Description

This invention relates to an improved process for hydroformylating an olefin with carbon monoxide and hydrogen in the presence of a rhodium catalyst.

Methods for producing aldehydes by the hydroformylation of an olefinically unsaturated organic compound with carbon monoxide and hydrogen in the presence of a rhodium-phosphorus complex catalyst and free phosphorus ligand are well known in the art as seen: e.g. by the basic low pressure oxo hydroformylation process of U.S.-A-3,527,809 and the rhodium-catalyzed liquid recycle hydroformylation process of U.S.-A-4,148,830.

In U.S.-A-4,148,830 it is disclosed that catalyst life can be enhanced and product yield improved by employing as a catalyst solvent for rhodium-catalyzed hydroformylation (or the "oxo" process), higher boiling aldehyde condensation products as defined therein. It was also found that the rhodium catalyst could be continuously or intermittently recycled to the hydroformylation reaction zone without significant loss of rhodium, catalyst life, reaction rates and efficiency.

Accordingly, US-A-4,148,830 disclosed that liquid effluent from the reaction zone containing catalyst, solvent and gases, is processed to strip and recover the aldehyde product. During this procedure some hydrogen, carbon monoxide, unreacted olefin, and other by-product and inert gases dissolved in the reactor effluent are removed by reducing pressure on the effluent stream to flash off such gases. The desired aldehyde product is then recovered from said effluent and the liquid residue fraction of unrecovered aldehydic product, catalyst and high boiling condensation product is recycled to the reactor. Accordingly, this process has sometimes been referred to as a liquid-recycle hydroformylation process (or "liquid recycle process").

U.S.-A-4,247,486, discloses a hydroformylation process which is directed to further modifications of the basic oxo process disclosed in U.S.-A-3,527,809 and 4,148,830.

In this process, unreacted feed, the aldehyde reaction product and higher boiling condensation products, inter alia, are allowed to distill out of the reaction medium. The aldehyde product and condensation products are condensed from the gas recycle stream and unreacted feed contained therein (i.e., syn gas and olefin) are recycled to the reaction zone. This process is a gas recycle hydroformylation process or, simply, "a gas-recycle process".

U.S.-A-4,247,486 discloses that a by-product of such a recycle hydroformylation process is saturated alkane formed by the hydrogenation of the olefin. Thus, for example, propane is a by-product in the hydroformylation of propylene. Accordingly, a purge stream is taken from a gas recycle stream therein to remove such propane and to control its concentration within the process. The purge stream also contains, inter alia, aldehyde product, unreacted olefin, inert gases, as well as carbon monoxide and hydrogen. It is said in the '486 Patent that the recovery of olefin from such a stream is impractical and that the purge stream is typically used as a fuel.

Likewise, to control total reactor pressure in a liquid recycle process due to build up of inerts and the like, a gaseous purge is generally taken from the liquid recycle hydroformylation reactor, where excess hydrogen, carbon monoxide, unreacted olefin, inerts and alkane by-products, such as propane, are vented as off-gases.

In addition, during the product separation step in a liquid recycle process, some gases, primarily unreacted olefin and alkane by-product, which remain dissolved in the liquid catalyst-containing effluent, are separated along with the desired aldehyde product. A portion of such separated gases are condensed with the desired aldehyde product. The remaining separated gases can be purged from the system.

The amount of olefin and syn gas components lost by purging in such recycle processes can amount to a significant economic disadvantage over the life of a commercial continous operation due to the efficiency loss of such purged desirables as unreacted olefin and syn gas.

In DE-B1-3,102,281, a cobalt-catalyzed high pressure hydroformylation of propylene was conducted and the waste gas, resulting from the decobalting of the reaction mix, containing propylene, carbon monoxide and hydrogen, was introducted into a low pressure rhodium catalyzed hydroformylation process, simultaneously conducted. In DE-A1-3,245,883 flue gas from a low pressure rhodium hydroformylation process containing propylene is compressed and introduced into a high pressure cobalt catalyzed reactor for conversion to aldehyde.

The US-A-3 271 458 discloses an oxo process wherein an olefin, carbon monoxide and hydrogen are contacted in a carbonylation zone with an oxo catalyst under conditions to produce an oxygenated reaction product comprising an aldehyde, the improvement which comprises withdrawing from said carbonylation zone an effluent stream having an olefin content higher than the final oxygenated reaction product, cooling and recycling about 20 to 90 % by volume of said stream to said carbonylation zone, and injecting at least a portion of the cooled recycle stream into the initial stages of said carbonylation zone.

In GB-A-1 387 657 the drawing shows the removal of gaseous reaction products from a reactor (i.e. reactor No. 1) to a cooler and then to a separator. A portion of gases removed from separator is recycled to reactor No. 1 and a portion is fed to reactor No. 2. The gas reaction product removed from reactor No. 2 is collected in separator and the aldehyde product obtained therefrom.

However, the reactor No. 2 of GB-A-1 387 657 is not involved in either a liquid recycle or a gas recycle process. Neither liquid nor gas from separator is recycled to reactor No. 2.

