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CA 2203311 C 2001/08/28

(11)(21) **2 203 311**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(22) Date de dépôt/Filing Date: 1997/04/22

(41) Mise à la disp. pub./Open to Public Insp.: 1997/10/30

(45) Date de délivrance/Issue Date: 2001/08/28

(30) Priorité/Priority: 1996/04/30 (196 17 257.8) DE

(51) Cl.Int.⁶/Int.Cl.⁶ C07C 47/02, C07C 45/50

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(54) Titre : PROCEDE D'HYDROFORMYLATION DE COMPOSES INSATURES OLEFINIQUES

(54) Title: PROCESS FOR THE HYDROFORMYLATION OF OLEFINICALLY UNSATURATED COMPOUNDS

(57) Abrégé/Abstract:

Waste gas which is obtained in the hydroformylation of olefinically unsaturated compounds in the presence of an aqueous catalyst solution comprising water-soluble rhodium complexes (1st reaction stage) is fed to a homogeneous reaction system in which residual amounts of the olefinically unsaturated compounds from the first reaction stage are reacted in a homogeneous reaction system (2nd reaction stage).



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Frankfurt, April 23, 1996

FPR/rcht-sei Hoe96/Y003

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Abstract

Waste gas which is obtained in the hydroformylation of olefinically unsaturated compounds in the presence of an aqueous catalyst solution comprising water-soluble rhodium complexes (1st reaction stage) is fed to a homogeneous reaction system in which residual amounts of the olefinically unsaturated compounds from the first reaction stage are reacted in a homogeneous reaction system (2nd reaction stage).

Process for the hydroformylation of olefinically
unsaturated compounds

The invention relates to an improved process for the hydroformylation of olefinically unsaturated compounds in the presence of an aqueous catalyst solution comprising water-soluble rhodium complexes and, in particular, the utilization of the unreacted olefins escaping with the waste gas from the hydroformylation zone.

The reaction of compounds containing olefinic double bonds with carbon monoxide and hydrogen is the current industrial process for preparing aldehydes (oxo process).

The process is not restricted to the use of olefinic hydrocarbons, but also extends to starting materials which have other functional groups in addition to the double bond, primarily functional groups which remain unchanged under the reaction conditions.

The classical oxo process uses cobalt as catalyst. Its effectiveness depends on the formation of cobalt carbonyl compounds in the presence of hydrogen and carbon monoxide at pressures above 20 MPa and temperatures of about 120°C and more over metallic cobalt or cobalt compounds.

In the last 30 years, cobalt has increasingly been replaced by rhodium as catalyst. The platinum metal is used as a complex containing, apart from carbon monoxide, preferably phosphines as ligands. Rhodium as catalyst enables the reaction to be carried out at low pressures and also gives higher yields and, when straight-chain terminal olefins are used as starting materials, preferentially forms the unbranched products which are more valuable for further processing.

A further improvement of the oxo process comprises the change from catalysts homogeneously dissolved in the reaction medium, i.e. in the starting material and in the reaction product, to aqueous catalyst solutions which are

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present as a separate phase from the starting material and reaction product. This variant of the reaction is described, for example, in DE-B-26 27 354. Its particular advantage is the easy separation of reaction product and catalyst which is carried out under mild conditions without use of thermal process steps and therefore avoids losses which occur as a result of further reactions of the aldehydes formed. Furthermore, very high yields are obtained and, when using unbranched terminal olefins, n-aldehydes are predominantly obtained.

For reasons of process economics, particularly to avoid large reactors or long reaction times, the reaction is not carried to complete consumption of the olefinically unsaturated compounds, but frequently only until from 60 to 95% of the starting material has been converted into the desired end product. The waste gas leaving the hydroformylation zone therefore comprises not only excess carbon monoxide and hydrogen but also unreacted olefinic starting material. While in the past these useful materials were frequently not recovered, efforts are nowadays made to utilize them as completely as possible. These efforts have led to the development of a series of processes of different types.

