into the reactor 1. The hydroformylation mixture 5 is expanded, the expansion gas 6 (unconsumed synthesis gas) is taken off and the expanded hydroformylation mixture is freed, in the catalyst removal stage 7, from the catalyst 4 which, if appropriate after supplementation by fresh catalyst, is recirculated to the reactor 1. The hydroformylation mixture 8 freed from the catalyst is passed into the hydrogenation 9 in which the aldehydes and also acetals of the aldehydes and esters of the alcohols, in particular their formates, present as byproducts, are hydrogenated to the alcohols. In the distillation stage 11, the low-boilers 12 are separated off from the hydrogenation mixture 10, which low-boilers very predominantly consist of unreacted isomeric olefins and are conducted, together with fresh olefins 13, into the reactor 1 as olefin mixture 2. Some of the low-boilers can be taken off from the olefin circuit as residual low-boilers 14. The crude alcohol mixture 15 is worked up to pure alcohol in a further distillation stage which is not shown.

Hydroformylation

The starting materials for the hydroformylation are mixtures of monoolefins having from 5 to 24 carbon atoms and a terminal or middle-position C-C

double bond, 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, 1-heptene, 2- or 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. Preferred starting materials are C_8 , C_9 , C_{12} or C_{16} olefin mixtures.

The invention does not lie in the type or the conditions of the hydroformylation. The olefins are rather hydroformylated in a manner known per se. Rhodium catalysts or preferably cobalt catalysts are therefore employed, with or without complex-stabilizing additions, such as organic phosphines or phosphites. The temperatures and the pressures can vary within broad ranges, depending on catalyst and olefin mixture. A description of the hydroformylation of olefins is given, for example, in J. Falbe, *New Syntheses with Carbon Monoxide*, Springer-Verlag, Heidelberg, New York, 1980, pages 99 ff., and in Kirk-Othmer, *Encyclopedia of Chemical Technology*, Volume 17, 4th edition, John Wiley & Sons, pages 902-919 (1996).

An essential feature of the invention is that the degree of conversion for one pass is restricted to from 40 to 90%. Advantageously, the olefins are from 65 to 80% converted. The preferred starting materials are C_8 , C_9 , C_{12} or C_{16} olefin mixtures which consist of a great number of different isomers. As

mentioned above, straight-chain olefins having terminal olefinic double bonds react most readily. The reactivity therefore decreases the more extensively the molecule is branched and/or the further the double bond is in the interior of the molecule. The restriction on conversion rate according to the invention has the effect that the reactive olefins preferentially react to completion, the less reactive remain in the reaction mixture and, after the selective hydrogenation of the reaction mixture, are recirculated to the hydroformylation. The restriction of conversion rate increases the selectivity of the hydroformylation. Olefin recycling increases the total residence time of the less-reactive olefins. As a consequence of the olefin recycling, higher overall olefin conversion rates with reduced byproduct formation and thus higher aldehyde yields are achieved and, after hydrogenation, higher alcohol yields are achieved. Furthermore, the smaller amount of byproducts facilitates work-up of the reaction mixtures. In comparison with the single-stage process without olefin recycling, the process according to the invention, owing to the selective hydrogenation and olefin recycling, increases the economic efficiency of the preparation of oxo alcohols.

The degree of conversion of the olefins is restricted to the desired value by changing appropriately the hydroformylation reaction conditions. By selecting lower reaction temperatures and/or catalyst concentrations as well as shorter reaction times, the olefin conversion rate can be decreased. The degree of conversion for one passage of the olefin mixture **2** (= fresh olefin mixture **13** + recirculated low-boilers **12**) is determined on the basis of the amount and composition of the olefin mixture **2** and on the amount and composition of the recirculated low-boilers **12** plus the withdrawn low-boilers **14**. The overall degree of conversion is determined on the basis of the amount and composition of the fresh olefin mixture **13** and on the amounts of olefin discharged with the residual low-boilers **14**. To determine the olefin contents in the various streams, gas-chromatographic analysis can be employed.