SUMMARY OF THE INVENTION

In a primary liquid recycle rhodium-catalyzed hydroformylation process for producing aldehydes, wherein an olefin, carbon monoxide and hydrogen are reacted in the presence of a solubilized rhodium-phosphorous complex catalyst, free phosphorous ligand and higher boiling aldehyde condensation by-products to produce an aldehyde product, wherein a gaseous effluent comprising unreacted olefin and any of said aldehyde product, hydrogen, carbon monoxide and an alkane by-product is vented from the process, the improvement which comprises: conducting a decoupled secondary liquid recycle or gas recycle rhodium-catalyzed hydroformylation process conjointly with the primary process, wherein the gaseous effluent together with make-up carbon monoxide and hydrogen is employed as the reactant feed to the secondary process and wherein the catalysts compositions employed in the primary and secondary process are different

In the present invention a low pressure hydroformylation process is provided with significantly reduced physical losses of valuable compounds, e.g. olefin and syn gas, and with enhanced process flexibility.

The present invention provides for operating 2 or more low pressure oxo (LPO) reactors in a "decoupled" series mode, with separate catalyst solutions and separate product removal steps for each reactor.

There are important advantages to the decoupled series reaction system. As noted, in a typical primary recycle oxo process, gaseous purges utilized to control total reactor pressures and/or remove saturated olefin by-product to prevent its build-up in the system, result in discarding valuable olefin feed and syn gas, which is also present in the gaseous purge stream.

It has now been found that such a purge stream can be employed as a feed stream in a second "decoupled" low pressure hydroformylation process employing a gas or a liquid recycle. The decoupled process of this invention requires its own independent catalyst system and independent product recovery system. It is a key feature of this invention that unreacted olefin contained in a vent stream from the primary system can be employed as the sole olefin feed to the decoupled secondary hydroformylation process, i.e. make-up quantities of olefin need not be added to the decoupled hydroformylation process. Improvements in overall aldehyde conversions and efficiencies may be increased from 2 to 10% or more employing the present inventive decoupled series system, as compared to a conventional hydroformylation system.

In a continuous rhodium-catalyzed hydroformylation process with a liquid recycle, use of a decoupled series reactor can permit more precise control over catalyst values, reaction parameters and operating conditions to obtain higher process performance.

Independent reaction catalyst systems and independent product removal systems also provide increased operating flexibility. Turndown capabilities for such a process are very broad, since either of the separate systems could be completely shut down for maintenance, modifications or the like and the remaining system run at a reduced rate. In addition, since the "decoupled system" operates at higher olefin and syn gas utilization efficiency, then by increasing olefin concentration, the production capacity can be increased more than would be economically attractive with a simple dependent "coupled" series system in which the catalyst and product recovery are shared.

Increased operating flexibility is obtained since there is separate product recovery capability for each reactor. Each reactor can also be operated independently, Since the two reactor units in the "decoupled series" of this invention can be operated independently of one another as two separate units, two different aldehyde product mixtures, (i.e., having different normal to branched isomer aldehyde product ratios) can be produced at the same time without significant cross-contamination.

If desired, the decoupled series reaction units could be run with a mixed olefin feedstock, such as a mixed butene feedstock, with the catalyst in the first reactor being appropriate to react the alpha-olefin, selectively, and the catalyst in the secondary decoupled reactor being designed to convert the internal olefin.

The ability of the system to handle upsets is also improved. Undesired sudden increases in the flow of inerts through the system (such as a drop in feed purity) would present less of a problem. In addition, the "decoupled series" system suffers less penalty due to catalyst poisoning or inhibition, since the catalyst solutions are independent.

DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic flow diagram of a primary single stage LPO liquid recycle process in which a gas vent from the primary reactor acts as a feed to a secondary decoupled LPO process employing a single stage reactor with a gas recycle.

DETAILED DESCRIPTION OF THE INVENTION

This invention is applicable to improving any conventional continuous liquid recycle rhodium-phosphorus complex catalyzed hydroformylation process for producing aldehydes, which process is conducted in the presence of free organic phosphorus ligand. Such oxo processes and the conditions thereof are well known in the art as illustrated, e.g. by the continuous liquid recycle process of U.S.-A-4,148,830. Such hydroformylation processes in general involve the production of aldehydes by reacting an olefinic compound with hydrogen and carbon monoxide gas in a liquid reaction medium which contains a soluble rhodium-phosphorus complex catalyst, free organophosphorus ligand and higher boiling aldehyde condensation by-products.

Of course it is to be understood that the particular manner in which the hydroformylation reaction is carried

out and particular hydroformylation reaction conditions employed in either the primary system or the secondary system are not critical to the subject invention and may be varied widely and tailored to meet individual needs and produce the particular aldehyde product desired.

It should also be understood that the makeup of the hydroformylation media and reaction conditions in the primary and secondary system can be the same or different. Accordingly, the olefinic starting material reactants encompassed by the process of this invention can be terminally or internally unsaturated and be of straight-chain or branched-chain structure. Such olefins preferably contain from 2 to 5 carbon atoms.

Illustrative olefins are ethylene, propylene, 1-butene, 1-pentene, 2-butene, 2-methyl propene (isobutylene), isoamylene, 2-pentene, 2-methyl-1-butene and 2-methyl-2-butene. Of course, it is understood that mixtures of different olefinic starting materials can be employed, if desired, by the hydroformylation process of the subject invention. More specifically, the secondary system can be dedicated to hydroformylating a different olefin from that designated to be hydroformylated in the primary system. Among the more preferred olefins are propylene, 1-butene, 2-butene (cis or trans), isobutene and mixtures thereof. The most preferred olefin is propylene.