In one known process (cf. EP 0 111 257 B1), waste gas coming from a hydroformylation stage in which olefin is reacted with carbon monoxide and hydrogen at low pressure in the presence of an aqueous catalyst solution comprising rhodium complexes is reacted in a second stage according to the classical oxide process at high pressure and in the presence of cobalt catalysts. This process has been found to be very useful in practice, particularly when it was possible to combine a modern formylation plant with an existing plant using cobalt as catalyst.

In another method of operation (cf. EP 01 88 246 B1), two rhodium-catalyzed hydroformylation stages are connected in series. In the first stage, olefin, carbon monoxide

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and hydrogen are reacted in the presence of a soluble rhodium-phosphorus complex catalyst, free phosphorus ligands and relatively high-boiling aldehyde condensation by-products with recirculation of liquid or gas. The waste gas comprising olefin, possibly aldehyde, also hydrogen, carbon monoxide and alkane by-product is fed to a decoupled, i.e. operated separately from the first stage, secondary rhodium-catalyzed hydroformylation process in which the waste gas is reacted with added carbon monoxide and hydrogen with recirculation of liquid or gas. This process has the restriction that the hydroformylation in both the first and second stages has to be carried out in the presence of a catalyst homogeneously dissolved in the reaction mixture. The substantial matching of the reaction conditions, in particular the catalyst system in the main and subsequent reaction, virtually rules out the presence in the waste gas from the first stage of components which could adversely affect the hydroformylation in the second stage.

The transfer of the two-stage reaction carried out in homogeneous phases to a process which employs aqueous catalyst solutions in the first and in the second stage is not possible with justifiable technical effort. It fails because the waste gas of the primary stage contains the olefin in a low concentration as a result of the high conversion. Therefore, when using a catalyst system dissolved in water, the processing of the waste gas requires either long reaction times or particular technical measures to restrict the reaction time while nevertheless achieving a high conversion.

It is therefore an object of the present invention to develop a process which allows, under economically justifiable conditions, the conversion of olefinic compounds present in the waste gas of a hydroformylation reaction carried out using an aqueous catalyst solution into carbonyl compounds.

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The invention provides a process for the hydroformylation of olefinically unsaturated compounds, in which the reaction in a first reaction stage is carried out in a heterogeneous reaction system using an aqueous solution comprising, as catalysts, rhodium compounds containing water-soluble organic phosphorus (III) compounds in complexed form at pressures of from 0.4 to 10 MPa and waste gas is formed. In this process, the waste gas from the first reaction stage is fed to a second reaction stage in which the residual amounts of the olefinically unsaturated compounds still present in the waste gas are reacted in a homogeneous reaction system in the presence of, as catalysts, rhodium complexes of organic phosphorus (III) compounds selected from the group consisting of aliphatic, aromatic or mixed aliphatic-aromatic phosphines, or phosphites or organic diphosphites at pressures of from 15 to 40 MPa.

The new process ensures that the major part of the olefinic compounds not reacted in the first stage and present in the waste gas is hydroformylated. In this way, frequently more than 98%, based on the total process, of the starting materials used can be converted into the desired carbonyl compounds, with the conversion essentially depending on the type of starting material and the reaction conditions in the two stages. Worthy of particular emphasis is the fact that by-products which cannot be utilized or are difficult to utilize are formed only in very subordinate amounts. The high efficiency of the process of the invention was not foreseeable. This is because, inter alia, the olefinic compounds are considerably diluted in the waste gas. Thus, for example, in the hydroformylation of lower olefins the proportion of the unreacted olefinic starting material in the waste gas is only from about 20 to 50% by weight. In this type of reaction, such concentrations stand in the way of substantial reaction of the

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unsaturated starting compound. The impurities carried out from the first reaction stage with the waste gas, which are, inter alia, degradation products of the catalyst system (e.g. mercaptans) and water, the solvent for the catalyst in the
5 first stage,

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surprisingly do not impair the effectiveness of the catalyst in the second stage. Such behavior was not to be expected because, in particular, organic derivatives of hydrogen sulfide are known as catalyst poisons. It needs
5 to be taken into account here that mercaptans are hardly soluble in water, as a result of which they do not get into the catalyst solution of the first reaction stage and therefore cannot damage the catalyst either. Instead, the mercaptans accumulate in the homogeneous catalyst-
10 containing reaction mixture of the second stage because of their good solubility in organic media. In addition, water also forms complexes with rhodium and can therefore at least partially replace the organic phosphorus ligands in the homogeneously dissolved rhodium complexes to form
15 catalytically inactive substances.

