

Improved process for the hydroformylation of olefins by
reducing the formic acid concentration

5 The invention relates to an improved process for the
hydroformylation of olefins in the presence of
unmodified cobalt carbonyl complexes by reducing the
formic acid content in the aqueous solution comprising
cobalt compounds which is recycled to the
hydroformylation reactor.

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Higher alcohols, in particular those having from 4 to
25 carbon atoms, are known to be able to be prepared by
catalytic hydroformylation (or oxo reaction) of the
olefins having one less carbon atom and subsequent
15 catalytic hydrogenation of the aldehyde- and alcohol-
containing reaction mixtures. They are used
predominantly for the production of plasticizers and
detergents.

20 The type of catalyst system and the optimum reaction
conditions for the hydroformylation depend on the
reactivity of the olefin used. The dependence of the
reactivity of the olefins on their structure is
described, for example, by J. Falbe, New Syntheses with
25 Carbon Monoxide, Springer-Verlag, Berlin, Heidelberg,
New York, 1980, page 95 ff. The differing reactivity
of, in particular, 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).

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Industrial olefin mixtures which are used as starting
materials for the oxo process comprise olefin isomers
of a variety of structures with different degrees of
branching, different positions of the double bond in
35 the molecule and possibly also different numbers of
carbon atoms. This is particularly true of olefin
mixtures which have been formed by dimerization or
trimerization or further oligomerization of C_2-C_5

olefins or other readily available higher olefins or by cooligomerization of such olefins. As examples of typical isomeric olefin mixtures which can be reacted by rhodium-catalyzed or preferably cobalt-catalyzed hydroformylation to give the corresponding aldehyde and alcohol mixtures, mention may be made of tripropenes and tetrapropenes and also dibutenes, tributenes and tetrabutenes.

10 If alcohols having a very low degree of branching are sought as hydroformylation product, the hydroformylation is advantageously carried out using unmodified cobalt catalysts. Compared to rhodium catalysts, use of cobalt catalysts and an identical
15 olefin mixture gives higher yields of the particularly valuable oxo products having a higher content of straight chains.

The hydroformylation of olefins catalyzed by unmodified
20 cobalt carbonyl complexes gives reaction mixtures comprising aldehydes, alcohols, their formic esters, unreacted olefins, free formic acid and further by-products as well as the catalyst. In order to obtain an almost cobalt-free reaction mixture which is suitable
25 for further processing, the cobalt compounds have to be removed from the hydroformylation product. In addition, for cost reasons, the cobalt compounds which have been separated off have to be recycled to the process.

30 During the hydroformylation and/or during removal of the catalyst, formic acid is formed by hydrolysis of formic esters. This reduces the rate of formation of the active catalysts, namely the cobalt carbonyls.

35 A conventional method of recovering the catalyst from the hydroformylation mixture comprises extracting cobalt compounds from the reactor output by means of aqueous base, liberating HCo(CO)_4 from the extract by acidification and returning it to the hydroformylation

(Kuhlmann process). A disadvantage of this process is that a salt of the base used is formed as by-product and has to be disposed of.

5 GB 2055371 describes a process comprising the following steps:

10 a) Part of the cobalt carbonyls present in the hydroformylation product is reacted with an aqueous cobalt(II) salt solution to form $\text{Co}[\text{Co}(\text{CO})_4]_2$. At the same time, the cobalt complex salt is extracted into the aqueous phase.

15 b) In a second step, the remaining cobalt carbonyls are oxidized by means of oxygen in the presence of an aqueous acid to give cobalt(II) salts. The aqueous extract formed is used in the first step.

20 c) The active cobalt compounds, i.e. the cobalt catalyst, are prepared from the extract of the first step by reaction with synthesis gas in the presence of an organic solvent.

25 A disadvantage of this process is that just the separation of the cobalt compounds from the hydroformylation product requires an oxidation step and two phase separations.

30 WO 93/24437 describes a process for catalyst removal and regeneration, which essentially comprises the following steps:

35 a) After depressurization of the hydroformylation product, the cobalt compounds are extracted from it under reductive or oxidative conditions (in the presence of oxygen) by extraction with an aqueous solution having a pH of not more than 7, in particular an aqueous solution comprising formic acid.