Likewise, any conventional rhodium-phosphorus complex catalyst can be employed and such catalysts as well as methods for their preparation are well known in the art. Such rhodium-phosphorus complex catalysts may include any rhodium-organophosphorus complex, such as the rhodium-organophosphine or rhodium-organophosphite complex hydroformylation catalysts heretofore advanced for such hydroformylation processes. Of course, mixtures of such catalysts can also be employed, if desired. Moreover, it is clear that the amount of complex catalyst present in the reaction medium of a given process need only be that minimum amount necessary to provide the rhodium metal concentration desired to be employed and which will furnish the basis for at least that catalytic amount of rhodium metal necessary to catalyze the particular hydroformylation process desired. In general, rhodium metal concentrations in the range of from 10 ppm to 1000 ppm, calculated as free metal, should be sufficient for most hydroformylation processes. It is generally preferred to employ from 10 to 700 ppm of rhodium, and more preferably, from 25 to 500 ppm of rhodium, calculated as free metal.

As noted above, the hydroformylation process of this invention is carried out in the presence of free phosphorus ligand, i.e. ligand that is not complexed with the rhodium complex catalyst employed. However, while it is generally preferred that the free phosphorus ligand be the same as the phosphorus ligand of the rhodium-phosphorus complex catalyst, such is not necessary and different ligands can be employed in a given process, if desired. Accordingly, as in the case of the rhodium-organophosphorus complex catalyst, any conventional organophosphorus ligand can be employed as the free ligand and such ligands, as well as methods for their preparation, are well known in the art. Such free phosphorus ligands may include any of the organophosphine or organophosphite ligands heretofore advanced for such hydroformylation processes. Of course, mixtures of such ligands can also be employed, if desired. Thus, the hydroformylation process of this invention may be carried out in any excess amount of free phosphorus ligand, e.g. at least 1 mole of free phosphorus ligand per mole of rhodium metal present in the reaction medium. The amount of free phosphorus ligand employed, in general, merely depends upon the aldehyde product desired, and the olefin and complex catalyst employed. Accordingly, amounts of free phosphorus ligand present in the reaction medium ranging from 1 to 300 or more per mole of rhodium present should be suitable for most purposes. For example, in general, large amounts of free triarylphosphine ligand, e.g. triphenylphosphine, such as more than 50 moles or, more preferably, more than 100 moles of free ligand per mole of rhodium have preferably been employed to achieve satisfactory catalytic activity and/or catalyst stabilization, while other phosphorus ligands, e.g. alkylarylphosphines and cycloalkylarylphosphines may help provide acceptable catalyst stability and reactivity without unduly retarding the conversion rates of certain olefins to aldehydes when the amount of free ligand present in the reaction medium is as little as 1 to 100 and, more preferably, 15 to 60 moles per mole of rhodium present.

More particularly, illustrative rhodium-phosphorus complex catalysts and illustrative free phosphorus ligands include, e.g. those disclosed in U.S.-A-3,527,809; 4,148,830; 4,247,486; 4,283,562; 4,400,548; 4,482,749: EP-Al-96,986; 96,987 and 96,988 PCT WO 80/01690 and U.S. Applications Serial Nos. 581,352, filed February 17, 1984 and 685,025, filed December 28, 1984. Among the more preferred ligands and complex catalysts that may be mentioned are, e.g. the triphenylphosphine ligand and rhodium-triphenylphosphine complex catalysts of U.S.-A-3,527,809 and 4,148,830 and 4,247,486; the alkylphenylphosphine and cycloalkylphenylphosphine ligands, and rhodium-alkylphenylphosphine and rhodium-cycloalkylphenylphosphine complex catalysts of U.S.-A-4,283,562; and the diorganophosphite ligands and rhodium-diorganophosphite complex catalysts of U.S. Applications Serials Nos. 581,352 filed February 17, 1984, and 685,025, filed December 28, 1984. The the most preferred ligand is triphenylphosphine (TPP), while the preferred catalyst is a rhodium-TPP complex.

As further noted above, the hydroformylation reaction is carried out in the presence of higher boiling aldehyde condensation by-products. It is the nature of such continuous hydroformylation reactions employable herein to produce such higher boiling aldehyde by-products (e.g. dimers, trimers and tetramers) in situ during the hydroformylation process as explained more fully, e.g. in U.S.-A-4,148,830 and 4,247,486. Such aldehyde by-products provide an excellent carrier for the liquid cat-

alyst recycle process. Indeed, while one may employ, if desired, any suitable solvent at the start up of a continuous process (aldehyde compounds corresponding to the desired aldehyde products being preferred), the primary solvent will normally eventually comprise both aldehyde products and higher boiling aldehyde condensation by-products due to the nature of such continuous processes. Of course, aldehyde condensation by-products can also be preformed if desired and used accordingly. It is also obvious that the amount of such higher boiling aldehyde by-products present in the reaction medium may vary over wide limits and is generally governed only by equipment constraints and the particular aldehyde product to be produced. For example, initially the hydroformylation reaction can be effected in the absence or in the presence of small amounts of higher boiling aldehyde condensation by-products as a solvent for the rhodium complex catalyst, or the reaction can be conducted in the presence of upwards of 70 weight percent, or even as much as 90 weight percent, and more of such condensation by-products, based on the total liquid reaction medium. In general, ratios of aldehyde to higher boiling aldehyde condensation by-products within the range of from 1:4 to 20:1 by weight should be sufficient for most purposes. Likewise it is to be understood that minor amounts of other conventional organic cosolvents may be present if desired.