The first reaction stage of the new process is carried out as a heterogeneous reaction in a two-phase system, a reaction which is described, for example, in DE-B-26 27 354. This process is characterized by the
20 presence of an organic phase comprising the olefinic starting material and the reaction product and an aqueous phase in which the catalyst is dissolved. Catalysts used are water-soluble rhodium complexes containing water-soluble organic phosphorus(III) compounds as ligands.
25 Examples of water-soluble phosphorus(III) compounds which form complexes with rhodium are triarylphosphines, trialkylphosphines and arylated or alkylated diphosphines whose organic radicals contain sulfonic acid groups or carboxyl groups. Their preparation and use is known, for
30 example, from DE-B 26 27 354, EP 0 103 810 B1, EP 0 163 234 B1 and EP 0 571 819 A1. Further groups of suitable compounds are sulfonated or carboxylated organic phosphites and also heterocyclic compounds of trivalent phosphorus (cf. for example EP 0 575 785 A1,
35 EP 0 646 588 A1).

The conditions under which the reaction in the first reaction stage proceeds can be varied within wide limits

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and be matched to the individual circumstances. They depend, inter alia, on the starting material, on the catalyst system selected and on the desired degree of conversion. The hydroformylation of the starting materials is usually carried out at temperatures of from 50 to 180°C. Preference is given to using temperatures of from 80 to 140°C and in particular from 100 to 130°C. The total pressure extends over a range from 0.4 to 10 MPa, preferably from 1 to 6 MPa and in particular from 1.5 to 5 MPa. The molar ratio of hydrogen to carbon monoxide is usually in a range from 1:10 to 10:1; mixtures comprising hydrogen and carbon monoxide in a ratio of from 3:1 to 1:3 and in particular about 1:1 are particularly suitable.

The rhodium concentration is from 20 to 1000 ppm by weight, preferably from 50 to 500 ppm by weight and in particular from 100 to 300 ppm by weight, in each case based on the aqueous catalyst solution. Although it is possible for the catalyst used to be the stoichiometric rhodium-phosphorus complex, the reaction is usually carried out in the presence of excess phosphorus ligands, i.e. ligand which has not undergone complex formation with rhodium. Preference is given to using from 3 to 200 mol of phosphorus in the form of a water-soluble organic phosphorus compound per mol of rhodium. Molar ratios of rhodium to phosphorus in the range from 1:50 to 1:100 have been found to be particularly useful. The rhodium-phosphorus complex catalyst does not have to have a uniform composition, but can, for example, comprise a mixture of rhodium complexes which have different types of phosphorus ligands. Likewise, the free phosphorus ligand present in the aqueous catalyst solution can be composed of a mixture of different water-soluble organic phosphorus compounds. The catalyst is usually formed in the reaction mixture under the conditions of the hydroformylation reaction from the components rhodium or rhodium compound, organic phosphorus compound and synthesis gas. However, it can also be introduced into the

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reaction stage in a preformed state, i.e. prepared separately.

In terms of process technology and apparatus too, the first stage of the new process can be varied within wide limits. A useful embodiment of the heterogeneous hydroformylation using an aqueous catalyst phase is described in EP 0 103 810 B1. It has been found to be advantageous to circulate the catalyst solution and to make up for any catalyst losses by feeding in fresh catalyst.

To increase the conversion per unit time of olefinically unsaturated compounds which are only sparingly soluble in the aqueous catalyst solution it can be advisable to add a phase transfer reagent (solubilizer) to the solution. The phase transfer reagent alters the physical properties of the interfaces between the two liquid phases and aids the transfer of the organic reactants into the aqueous catalyst phase.