Catalyst removal

The hydroformylation reaction mixtures are expediently firstly freed from the catalyst, again in a manner known per se. If a cobalt catalyst was used, this can be achieved by pressure reduction, separating off the aqueous catalyst phase, oxidizing with air or oxygen the cobalt carbonyl compounds remaining in the hydroformylation mixture and extracting the resulting cobalt compounds with water or aqueous acid. Cobalt-depletion processes are well known, see, for example, J. Falbe, loc. cit., 164, 165 (BASF Process), Kirk-Othmer, loc. cit. and EP-0 850 905 A1. If a rhodium compound served as hydroformylation catalyst, it can be removed from the hydroformylation mixture as distillation residue by means of thin-film evaporation.

The hydroformylation reaction mixtures freed from catalyst, depending on the degree of conversion, generally comprise 3-40% by weight, usually from 5 to 30% by weight, of low-boilers having a lower boiling point than the aldehydes, principally olefins, in addition the corresponding saturated hydrocarbons and water with or without methanol, in addition 30-90% by weight of aldehydes, 5-60% by weight of alcohols, up to 10% by weight of formates of these alcohols and 5-15% by weight of high-boilers having a higher boiling point than the alcohols. However, it may be emphasized that the process according to the invention can also be carried out using hydroformylation mixtures whose composition does not correspond with these specifications in this and/or that regard.

Selective hydrogenation

The selective hydrogenation of the hydroformylation mixtures expediently freed from the hydroformylation catalyst is a further essential feature of the process according to the invention. In this hydrogenation, the aldehydes and certain accompanying substances, including acetals of the aldehydes and esters of the alcohols, and of these particularly the formates, are hydrogenated to the desired alcohols. Since the conversion rate in the

hydroformylation stage is restricted, it is critical for the economic efficiency of the process that in the hydrogenation the unreacted olefins are not hydrogenated, or are virtually not hydrogenated, so that they can be separated off from the hydrogenation mixture and recirculated to the hydroformylation.

A selective hydrogenation of hydroformylation mixtures is subject-matter of the co-pending patent application 198 42 370.5 (O.Z. 5356). The hydroformylation reaction mixtures are, according to this, hydrogenated by means of hydrogen at elevated temperature and at elevated pressure at a supported catalyst which comprises, as active components, copper, nickel and chromium.

Preferred catalysts of this type are supported catalysts which comprise, as active components, copper and nickel at concentrations in each case of 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, advantageously of 0.02-1.2% by weight, in each case based on the supported catalyst. Another advantageous supported catalyst comprises copper, nickel and chromium in the specified amounts, but no alkali metal component. Suitable support substances are, in particular, silicon dioxide and aluminum oxide. The amounts specified are based on the catalyst which is prepared as described below and has not yet been reduced.

In the hydrogenation, the aldehydes in the hydroformylation mixtures are hydrogenated to the corresponding alcohols in only one hydrogenation stage at conversion rates greater than 98% at a selectivity of greater than 99%. The esters and acetals are likewise converted into the desired alcohols. The starting olefins present in the mixture remain surprisingly by far for the most part unchanged, although precisely the preferred supported catalysts, under

comparable conditions, also hydrogenate virtually quantitatively the olefinic double bond in 2-ethylhex-2-enal (EP 0 326 674 A2). The hydrogenation can be carried out in the low-pressure region of below 30 bar and at high space-time yields.

Said catalyst components can be distributed homogeneously 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 expediently roughly corresponds to 0.8 times the pore volume of the support material. As copper salts, nickel salts and 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 onto the non-preheated support material, situated in a coating drum and penetrates into the pores thereof. The catalyst is then dried.

If it is desired to have a catalyst with 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 of both said types are calcined, i.e. depending on the catalyst precursor used, heated to temperatures of 200-400°C, the catalyst precursors being converted to the oxides. The catalyst is then reduced with hydrogen. The reduction can be performed just after the

catalyst is prepared or expediently not until the hydrogenation reactor.

The catalysts are advantageously 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 expediently activated prior to use by heating in a hydrogen stream, e.g. at said hydrogenation temperatures, from 150 to 250°C, if they have not been reduced in the reactor.

The hydrogenation 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 there is the fact that evaporating aldehydes having an increasing carbon number requires more and more energy, and, in addition, the starting material loading in the reduction gas decreases, so that a gas-phase process in the case of aldehydes having a carbon number greater than about 8 makes it scarcely possible still to carry out the overall process economically.

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, expediently 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 concurrent 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 m³, in particular 15-50 m³ per m² of cross section of the 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, with correspondingly greater gas volumes. The reaction temperatures, in the case of hydrogenations in the liquid or gas phase, are generally between 120 and 220°C, in particular between 140 and 180°C.