While the hydroformylation reaction conditions may vary over wide limits, as discussed above, in general it is more preferred that the process may be operated at a total gas pressure of hydrogen, carbon monoxide and olefinic unsaturated starting compound of less than 31 bar abs (450 psia) and more preferably less than 24 bar abs (350 psia). The minimum total pressure of the reactants is not particularly critical and is limited mainly only by the amount of reactants necessary to obtain a desired rate of reaction. More specifically, the carbon monoxide partial pressure of the hydroformylation process of this invention is preferably from 0.069 to 8.3 bar abs. (1 t 120 psia)and, more preferably, from 0.2 to 6,2 bar abs. (3 to 90 psia), while the hydrogen partial pressure is preferably 0,69 to 11 bar abs.(10 to 160 psia)and more preferably from 1 to 6.9 bar abs.(15 to 100 psia). In general H_2:CO molar ratio of gaseous hydrogen to carbon monoxide may range from 1:10 to 100:1 or higher, the more preferred hydrogen to carbon monoxide molar ratio being from 1:1 to 50:1.

Further, as noted above, the hydroformylation process of this invention may be conducted at a reaction temperature from 50° C to 145° C. However, in general, hydroformylations at reaction temperatures of 60° C to 120° C and more preferably 75° C to 115° C are preferred.

In one embodiment of this invention, the hydroformylation process employed in either the primary or secondary system can involve a continuous liquid recycle. In the continuous liquid recycle, a portion of the liquid reaction aldehyde product solution containing aldehyde product, solubilized rhodium-phosphorus complex catalyst, free phosphorus ligand and higher boiling aldehyde condensation by-products is removed from the reactor. The desired aldehyde product is separated via vaporization or distillation, in one or more stages, under normal, reduced or elevated pressure from the liquid reaction solution. The aldehyde product is condensed and collected in a product receiver, and further purified if desired. The remaining nonvolatilized catalyst-containing liquid reaction product solution is recycled back to the reactor. Such types of continuous hydroformylation systems and methods for carrying them out are well known in the art and thus need not be particularly detailed herein.

In employing a liquid recycle step in the primary system, a solution of rhodium species catalyst in high boiling liquid condensation products with aldehydic products resulting from hydroformylation, syn gas, inerts, saturated olefinic by-products and the like is continuously or intermittently recycled to the hydroformylation zone. The solution is removed from the reactor at a rate sufficient to keep a relatively constant level of liquid in the reactor. The pressure on the effluent stream is then reduced to flash-distill off light gaseous hydroformylation products, including some unreacted olefin, hydrogen, saturated olefin by-products and the like. The flashed off-gases are compressed and returned to the reactor. Of course it is to be understood that such an intermediate step as said flash-distillation and return of the off-gases to the reactor is not critical to the process and can be omitted, if desired. Alternatively said off-gases can merely be purged, if desired. For example, said flash distillation intermediate step and return of said off-gas to the reactor may or may not be of any great benefit to a secondary system employing a liquid recycle process.

The effluent stream is then fed to a product separation zone wherein the crude aldehyde product is recovered by conventional techniques., e.g., distillation. Undissolved light gases are also vented off in the product separation zone and are returned to the reactor. Again, these off-gases may be merely purged, if desired, and such may be the case in the secondary system.

The remaining concentrated catalyst is recycled as a liquid stream to the reaction zone. Make-up syn gas and olefin are fed into the reaction medium, as required. In refining of the crude aldehyde, it is further preferred to recycle the light gases dissolved in the crude product to the reactor after their removal via conventional techniques: e.g. distillation, although they too may be wasted, if desired.

In the primary liquid recycle process, a vent line is provided in the head space above the liquid level in the primary reactor to control the internal pressure build-up in the reactor and as the means for conveying the unreacted olefin feed to the secondary decoupled reactor. In the case of the secondary system employing a liquid recycle process this vent line from the headspace of the reactor can serve as the purge line for controlling internal pressure build-up in the secondary reactor.

It should be understood that the olefin starting material for the secondary decoupled system can be taken from any gaseous stream which could be vented from the primary process as off-gas. While such olefin starting material for the secondary decoupled process can be derived from any appropriate gas vent containing unreacted olefin and incidental alkane by-products taken from any suitable location in the primary reaction system, it is preferred to employ the vent stream from either the reactor headspace and/or from the product separation step as the feed for the secondary decoupled rhodium-catalyzed hydroformylation process. In the secondary process, olefin-containing vented gas from the primary system is admixed with make-up syn gas and the resulting feed is introduced into the reactor of the secondary system which contains a catalyst system of the present invention. Reaction products are removed and recovered employing a gas recycle or a liquid recycle step of this invention.

The process carried out in the secondary decoupled system, as set forth previously, can employ the same or different reaction conditions as utilized in the primary hydroformylation process discussed above. A liquid recycle or gas recycle can be employed in the secondary process in accordance with the same or different conditions as noted hereinbefore.