Known solubilizers are compounds whose hydrophilic groups are ionic (anionic or cationic) or nonionic. The anionic compounds include sodium, potassium or ammonium salts of carboxylic acids, preferably those having from 8 to 20 carbon atoms, and in particular salts of saturated fatty acids having from 12 to 18 carbon atoms, also alkylsulfates, alkylbenzenesulfonates and alkylbenzenephosphates. Examples of cationic solubilizers are tetraalkylammonium and N-alkylpyridinium salts. The nonionic phase transfer reagents do not dissociate into ions in aqueous solution. They include alkylpolyethylene glycols, alkylphenylpolyethylene glycols, fatty acid alkylolamines and trialkylamine oxides. Ampholytes such as aminocarboxylic acids, betaines and sulfobetaine can also be employed as solubilizers. Corresponding processes are described, for example, in EP 0 157 316 B1.

Finally, it is also possible to use rhodium complexes which simultaneously act as catalyst and phase transfer

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reagent. Such a procedure is, for example, subject matter of EP 0 163 234 B1.

5 In the first reaction stage, a very substantial conversion of the olefinically unsaturated compounds is usually sought. However, in some cases the reaction can also be carried out to some degree of partial conversion.

10 The waste gas (waste gas stream) leaving the first reaction stage is composed of the waste gas taken directly from the reactor (reactor waste gas) in order to avoid accumulation of inerts in the circulated gas mixture and the gaseous components arising in the separation of catalyst solution and crude reaction product in the phase separator (product waste gas). The waste gas stream consists essentially of unreacted olefinic compound, carbon monoxide, carbon dioxide, hydrogen and the hydrogenation products of the olefin. This gas mixture is fed, without further intermediate treatment, in particular without purification, but possibly after mixing in hydrogen alone or a mixture of hydrogen and carbon monoxide, as starting material to a second hydroformylation stage.

25 The second reaction stage is operated independently of the first stage. In the second stage, the residual amounts of the olefinically unsaturated compounds present in the waste gas stream are reacted with carbon monoxide and hydrogen in a homogeneous reaction system. The term homogeneous reaction system means a homogeneous solution composed essentially of solvent, catalyst, olefinically unsaturated compound and reaction product. The catalysts used are rhodium complexes containing organic phosphorus(III) compounds as ligands. Such complexes and their preparation are known (cf. for example US 3 527 809 A1, US 4 148 830 A1, US 4 247 486 A1, US 4 283 562 A1). They can be used as uniform complexes or as a mixture of different complexes. The rhodium concentration in the reaction medium extends over a range

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from about 1 to about 1000 ppm by weight and is preferably from 10 to 700 ppm by weight. In particular, rhodium is employed in concentrations of from 25 to 500 ppm by weight, in each case
5 based on the homogeneous reaction mixture. As in the first stage, the catalyst employed can be the stoichiometric rhodium complex. However, it has been found to be advantageous to carry out the hydroformylation in the presence of a catalyst system comprising rhodium-phosphorus complex and free, i.e.
10 excess, phosphorus ligand which no longer forms a complex with rhodium. The free phosphorus ligand can be the same as in the rhodium complex, but ligands different from this can also be used. The free ligand can be a uniform compound or comprise a mixture of various organophosphorus compounds. Examples of
15 rhodium-phosphorus complexes which can be employed as catalysts are described in US 3 527 809 A1. Preferred ligands in the rhodium complex catalysts include, for example, triarylphosphines such as triphenylphosphine, trialkylphosphines such as tri(n-octyl)phosphine,
20 trilaurylphosphine, tri(cyclohexyl)phosphine, alkylphenylphosphines, cycloalkylphenylphosphines, phosphites and organic diphosphites. Owing to its ready availability, triphenylphosphine is employed particularly frequently.

The molar ratio of rhodium to phosphorus is usually
25 from 1:1 to 1:300, but the molar proportion of the phosphorus in the form of organic phosphorus compounds can also be higher. Preference is given to using rhodium and organically bound phosphorus in molar ratios of from 1:3 to 1:200. When using triarylphosphines, Rh/P molar ratios of from 1:50 to 1:150 have
30 been found to be particularly useful. If trialkylphosphines are used as ligands, the molar ratio of rhodium to phosphorus is preferably from 1:3 to 1:20.