Separation of the hydrogenation mixture by distillation

After the hydrogenation, the reaction mixtures are worked up by distillation in a manner known per se. This is expediently performed under reduced pressure, e.g. at an absolute pressure of from 400 to 900 mbar. In this distillation, the olefins are recovered as by far the most predominant constituent of the low-boiler fraction. Expediently, the majority of the low-boiler fraction, generally from 60 to 98%, is recirculated to the hydroformylation. The remaining portion of the low-boiler fraction, that is from 2 to 40%, can be discharged from the olefin circuit so that the concentration of the inert saturated hydrocarbons which have been formed by hydrogenation of the olefins in the hydroformylation stage does not exceed 70%, preferably is kept below 60%.

Comparative Example

Hydroformylation of di-n-butene

In a 5 l high-pressure autoclave provided with a stirrer and electrical heating, 2000 g of di-n-butene (C_4 olefin from the OXENO Octol process) were hydroformylated in the presence of a cobalt catalyst at 180°C and a synthesis gas pressure of 280 bar, which was held constant. The synthesis gas contained 50% by volume CO and 50% by volume H_2 .

To prepare the cobalt hydridocarbonyls which are used as catalyst, use was made as catalyst precursor of an aqueous cobalt acetate solution containing 0.95% by weight of Co. The cobalt acetate solution was treated with synthesis gas at 170°C and 280 bar with stirring for 7 h. After cooling to room temperature and depressurization, the cobalt hydridocarbonyls formed were transferred to the organic phase by extraction with the di-n-butene starting material. Following separation of the aqueous phase, the di-n-butene, loaded with cobalt hydridocarbonyls with a Co content of 0.025% by weight (calculated as the metal), was hydroformylated for 3 hours under the abovementioned reaction conditions.

After cooling to room temperature, the reaction mixture was depressurized, removed from the autoclave and freed from the Co catalyst by treatment with 5% strength acetic acid and air at 80°C. This gave 2488 g of hydroformylation mixture which was analyzed by means of gas chromatography (GC). The results are set out in Table 1. According to those results, a di-n-butene conversion of 89.3% was achieved with a target-product selectivity of 90.7%, corresponding to a target-product yield of 81.0% based on the di-n-butene employed.

C_5 aldehydes, C_5 alcohols, and isononyl formates are regarded as target products.

Example (in accordance with the invention)

Hydroformylation of di-n-butene with recycled C_4 olefin

2488 g of the hydroformylation mixture from the comparative example were hydrogenated selectively to the target product C_5 alcohol with retention of the olefins. The hydrogenation was conducted batchwise in a 5 l autoclave at 180°C and an H_2 pressure of 20 bar in the liquid phase in the presence of a supported catalyst comprising 12.1% by weight Cu, 3.0% by weight Ni and 2.5% by weight Cr on alumina as support material. Subsequently, the unreacted olefins from the hydrogenation mixture were removed, as low boilers, from the target products and the high boilers by distillation in a laboratory distillation column.

This gave 250 g of a low-boiling fraction which according to GC analysis contained around 1.3% by weight of methanol (follow-on product of the hydrogenation of isononyl formate) in addition to 98.7% by weight of C_5 hydrocarbons, of which 78.4% by weight comprised C_4 olefins.

The low-boiling fraction and 2000 g of di-n-butene, i.e., 2250 g of starting

material in all containing

2193 g of C₈ olefin, were hydroformylated in a 5 l autoclave at 180°C under a synthesis gas pressure of 280 bar in the presence of a cobalt catalyst in the manner described in the comparative example. Again, a synthesis gas containing 50% by volume CO and 50% by volume H₂ was used. This mixture was hydroformylated for 3 hours with a cobalt content of 0.024% by weight Co based on the C₈ olefin mixture.

After cooling to room temperature, the reaction mixture was depressurized, removed from the autoclave and freed from the Co catalyst by treatment with 5% strength acetic acid and air at 80°C. This gave 2731 g of hydroformylation mixture, which was analyzed by means of gas chromatography. The results are set out in Table 1. According to those results, a C₈ olefin conversion of 88.2% was achieved with a target-product selectivity of 90.9%, corresponding to a target-product yield of 80.2%, based on the C₈ olefin employed. Again, C₈ aldehydes, C₉ alcohols and isononyl formates were regarded as target products.