Accordingly, one embodiment of this invention can be further illustrated by reference to Figure 1 which schematically shows a diagrammatic flowsheet suitable for practicing this invention.

Referring to Fig. 1, a stainless steel reactor 10 is provided with a sparger 12 having holes for providing a sufficient gas flow of olefin and synthesis gas. Additional spargers may be employed depending upon the size of the reactor, if desired. In the system illustrated, propylene is converted to butyraldehyde. A feed line 13 supplies make-up propylene and syn gas. An impeller (not shown) is employed to mix the reactor contents. An internal or external cooler (not shown) is employed to help control reaction temperature. A liquid effluent stream is removed via line 16 to a flash evaporator 18, wherein light gaseous hydroformylation components are vaporized, conducted through line 17 to compressor 20, compressed therein and recycled to the reactor via line 22 and feed line 14. The remaining liquid effluent is then passed via line 19 a a product removal zone 23.

In the product removal zone 23 which generally comprises a vaporizer/separator, aldehyde product is vaporized out of the catalyst stream via line 25 and, thereafter condensed and refined. Some olefin, syn gas and other gases dissolved in the catalyst stream are distilled off. A portion of the distilled-off gases are condensed with the aldehyde and said gases can be recovered during refining of the crude aldehyde product and recycled to the reactor (not shown). However, a significant portion of said distilled-off gases; e.g. the olefin, is not condensed with the aldehyde product, but is removed in a purge or vent stream 24 which is compressed in compressor 21 and recycled to line 22. The concentrated catalyst from the product removal step is recycled to the reactor via line 26.

In Fig. 1 a vent line 28 originating in the reactor headspace conducts unconverted olefin and syn gas to inlet line 30 of secondary decoupled reactor 32. Reactor 32 may be equipped in the same manner as reactor 10, e.g. sparger 34, agitator, inlet syn gas feed line 36, and means for temperature control.

The decoupled reactor 32 has an effluent line 38 to conduct gaseous effluents containing aldehyde product to a dedicated product recovery zone. A condenser 40 is utilized to condense the aldehyde product from the effluent gases. A separator-catchpot 39 is used to separate the condensed, crude aldehyde product from the non-condensed effluent gases. Gaseous materials are passed via line 42 to a compressor 44 and then recycled to inlet line 30 for reintroduction into the reactor. A purge line 46 is provided to remove excess by-products, such as propane and other gases, from the system. The crude aldehyde is recovered via line 41 and refined, as desired.

If desired, vent line 24 and/or vent line 17 in the primary system can be employed singularly, plurally or in conjunction with vent line 28 as the feed line for the decoupled system.

The primary and secondary reactors each contain, as will be appreciated, a solubilized rhodium catalyst composition comprising a solubilized rhodium-phosphorous complex catalyst, free phosphorous ligand and a solvent, e.g. aldehyde and/or aldehyde high boiling condensation by-products. The catalyst compositions are different in the 2 reactors as shown and discussed above.

It is a unique feature of this invention that the secondary decoupled reactor can employ partially deactivated catalyst. For example, it is known that, despite the obvious advantages of the above invention, during use the rhodium complex catalyst loses activity (i.e. becomes partially deactivated) and eventually, after prolonged use, the activity of the catalyst will have decreased to such a point that it is no longer economically desirable to operate the hydroformylation process, and the catalyst will have to be discharged and replaced with fresh catalyst. Accordingly, due to the high cost of rhodium values, the ability to employ partially deactivated catalyst in the secondary, decoupled reactor, which catalyst might be so deactivated as not to be preferably employable in the primary reactor, is obviously of high benefit to the state of this art.

It will be understood that for the purposes of this invention more than one reactor can be employed in series or in parallel in both the primary or secondary systems of this invention.

The process carried out in the secondary decoupled system, as set forth previously, can employ the same or different reaction conditions as utilized in the primary hydroformylation process discussed above. A liquid recycle or gas recycle can be employed in the secondary process in accordance with the same or different conditions as noted hereinbefore.

The primary and secondary reactors each contain, as will be appreciated, a solubilized rhodium catalyst composition comprising a solubilized rhodium-phosphorous complex catalyst, free phosphorous ligand and a solvent, e.g. aldehyde and/or aldehyde high boiling condensation by-products. The catalyst compositions are different in the primary or secondary reactors.

It is a unique feature of this invention that the secondary decoupled reactor can employ partially deactivated catalyst as discussed before. It will also be understood that more than one reactor can be employed in series or in parallel in the primary or secondary systems of this embodiment.

Again, the concept of the decoupled series mode of this invention is applicable to any combination of reactor systems whether they be liquid recycle-liquid recycle or liquid recycle-gas recycle. It is also possible to employ a heterogeneous rhodium catalyst system on a solid support in the secondary decoupled reactor.

In general the olefin efficiency provided by this invention improves as the secondary decoupled reactor catalyst volume increases relative to the primary reactor catalyst volume. More catalyst is required as the secondary decoupled reactor catalyst volume is increased. For most purposes the secondary reactor is no larger in catalyst volume than the primary reactor and may be quite small relative to the primary reactor. Usually the ratio of secondary reactor system catalyst volume to primary reactor system catalyst volume is from 0.05:1 to 1:1. Preferred ratios are from 0.1:1 to 1:1 and most preferably, about 0.33:1 to 1:1.