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The hydroformylation reaction is carried out in the presence of a solvent. Solvents used are organic compounds in which starting material, reaction product and

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catalyst system are soluble. Examples of such compounds are aromatic hydrocarbons such as benzene, toluene or the xylenes. Other solvents which can be used are paraffin oil, ketones or ethers. Solvents which have been found to be particularly useful are the relatively high-boiling condensation compounds of the aldehydes which are formed as by-products in the hydroformylation. The proportion of solvent in the reaction medium can be varied over a wide concentration range and is usually between 20 and 90% by weight, preferably from 50 to 80% by weight, based on the reaction mixture.

The reaction pressure in the second stage of the total process is in the range from 15 to 40 MPa. It has been found to be particularly useful to employ pressures between 15 and 35 MPa, preferably from 20 to 30 MPa. Such ranges are unusual for hydroformylations in homogeneous reaction systems and in the presence of complexes of rhodium and organic phosphorus compounds, regardless of whether the reaction is carried out in one or more stages. The volume ratio of hydrogen to carbon monoxide is from 1:10 to 10:1, preferably from 1:3 to 3:1 and in particular 1:1.

The reaction temperatures in the second stage of the new process are from 50 to 160°C. Temperatures of from 60 to 150°C and in particular from 75 to 140°C are preferred.

As already mentioned, the reaction product from the first reaction stage is separated in a phase separator from the aqueous catalyst solution which is returned to the process. According to a useful embodiment, the crude aldehyde is passed through a stripping column in counter-current to fresh synthesis gas. In this way, heat is transferred from the aldehyde to the synthesis gas and the olefinic compound dissolved in the aldehyde is stripped from the crude product and is, together with the heated synthesis gas, again fed to the reaction. The reaction product of the second reaction stage is

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distilled off from the catalyst. It can be combined with the product of the first stage and processed further, e.g. distilled. The catalyst-containing distillation residue from the second reaction stage which remains
5 after separating off the aldehyde is, if appropriate, after addition of fresh catalyst and removal of part of the aldehyde condensation products formed during the course of the reaction, recirculated to the reaction zone.

10 The reaction of straight-chain terminal olefinically unsaturated compounds in the second reaction stage, i.e. using catalyst homogeneously dissolved in the reaction medium, gives as reaction product an aldehyde mixture containing a higher proportion of iso compound than the
15 product of the first stage, i.e. the reaction using a heterogeneous catalyst phase. The new process therefore makes it possible to match the proportions of n- and iso-compound in the reaction product of the overall process to the actual requirements by selection of the olefin
20 conversion in the first stage. According to a further embodiment of the process of the invention, the ratio of n- and iso- compound in the overall process can also be influenced by addition of olefin to the waste gas mixture which is fed to the second reaction stage. Regardless of
25 the type of olefinically unsaturated starting materials, the formation of relatively high molecular weight further reaction products of the aldehydes (thick oil) in the secondary stage is very low.

The process of the invention can be applied to olefinically unsaturated compounds of any structure.
30 Accordingly, suitable starting materials are olefins having an internal or terminal double bond and likewise straight-chain or branched olefins. Furthermore, the olefins can also be additionally substituted by
35 functional groups, in particular those which are not changed during the course of the reaction. Olefinically unsaturated compounds having a plurality of double bonds

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are also suitable as starting materials. The process has been found to be particularly useful in the hydroformylation of olefinically unsaturated hydrocarbons having from 3 to 6 carbon atoms in the molecule, preferably propylene and the isomeric butenes.

The invention is illustrated by the following examples, but is not restricted to the embodiments described.

Example 1

1st reaction stage

10 In a reactor, rhodium acetate and triphenylphosphinetrisulfonate sodium salt (TPPTS) are reacted while stirring vigorously at a synthesis gas pressure ($\text{CO:H}_2 = 1:1$) of 5 MPa and a temperature of 122°C to form the active, water-soluble catalyst HRhCO(TPPTS)_3 . Rhodium compound and TPPTS are used in such an amount that the rhodium concentration in the aqueous catalyst solution is 300 ppm by weight and the molar ratio of rhodium to phosphorus is about 1:100.