In the oxidative extraction, the following work-up procedure is used:

- 5 b) The aqueous extract comprising the cobalt compounds is concentrated by distillation. The top product is a mixture of water and acids (formic acid) which is partly returned to the extraction step a).
- 10 c) The aqueous concentrate from b) is reacted with synthesis gas at elevated temperature and super-atmospheric pressure to give a mixture comprising cobalt carbonyls.
- 15 d) The cobalt carbonyls are stripped from the mixture obtained from c). The remaining aqueous stream is recirculated to a).
- 20 e) The cobalt carbonyls are extracted from the strip gas using starting olefin (for the hydroformylation).

25 In the nonoxidative work-up, the same process steps are carried out, but in a different order (a-d-c-b) and with the further difference that the largely cobalt-free aqueous stream from step d) is divided into two substreams which are recirculated to the steps a) and b).

30 WO 93/24438 and US 5 321 168 describe further developments of the process disclosed in WO 93/24437. In the same sequence of work-up steps, a palladium catalyst is additionally used in the catalyst preformation (step c). US 5 321 168 additionally
35 describes the restoration of the activity of the palladium catalyst.

These work-up methods are very complex and incur high capital costs and operating costs.

A further process is described in J. Falbe, New Syntheses with Carbon Monoxide, Springer-Verlag, Berlin, Heidelberg, New York, 1980, page 164, 165 (BASF process) and comprises the following steps:

- a) Oxidation of the cobalt carbonyls by oxygen in the presence of acids, in particular formic acid formed in the process, to give cobalt(II) salts and their extraction from the hydroformylation mixture.
- b) Reduction of the cobalt(II) salts in the aqueous extract from step a) in the presence of an organic solvent to give cobalt carbonyls.
- c) Extraction of the cobalt carbonyls into an organic phase, advantageously the starting olefin, and feeding them into the hydroformylation reactor.

DE 196 54 340 describes a hydroformylation process in which the steps b) and c) are carried out in situ in the hydroformylation reactor, as a result of which the capital costs and operating costs are reduced. The space-time yields of this process also depend on the formation and stability of the catalyst complex in the hydroformylation reactor. This is still capable of improvement.

In all the existing processes, the formic acid concentration is either not influenced or controlled at all and remains at the concentration established as a result of the reaction conditions, or is reduced by a further process step such as distillation.

It is therefore an object of the invention to develop a hydroformylation process for olefins which has a closed cobalt catalyst circuit and makes simple catalyst recirculation and a high space-time yield possible.

It has surprisingly been found that the space-time yield of a hydroformylation reaction can be increased

if the formic acid concentration is reduced in the aqueous cobalt(II) salt solution which is fed to the hydroformylation reactor or in the total process.

5 The present invention accordingly provides a process for preparing aldehydes having from 4 to 25 carbon atoms by hydroformylation of the corresponding olefins in the presence of a cobalt catalyst, wherein the formic acid formed in the hydroformylation or in the
10 subsequent catalyst work-up is decomposed catalytically.

The decomposition of the formic acid is preferably carried out in an aqueous phase which is subsequently,
15 i.e. after decomposition of the formic acid has occurred, returned in full or in part to the hydroformylation process.

The crude aldehydes prepared by the process of the
20 invention are preferably used for preparing alcohols by hydrogenation.

The hydroformylation and the separation of the cobalt catalyst from the hydroformylation product can be
25 carried out, for example, as described in DE 196 54 340 A1. This is a single-stage process in which the olefins are reacted with an aqueous cobalt salt solution and synthesis gas in a homogeneous phase, preferably in a cascaded reactor, particularly
30 preferably by means of a mixing nozzle. The reaction product is subsequently treated oxidatively in the presence of an aqueous solution of carboxylic acids, predominantly formic acid; after phase separation, part of the aqueous phase comprising the cobalt salts is
35 returned to the single-stage process and the organic phase is worked up further to give the products (aldehyde) or hydrogenated to the corresponding alcohols. The aqueous solution recirculated to the hydroformylation reactor contains virtually the same

amount of cobalt as is discharged with the hydroformylation mixture.

For the catalytic decomposition of the formic acid, it
5 is in principle possible to use the formic acid-
containing reaction mixture formed in the hydro-
formylation before or after oxidation of the cobalt
carbonyls. The cobalt compounds are separated from the
hydroformylation product only afterward. However, this
10 procedure is not advisable with a view to the total
process.