Claims

1. A primary liquid recycle rhodium-catalyzed hydroformylation process for producing aldehydes, wherein an olefin, carbon monoxide and hydrogen are reacted in the presence of a solubilized rhodium-phosphorus complex catalyst, free phosphorus ligand and higher boiling aldehyde condensation by-products, wherein a gaseous effluent comprising unreacted olefin and any of the aldehyde product, hydrogen, carbon monoxide and an alkane by-product is vented from the process,
characterized by
conducting a decoupled secondary liquid recycle or gas recycle rhodium-catalyst hydroformylation process conjointly with the primary process, wherein the gaseous effluent together with make-up carbon monoxide and hydrogen is employed as the reactant feed to the secondary process and wherein the catalysts compositions employed in the primary and secondary process are different.

2. The process of claim 1,
characterized by
employing as the reactant feed to the decoupled secondary process a gaseous effluent containing unreacted olefin vented solely from the headspace of the primary reactor together with make-up quantities of carbon monoxide and hydrogen.

3. The process of claim 2 wherein the decoupled secondary rhodium-catalysed hydroformylation process comprises a gas recycle process or a liquid recycle process, respectively.

4. The process of claim 3 wherein the free phosphorus ligand and phosphorus ligand of the rhodium-phosphorus complex catalyst is a triorganophosphine compound, preferably triphenylphosphine.

5. The process of claim 3 wherein make-up olefin is not added to the decoupled secondary process.

6. The process of claims 1 to 5 in which the ratio of secondary decoupled reactor catalyst volume to primary reactor catalyst volume is from 0.05:1 to 1:1 or from 0.1:1 to 1:1.

7. The process of claims 1 to 6 in which the hydroformylation reaction in the primary and secondary process is conducted at a reaction temperature from 50°C to 145°C or from 75°C to 115°C.

8. The process of claims 1 to 7 in which the rhodium concentration in the primary and secondary process is from 10 to 700 ppm. or from 25 to 500 ppm. calculated as free rhodium metal.

9. The process of claims 1 to 8 in which from 1 to 300 moles of free ligand are present per mole of rhodium.

10. The process of claims 1 to 9 in which the total pressure of olefin, carbon monoxide and hydrogen in each of the primary and decoupled secondary process is less than 31 bar abs. (450 psia) and the molar ratio of hydrogen to carbon monoxide is from 1:10 to 100:1.

11. The process of claim 10 in which the total pressure of olefin, carbon monoxide and hydrogen is less than about 24 bar abs. (350 psia) and the molar ratio of hydrogen to carbon monoxide is from 1:1 to 50:1.

12. The process of claims 1 to 11 in which the ratio of the aldehyde product to the high boiling aldehyde condensation by-products in the hydroformylation reaction zone of each reactor is from 1:4 to 20:1 in the hydroformylation process.

13. The process of claims 1 to 12 in which the olefin has from 2 to 5 carbon atoms.

Patentansprüche

1. Ein primäres Rhodium-katalysiertes Hydroformylierungsverfahren unter Rückführung von Flüssigkeit

The primary and secondary reactors each contain, as will be appreciated, a solubilized rhodium catalyst composition comprising a solubilized rhodium-phosphorous complex catalyst, free phosphorous ligand and a solvent, e.g. aldehyde and/or aldehyde high boiling condensation by-products. The catalyst compositions are different in the primary or secondary reactors.

It is a unique feature of this invention that the secondary decoupled reactor can employ partially deactivated catalyst as discussed before. It will also be understood that more than one reactor can be employed in series or in parallel in the primary or secondary systems of this embodiment.

Again, the concept of the decoupled series mode of this invention is applicable to any combination of reactor systems whether they be liquid recycle-liquid recycle or liquid recycle-gas recycle. It is also possible to employ a heterogeneous rhodium catalyst system on a solid support in the secondary decoupled reactor.

In general the olefin efficiency provided by this invention improves as the secondary decoupled reactor catalyst volume increases relative to the primary reactor catalyst volume. More catalyst is required as the secondary decoupled reactor catalyst volume is increased. For most purposes the secondary reactor is no larger in catalyst volume than the primary reactor and may be quite small relative to the primary reactor. Usually the ratio of secondary reactor system catalyst volume to primary reactor system catalyst volume is from 0.05:1 to 1:1. Preferred ratios are from 0.1:1 to 1:1 and most preferably, about 0.33:1 to 1:1.

Claims

1. A primary liquid recycle rhodium-catalyzed hydroformylation process for producing aldehydes, wherein an olefin, carbon monoxide and hydrogen are reacted in the presence of a solubilized rhodium-phosphorus complex catalyst, free phosphorus ligand and higher boiling aldehyde condensation by-products, wherein a gaseous effluent comprising unreacted olefin and any of the aldehyde product, hydrogen, carbon monoxide and an alkane by-product is vented from the process,
characterized by
conducting a decoupled secondary liquid recycle or gas recycle rhodium-catalyst hydroformylation process conjointly with the primary process, wherein the gaseous effluent together with make-up carbon monoxide and hydrogen is employed as the reactant feed to the secondary process and wherein the catalysts compositions employed in the primary and secondary process are different.