20 Via a distributor ring at the bottom of the reactor, preheated propylene is fed into the reaction zone and the olefin is reacted there with carbon monoxide and hydrogen at 122°C and 5 MPa. The product stream comprising gaseous and liquid constituents is taken from the upper part of the reactor and conveyed to a phase separator in which the separation of the aqueous catalyst solution from the crude organic reaction product and from product waste gas takes place. The product waste gas is combined with the reactor waste gas to form the waste gas stream. Reactor waste gas is taken from the reactor to avoid accumulation of inerts in the gas mixture which is circulated. On further cooling, a liquid condensate (waste gas condensate) consisting essentially of propylene and propane separates from the waste gas stream.

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The catalyst solution obtained in the phase separator is pumped back into the reactor. The crude aldehyde is passed through a downstream stripping column in counter-current to synthesis gas. In this column, heat is transferred from the aldehyde to the synthesis gas and at the same time the synthesis gas stream carries out propylene and propane dissolved in the crude aldehyde. As a result of this cooling, water separates from the aldehyde and is returned to the catalyst circuit. Under the reaction conditions selected, the propylene conversion is, depending on throughput and purity of the olefin, between 81 and 91%. The ratio of n-aldehyde to i-aldehyde is about 20:1.

2nd reaction stage

Waste gas stream and waste gas condensate from the first reaction stream are, if appropriate, supplemented by hydrogen and/or carbon monoxide and/or propylene and together with the catalyst solution are compressed to 21 MPa and fed to the second reactor. The catalyst comprises relatively high-boiling aldehyde condensation products in which triphenylphosphine (TPP) and the rhodium complex $\text{HRhCO}(\text{TPP})_3$ are dissolved. The feed mixture is introduced into the reactor from the bottom at a space velocity of 0.5 v/v·h. It has about the following composition (all figures in % by weight).

	Hydrogen	2.20
	Carbon monoxide	29.94
	Carbon dioxide	0.31
	Inerts	1.29
30	Propylene	40.01
	Propane	10.19
	n-Butyraldehyde	6.98
	Isobutyraldehyde	0.54
	Butanols	0.77
35	C8 components	1.60
	>C8 components	2.76

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Triphenylphosphine	1.21
Triphenylphosphine oxide	0.50
Water	1.69
Sulfur	Traces

- 5 The molar ratio of phosphorus to rhodium is about 80:1. The reactants are reacted at 132°C. 99% of the propylene used (i.e. the unreacted propylene from the first reaction stage and any propylene added to the waste gas stream before it enters the second reactor) are converted
- 10 into aldehyde. The product stream leaving the second reactor is depressurized via a separator. Apart from a liquid phase, the crude aldehyde product, this gives a gaseous phase, the depressurization gas, which is fractionally condensed to separate off remaining aldehydes.
- 15 The crude aldehyde is distilled off from the catalyst in a first column and separated into n- and i-butyraldehyde in a second column. The catalyst, which is obtained as a liquid residue in the first column, is mostly returned to the reactor. Only a small substream is bled off in such
- 20 an amount that the concentration of the relatively high-boiling aldehyde condensation products used as solvent for the rhodium catalyst remains approximately constant in the second reactor.

25 Under the reaction conditions selected, the ratio of n-aldehyde:i-aldehyde is 65:35.

Example 2

1st reaction stage

In the first reaction stage, the reactants are reacted in the same way as described in Example 1.

30 2nd reaction stage

Waste gas stream and waste gas condensate are, if

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appropriate, supplemented by hydrogen and/or carbon
monoxide and/or propylene and reacted in an autoclave at
a pressure of from 25 to 27 MPa and a temperature of
130°C. Per 1500 g of propylene, use is made of 80 mg of
5 rhodium and different amounts of trilaurylphosphine so
that the molar ratio of rhodium to phosphine is 1:5 or
1:10.

The results are shown in the table below. They are
compared with the results obtained when using Rh/TPP as
10 catalyst.