The process of the invention is advantageously carried
out by separating the reaction mixture formed in the
15 hydroformylation in the presence of an aqueous phase by
oxidative treatment and subsequent phase separation
into an organic product phase and an aqueous phase
comprising cobalt salts and formic acid and using all
or part of the aqueous phase for the catalytic
20 decomposition of the formic acid.

The proportion of aqueous phase which is not used for
the decomposition of the formic acid can be returned to
the cobalt removal step.

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The aqueous solution obtained in this way, which has
been largely freed of formic acid, can be recirculated
to the hydroformylation process.

30 To reduce the concentration of formic acid in the
overall process, it can be sufficient to use part of
the aqueous phase which is to be recirculated to the
hydroformylation reactor or part of the
hydroformylation mixture for the catalytic
35 decomposition of the formic acid. Likewise, it is
possible to decompose only part of the formic acid in
the decomposition reactor. In most cases, it is
sufficient for at least 50%, preferably from 50 to 80%,

of the formic acid formed in the process to decompose catalytically.

In any case, the solution or mixture used for the decomposition of the formic acid contains cobalt compounds, either as cobalt carbonyl or, after the oxidative work-up, as cobalt(II) salt. The concentration of these cobalt compounds can be varied within a wide range. It only has to be ensured that no cobalt compounds are precipitated during the work-up. The concentration of the cobalt salt solution is partly determined by the amount of water which is discharged from the reactor with the hydroformylation mixture. Since water is discharged from the process with the decobalted hydroformylation mixture, i.e. the organic phase after the catalyst has been separated off, water has to be metered in to avoid an increase in the concentration. Possible feed points for this water are, for example, the reactor feed, the cobalt removal unit or the crude product scrubber.

If desired, part of the formic acid can be separated off by distillation and the formic acid in the distillate can be decomposed by the process of the invention.

It is known that formic acid reacts with oxygen over heavy metal catalysts, in particular Pd catalysts, to form carbon dioxide and water. Likewise, formic acid can be oxidized in the absence of catalysts, e.g. using hydrogen peroxide.

Suitable catalysts for the decomposition of the formic acid in the process of the invention are catalysts comprising Al_2O_3 , SiO_2 , TiO_2 , MgO and their mixed oxides, zeolites or activated carbon as support materials. As active metals, the catalysts used in the process can comprise metals of groups VIII, VIIa and Ib of the Periodic Table of the Elements. These metals can be

used in elemental or oxidic form, in each case as a mixture or as a mixed oxide. In the process of the invention, preference is given to using supported catalysts, in particular Pd/Al₂O₃ catalysts.

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In the oxidative removal of formic acid in aqueous cobalt salt solutions, cobalt(II) is partly oxidized to cobalt(III). This leads to precipitation of Co(III) compounds with increasing pH. When the decomposition is
10 carried out in the absence of oxygen or another oxidant, this reaction does not take place. For this reason, the invention gives preference to nonoxidative methods, e.g. decomposition of the formic acid in the presence of synthesis gas, hydrogen, carbon monoxide,
15 carbon dioxide or nitrogen.

In particular, the formic acid in the aqueous cobalt salt solution obtained after the oxidative removal of cobalt from the hydroformylation product can be
20 decomposed catalytically.

The process of the invention for hydroformylation with formic acid decomposition can be carried out continuously or batchwise and either in the liquid
25 phase or at least partly in the gas phase. Continuous decomposition in the liquid phase is the preferred method of carrying out the process.

The decomposition of the formic acid can be carried out
30 in stirred reactors or preferably in tube reactors. In the second case, the decomposition reaction can be carried out in a single pass or with recirculation of the solution (loop). The reactors can be operated as cocurrent reactors with trickle flow or with high
35 liquid throughputs (pulse flow). It is also possible to connect a plurality of reactors with one another. These can be operated in the same mode or in different modes.

The decomposition of the formic acid is carried out in a temperature range from 100°C to 300°C, preferably in the range from 120°C to 200°C. The total pressure is generally from 1 bar to 350 bar, in particular from 1 bar to 25 bar.

The space velocities over the catalyst in the formic acid decomposition are from 0.5 h⁻¹ to 5 h⁻¹, in particular from 1 h⁻¹ to 3 h⁻¹.