2. The process of claim 1,
characterized by
employing as the reactant feed to the decoupled secondary process a gaseous effluent containing unreacted olefin vented solely from the headspace of the primary reactor together with make-up quantities of carbon monoxide and hydrogen.

3. The process of claim 2 wherein the decoupled secondary rhodium-catalysed hydroformylation process comprises a gas recycle process or a liquid recycle process, respectively.

4. The process of claim 3 wherein the free phosphorus ligand and phosphorus ligand of the rhodium-phosphorus complex catalyst is a triorganophosphine compound, preferably triphenylphosphine.

5. The process of claim 3 wherein make-up olefin is not added to the decoupled secondary process.

6. The process of claims 1 to 5 in which the ratio of secondary decoupled reactor catalyst volume to primary reactor catalyst volume is from 0.05:1 to 1:1 or from 0.1:1 to 1:1.

7. The process of claims 1 to 6 in which the hydroformylation reaction in the primary and secondary process is conducted at a reaction temperature from 50°C to 145°C or from 75°C to 115°C.

8. The process of claims 1 to 7 in which the rhodium concentration in the primary and secondary process is from 10 to 700 ppm. or from 25 to 500 ppm. calculated as free rhodium metal.

9. The process of claims 1 to 8 in which from 1 to 300 moles of free ligand are present per mole of rhodium.

10. The process of claims 1 to 9 in which the total pressure of olefin, carbon monoxide and hydrogen in each of the primary and decoupled secondary process is less than 31 bar abs. (450 psia) and the molar ratio of hydrogen to carbon monoxide is from 1:10 to 100:1.

11. The process of claim 10 in which the total pressure of olefin, carbon monoxide and hydrogen is less than about 24 bar abs. (350 psia) and the molar ratio of hydrogen to carbon monoxide is from 1:1 to 50:1.

12. The process of claims 1 to 11 in which the ratio of the aldehyde product to the high boiling aldehyde condensation by-products in the hydroformylation reaction zone of each reactor is from 1:4 to 20:1 in the hydroformylation process.

13. The process of claims 1 to 12 in which the olefin has from 2 to 5 carbon atoms.

Patentansprüche

1. Ein primäres Rhodium-katalysiertes Hydroformylierungsverfahren unter Rückführung von Flüssigkeit

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zur Herstellung von Aldehyden, wobei ein Olefin, Kohlenmonoxid und Wasserstoff in Gegenwart eines löslich gemachten Rhodium-Phosphorkomplex-Katalysators, freiem Phosphor-Liganden und höhersiedenden Aldehyd-Kondensationsnebenprodukten umgesetzt werden, wobei ein Abgas, das nicht-umgesetztes Olefin und etwaiges Aldehydprodukt, Wasserstoff, Kohlenstoffmonoxid und ein Alkan-Nebenprodukt umfaßt, aus dem Verfahren abgegeben wird,
dadurch gekennzeichnet, daß man ein entkoppeltes sekundäres Rhodium-katalysiertes Hydroformylierungsverfahren unter Rückführung von Flüssigkeit oder Gas gleichzeitig mit dem primären Verfahren durchführt, wobei das Abgas zusammen mit zugesetztem Kohlenstoffmonoxid und Wasserstoff als Reaktantenspeisung für das sekundäre Verfahren eingesetzt wird, und wobei die in dem primären und sekundären Verfahren eingesetzten Katalysatorenzusammensetzungen verschieden sind.

2. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, daß man als Reaktantenspeisung zu dem entkoppelten sekundären Verfahren einen Gas-Abstrom verwendet, der nicht-umgesetztes Olefin enthält, das nur aus dem Kopfraum des primären Reaktors abgeblasen worden ist zusammen mit Zusatzmengen an Kohlenstoffmonoxid und Wasserstoff.

3. Verfahren nach Anspruch 2, worin das entkoppelte sekundäre Rhodium-katalysierte Hydroformylierungsverfahren ein Gas-Kreislaufverfahren oder ein Flüssigkeits-Kreislaufverfahren umfaßt.

4. Verfahren nach Anspruch 3, worin der freie Phosphor-Ligand und der Phosphor-Ligand des Rhodium-Phosphorkomplex-Katalysators eine Triorganophosphinverbindung, vorzugsweise Triphenylphosphin, ist.

5. Verfahren nach Anspruch 3, worin das zugesetzte Olefin nicht dem entkoppelten sekundären Verfahren zugesetzt wird.

6. Verfahren nach den Ansprüchen 1 bis 5, worin das Verhältnis von sekundären entkoppeltem Reaktorkatalysatorvolumen zu primären Reaktorkatalysatorvolumen 0,05 : 1 bis 1 : 1 oder 0,1 : 1 bis 1 : 1 beträgt.

7. Verfahren nach den Ansprüchen 1 bis 6, worin die Hydroformylierungsreaktion in primären und sekundären Verfahren bei einer Reaktionstemperatur von 50 bis 150°C oder von 75 bis 115°C ausgeführt wird.

8. Verfahren nach den Ansprüchen 1 bis 7, worin die Rhodium-Konzentration im primären und sekundären Verfahren 10 bis 700 ppm oder 25 bis 500 ppm beträgt, berechnet als freies Rhodiummetall.