In order to be able to estimate the influence of the recycling of olefins, in accordance with the present invention, on the yield of target products, the yield based on C₈ olefin (di-n-butene and recycled C₈ olefin) was calculated on the basis of the amount of fresh di-n-butene (2000 g) employed. Accordingly, the di-n-butene-related yield is found to be 88.0%.

Relative to the hydroformylation without olefin recycling, as in the comparative example, olefin recycling produces an increase in the target-product yields of around 8%. In practice, the C₈ paraffins and a fraction of the C₈ olefins are removed by means of a purge, which is a consequence of the continuous procedure.

Table 1
Composition of hydroformylation mixtures

Composition by GC analysis	Comparative example % by weight	Inventive example % by weight (without paraffins from the 1st hydroformylation cycle)
C ₈ olefins	8.6	9.5
C ₈ paraffins	2.2	2.0 only paraffins from the 2nd hydroformylation cycle)
Isononanal	55.8	57.0
Ester/isononyl formates	4.5	4.8
Isononanol	23.4	21.2
Residue	5.5	5.5

Accordingly, in a single-stage process, the target-product yield can no longer be improved significantly through a higher conversion of di-n-butene, since

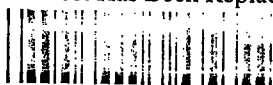
the increase in conversion results in a reduction in selectivity owing to follow-on reactions.

In contrast, the process of the invention allows a higher conversion of di-n-butene to target products without reduction in selectivity.



CLAIMS

1. A process for preparing higher oxo alcohols from mixtures of isomeric olefins having from 5 to 24 carbon atoms by hydroformylation in the presence of a catalyst at elevated temperature and at elevated pressure, which comprises carrying out the hydroformylation in one stage, restricting the olefin conversion rate for one passage to from 40 to 90%, selectively hydrogenating the reaction mixture, expediently after catalyst removal, separating the hydrogenation mixture by distillation and recirculating the olefin fraction to the hydroformylation.
2. The process as claimed in claim 1, wherein use is made of C₈, C₉, C₁₂ or C₁₆ olefin mixtures as the starting materials for the hydroformylation.
3. The process as claimed in claim 1 or 2, wherein the hydroformylation reaction mixture is hydrogenated at elevated temperature and at elevated pressure at a supported catalyst which comprises, as active components, copper, nickel and chromium.
4. The process as claimed in claim 3, wherein use is made of a supported catalyst which comprises, as active components, copper and nickel at concentrations in each case of 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.
5. The process as claimed in claim 4, wherein the concentration of the alkali metal component is from 0.2 to 1.2% by weight.
6. The process as claimed in claim 4, wherein the supported catalyst



does not contain an alkali metal component.

7. The process as claimed in one of claims 1 to 6, wherein the catalyst support material is silicon dioxide or aluminum oxide.
8. The process as claimed in one of claims 1 to 7, wherein the active catalyst components are homogeneously distributed in the pores of the support material.
9. The process as claimed in one of claims 1 to 7, wherein said catalyst components are homogeneously enriched in the edge zones of the support material.
10. The process as claimed in one of claims 1 to 9, wherein the hydrogenation is carried out continuously or batchwise in the liquid phase.
11. The process as claimed in one of claims 1 to 10, wherein the hydrogenation is carried out in the liquid phase at an overall pressure of from 5 to 30 bar.
12. The process as claimed in claim 11, wherein the overall pressure is from 15 to 25 bar.
13. The process as claimed in one of claims 1 to 12, wherein the hydrogenation is carried out at from 120 to 220°C.
14. The process as claimed in claim 13, wherein the temperature is from 140 to 180°C.
15. The process as claimed in one of claims 1 to 14, wherein the hydrogenation is carried out in the liquid phase and at liquid loadings of 5-100 m³ per m² of cross section of the empty reactor and hour.



16. The process as claimed in claim 15, wherein the liquid loading is 15-50 m³ per m² of cross section of the empty reactor and hour.
17. The process as claimed in one of claims 1 to 16, wherein the hydrogenation mixture is separated by distillation and the olefins are recirculated to the hydroformylation.
18. The process as claimed in claim 17, wherein from 2 to 40% of the low-boilers are discharged from the olefin circuit.

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