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If desired, the formic acid decomposition can be carried out in the presence of a purge gas, for example carbon monoxide, nitrogen, hydrogen or synthesis gas.

15 The aqueous solutions which have been depleted in or freed of formic acid can, if appropriate after having been concentrated, if desired after premixing with starting material and possibly synthesis gas, be fed back into the hydroformylation reactor.

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In another embodiment of the present invention, the catalytic decomposition of the formic acid is carried out in the presence of synthesis gas to form the cobalt catalyst used in the hydroformylation of the respective olefins (known as preformation).

25 The preparation of this cobalt catalyst (HCo(CO)₄ and Co₂(CO)₈) by reacting aqueous cobalt(II) salt solutions with synthesis gas at elevated pressures and temperatures is, as described above, known. This reaction can be accelerated by means of Pd catalysts, as is described in the patents US 5 321 168, US 5 434 318 and WO 93/24438. Here, an aqueous cobalt(II) salt solution is reacted with synthesis gas over a Pd catalyst in the presence of an organic solvent, preferably an alcohol. A disadvantage of these methods is that the catalyst is deactivated and has to be regenerated at intervals. The regeneration is carried out as described in US 5 321 168 by scrubbing

with water, with or without addition of formic acid, under synthesis gas at a pressure of 138-310 bar and a temperature of 120-170°C. According to US 5 434 318, scrubbing is carried out under the abovementioned
5 conditions using a mixture of alcohol and aqueous formic acid.

The processes mentioned encompass only the formation of cobalt carbonyls from cobalt(II) salt solutions, but
10 not the decomposition of formic acid.

In a particular embodiment of the present invention, the decomposition of formic acid can be carried out with simultaneous formation of cobalt carbonyl
15 compounds, in each case either batchwise or continuously.

This reaction, too, can be carried out in stirred reactors or preferably in tube reactors. In the second
20 case, the reaction can be carried out in a single pass or with recirculation of the solution (loop). The reactors can be operated as cocurrent reactors with trickle flow or with high liquid throughputs (pulse flow). It is also possible for a plurality of reactors
25 to be connected to one another. These can be operated in the same mode or in different modes. The combined reactions can be carried out in the presence of synthesis gas at a total pressure of from 150 bar to 330 bar, in particular from 200 bar to 300 bar.

30 The molar ratio of carbon monoxide to hydrogen in the synthesis gas used can be in the range from 2/1 to 1/2.

The reaction temperatures in the combined formic acid
35 decomposition and preformation can be in the range from 140°C to 220°C, preferably from 160°C to 180°C. The space velocities over the catalyst (LHSV) are from 0.5 h⁻¹ to 5 h⁻¹, preferably from 1 h⁻¹ to 3 h⁻¹.

As catalysts for the decomposition of formic acid with simultaneous formation of the cobalt catalyst, it is possible to use the same ones which are used in the decomposition of the formic acid alone.

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The liquid reaction product from the combined decomposition and preformation reactor is introduced into the hydroformylation reactor. The waste gas obtained is fed to the oxidizer or preferably likewise
10 to the hydroformylation reactor.

If desired, the decomposition of the formic acid, possibly with simultaneous formation of cobalt carbonyls, can be carried out in the presence of
15 organic solvents comprising, for example, alcohols or aldehydes, in particular the starting materials and products of the hydroformylation reaction. These are advantageously liquid hydrocarbons which are liquid under the reaction conditions of the hydroformylation
20 and/or the corresponding olefins.

In any case, it is possible to recirculate the cobalt catalyst formed in the decomposition of formic acid to the hydroformylation reaction.

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A hydroformylation plant operating according to the process of the invention requires a somewhat higher capital investment compared to a conventional plant. This small disadvantage is more than compensated for by
30 the higher space-time yield and also further advantages:

The formic acid concentration in the overall plant, in particular in the lower part of the hydroformylation
35 reactor and in the downstream oxidizer (cobalt removal unit), is reduced.

The hydroformylation rate and thus the space-time yield of the hydroformylation reaction is increased, since

the mean concentration of active cobalt compounds in the hydroformylation reactor is greater.

5 A further advantage is that the decomposition of the major part of the formic acid generated in the process results in only waste streams containing less formic acid being obtained. This reduces environmental pollution.