9. Verfahren nach den Ansprüchen 1 bis 8, worin 1 bis 300 mol freier Ligand je mol Rhodium vorhanden sind.

10. Verfahren nach den Ansprüchen 1 bis 9, worin der Gesamtdruck von Olefin, Kohlenmonoxid und Wasserstoff in jedem der primären und entkoppelten sekundären Verfahren weniger als 31 bar abs. (450 psia) beträgt und das Molverhältnis von Wasserstoff zu Kohlenmonoxid 1 : 1 bis 100 : 1 ausmacht.

11. Verfahren nach Anspruch 10, worin der Gesamtdruck von Olefin, Kohlenmonoxid und Wasserstoff weniger als etwa 24 bar abs. (350 psia) beträgt und das Molverhältnis von Wasserstoff zu Kohlenmonoxid 1 : 1 bis 50 : 1 ausmacht.

12. Verfahren nach den Ansprüchen 1 bis 11, worin das Verhältnis von Aldehydprodukt zu den hochsiedenden Aldehyd-Kondensationsnebenprodukten in der Hydroformylierungsreaktionszone jedes Reaktors 1 : 4 bis 20 : 1 im Hydroformylierungsverfahren beträgt.

13. Verfahren nach den Ansprüchen 1 bis 12, worin das Olefin 2 bis 5 Kohlenstoffatome enthält.

Revendications

1. Procédé d'hydroformylation primaire catalysé au rhodium avec recyclage de liquide pour la production d'aldéhydes, dans lequel une oléfine, de l'oxyde de carbone et de l'hydrogène sont mis en réaction en présence d'un catalyseur complexe rhodium-phosphore solubilisé, d'un ligand phosphoré libre et de sous-produits de condensation d'aldéhydes de point d'ébullition élevé, dans lequel un effluent gazeux comprenant de l'oléfine n'ayant pas réagi et du produit aldéhydique, de l'hydrogène, de l'oxyde de carbone et un sous-produit formé d'un alcane est évacué du procédé, caractérisé par la conduite d'un procédé secondaire découplé d'hydroformylation en présence d'un catalyseur au rhodium avec recyclage de liquide ou recyclage de gaz conjointement avec le procédé primaire, où l'effluent gazeux est utilisé conjointement avec de l'oxyde de carbone et de l'hydrogène d'appoint comme charge réactionnelle envoyée au procédé secondaire et où les catalyseurs utilisés dans les procédés primaire et secondaire ont des compositions différentes.

2. Procédé suivant la revendication 1, caractérisé par l'utilisation, comme charge réactionnelle du procédé secondaire découplé, d'un effluent gazeux contenant de l'oléfine n'ayant pas réagi évacué uniquement de l'espace en tête du réacteur primaire

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conjointement avec des quantités d'appoint d'oxyde de carbone et d'hydrogène.

3. Procédé suivant la revendication 2, dans lequel le procédé secondaire découplé d'hydroformylation catalysé au rhodium comprend un procédé de recyclage de gaz ou respectivement un procédé de recyclage de liquide.

4. Procédé suivant la revendication 3, dans lequel le ligand phosphoré libre et le ligand phosphoré du catalyseur complexe rhodium-phosphore est un composé triorganophosphinique, de préférence la triphénylphosphine.

5. Procédé suivant la revendication 3, dans lequel de l'oléfine d'appoint n'est pas ajoutée au procédé secondaire découplé.

6. Procédé suivant les revendications 1 à 5, dans lequel le rapport du volume de catalyseur du réacteur découplé secondaire au volume de catalyseur du réacteur primaire a une valeur de 0,05:1 à 1:1 ou de 0,1:1 à 1:1.

7. Procédé suivant les revendications 1 à 6, dans lequel la réaction d'hydroformylation dans le procédé primaire et dans le procédé secondaire est conduite à une température de réaction de 50 à 145°C ou de 75 à 115°C.

8. Procédé suivant les revendications 1 à 7, dans lequel la concentration en rhodium dans le procédé primaire et le procédé secondaire va de 10 à 700 ppm ou de 25 à 500 ppm, exprimée en rhodium métallique libre.

9. Procédé suivant les revendications 1 à 8, dans lequel 1 à 300 moles de ligand libre sont présentes par mole de rhodium.

10. Procédé suivant les revendications 1 à 9, dans lequel la pression absolue totale d'oléfine, d'oxyde de carbone et d'hydrogène dans chacun des procédés primaire et secondaire découplé est inférieure à 31 bars (450 lb/in^2) et le rapport molaire de l'hydrogène à l'oxyde de carbone va de 1:10 à 100:1.

11. Procédé suivant la revendication 10, dans lequel la pression absolue totale d'oléfine, d'oxyde de carbone et d'hydrogène est inférieure à environ 24 bars (350 lb/in^2) et le rapport molaire de l'hydrogène à l'oxyde de carbone va de 1:1 à 50:1.

12. Procédé suivant les revendications 1 à 11, dans lequel le rapport du produit aldéhydique aux sous-produits de condensation aldéhydiques de haut point d'ébullition dans la zone de réaction d'hydroformylation de chaque réacteur va de 1:4 à 20:1 dans le procédé d'hydroformylation.

13. Procédé suivant les revendications 1 à 12, dans lequel l'oléfine a 2 à 5 atomes de carbone.

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