Table

	Trilaurylphosphine		Triphenylphosphine
Rh/P ratio	1 : 5	1 : 10	1 : 10
Conversion (%)	96	98	95
n/iso ratio	64/36	64/36	61/39

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CLAIMS:

1. A process for the hydroformylation of olefinically unsaturated compounds, in which the reaction in a first reaction stage is carried out in a heterogeneous reaction system using an aqueous solution comprising, as catalysts, rhodium compounds containing water-soluble organic phosphorus (III) compounds in complexed form at pressures of from 0.4 to 10 MPa and waste gas is formed, wherein the waste gas from the first reaction stage is fed to a second reaction stage in which the residual amounts of the olefinically unsaturated compounds still present in the waste gas are reacted in a homogeneous reaction system in the presence of, as catalysts, rhodium complexes of organic phosphorus (III) compounds selected from the group consisting of aliphatic, aromatic or mixed aliphatic-aromatic phosphines, or phosphites or organic diphosphites at pressures of from 15 to 40 MPa.
2. The process as claimed in claim 1, wherein the hydroformylation in the first reaction stage is carried out at temperatures of from 50 to 180°C and a rhodium concentration of from 20 to 1000 ppm by weight, based on aqueous catalyst solution, and the molar ratio of rhodium to phosphorus in the catalyst solution is from 1:3 to 1:200.
3. The process as claimed in claim 1 or 2, wherein the pressure in the first reaction stage is from 1 to 6 MPa.
4. The process as claimed in claim 3, wherein the pressure in the first reaction stage is from 1.5 to 5 MPa.
5. The process as claimed in any one of claims 1 to 4, wherein the temperature in the first reaction stage is from 80 to 140°C.

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6. The process of claim 5 wherein the temperature in the first reaction stage is from 100 to 130°C.

7. The process as claimed in any one of claims 1 to 6, wherein the concentration of the rhodium in the aqueous catalyst solution is from 50 to 500 ppm by weight.

8. The process of claim 7 wherein the concentration of rhodium in the aqueous catalyst solution is from 100 to 300 ppm by weight.

9. The process as claimed in any one of claims 1 to 8, wherein the molar ratio of rhodium to phosphorus in the aqueous catalyst solution is from 1:50 to 1:100.

10. The process as claimed in any one of claims 1 to 9, wherein the water-soluble organic phosphorus (III) compounds used are sulfonated or carboxylated aliphatic, aromatic or mixed aliphatic-aromatic phosphines or phosphites.

11. The process as claimed in any one of claims 1 to 10, wherein the hydroformylation in the second reaction stage is carried out in the presence of a solvent at temperatures of from 50 to 160°C and a rhodium concentration of from 1 to 1000 ppm by weight, based on the homogeneous reaction mixture, and the molar ratio of rhodium to phosphorus in the reaction mixture is from 1:1 to 1:300.

12. The process as claimed in claim 11, wherein the pressure in the second reaction stage is from 15 to 35 MPa.

13. The process as claimed in claim 12, wherein the pressure in the second reaction stage is from 20 to 30 MPa.

14. The process as claimed in claim 11, 12 or 13, wherein the temperature in the second reaction stage is from 60 to 150°C.

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15. The process as claimed in claim 14, wherein the temperature in the second reaction stage is from 75 to 140°C.

16. The process as claimed in any one of claims 11 to 15,
5 wherein the rhodium concentration in the second reaction stage is from 10 to 700 ppm by weight based on the reaction mixture.

17. The process as claimed in claim 16 wherein the rhodium concentration in the second reaction stage is from 25 to 500 ppm by weight.

18. The process as claimed in any one of claims 11 to 17,
10 wherein, in the second reaction stage, the molar ratio of rhodium to phosphorus in the reaction mixture is from 1:3 to 1:200.

19. The process as claimed in claim 1, wherein the organic phosphorus (III) compound used is a triarylphosphine
15 and the molar ratio of rhodium to phosphorus in the reaction mixture is from 1:50 to 1:150.

20. The process as claimed in claim 19, wherein the triarylphosphine is triphenylphosphine.

21. The process as claimed in claim 1, wherein the
20 organic phosphorus (III) compound is a trialkylphosphine and the molar ratio of rhodium to phosphorus in the reaction mixture is from 1:3 to 1:20.

22. The process as claimed in claim 21, wherein trialkylphosphine is trilaurylphosphine.

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