10 The following examples illustrate the invention but do not restrict its scope which is defined by the claims.

Example 1:

15 A Co-containing process water (3850 g) after cobalt removal from the hydroformylation of dibutene, which contained the cobalt salt (cobalt formate) with 0.85% by weight of Co (calculated as Co metal) and about 1.0% by weight of free formic acid, was treated in an intermediate-pressure circulation apparatus in the
20 presence of 198 g of supported Pd/Al₂O₃ catalyst (1.0% by weight of Pd, Al₂O₃ extrudates, 4 mmx4 mm) to reduce the formic acid contents at a temperature of 135°C and a pressure of 15 bar. The change in the cobalt and formic acid contents and the pH of the Co process water
25 over time were followed by appropriate sampling. The starting material and product analyses are shown in Table 1 below.

Residence time [min]	Formic acid [% by weight]	Cobalt content [% by weight]	pH
0	1.0	0.85	3.45
5	0.65	0.85	3.82
10	0.47	0.84	4.01
15	0.32	0.85	4.22
20	0.22	0.84	4.45
30	0.10	0.85	4.81

Table 1: Decomposition of formic acid in the presence of Pd/Al₂O₃ catalyst

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It can be seen that the contents of free formic acid in the Co process water can be reduced by catalytic decomposition without oxygen in the presence of Pd/Al₂O₃ catalyst.

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The decrease in the formic acid concentration from 1.0% by weight to 0.10% by weight results in an increase in the pH from 3.45 to 4.81.

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Example 2:

In a 2 liter high-pressure autoclave, the Co-containing process water having a composition as described in Example 1 was carbonylated before and after the formic acid decomposition described in Example 1 at 180°C and 270 bar with synthesis gas (50% by volume of CO, 50% by volume of H₂) to prepare cobalt carbonyls, i.e. a catalyst system active for hydroformylation of olefins. The Co process water contained 0.85% by weight of Co in the form of cobalt formate and 1.0 or 0.10% by weight of formic acid. After a treatment time of 3 hours, the carbonylation was stopped and the reaction product was analyzed to determine the cobalt carbonyl content. To determine the "active" cobalt in the Co water, the reaction product was reacted with iodine to liberate CO

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from the cobalt carbonyls. The amounts of CO liberated enabled the concentration of the cobalt carbonyls and thus the proportion of "active" cobalt in the total amount of Co to be determined.

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After a treatment time of 3 hours, the formic acid-rich Co water had an activity of 21%, i.e. 21% of 0.85% by weight of Co is present as cobalt carbonyl, i.e. in a form which can be used as catalyst for the hydroformylation of olefins. In comparison, the use of Co water having a low formic acid content after formic acid decomposition achieved a significantly higher activity with 38% of "active" cobalt.

15 Example 3:

A Co-containing process water from the cobalt removal step of a hydroformylation of dibutene, containing 1.05% by weight of Co (calculated as Co metal) and about 0.95% by weight of free formic acid, was carbonylated at 180°C and 270 bar with synthesis gas (50% by volume of CO, 50% by volume of H₂) in the presence of a supported Pd/Al₂O₃ catalyst (1.0% by weight of Pd) in powder form in a 2 liter high-pressure autoclave (1 l of Co water, 10 g of Pd/Al₂O₃) to prepare cobalt carbonyls, i.e. a catalyst system active for the hydroformylation of olefins. After a treatment time of 3 hours, the reaction was stopped and the reaction product was analyzed to determine the cobalt carbonyl content as described in Example 2. The analysis of the reaction product indicated an activity of about 40%.

This result shows that the reduction of the formic acid contents by decomposition and the Co carbonylation can be carried out in one process step.

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Example 4:

The Co water carbonylated in Example 2, containing 0.85% by weight of Co (total Co calculated as metal) and having a Co activity of 21%, was used as catalyst

for the hydroformylation of dibutene (C_8 -olefin mixture) to give C_9 -aldehydes. For this purpose, the active cobalt carbonyls were firstly extracted with stirring from the Co water into the starting material
5 dibutene (1000 g of dibutene, 250 g of Co water) in a 2 liter high-pressure autoclave. After separating off the aqueous phase, the dibutene laden with cobalt carbonyls was hydroformylated for 5 hours at a temperature of $185^\circ C$ and a synthesis gas pressure of
10 270 bar. After cooling to room temperature, the reaction mixture was depressurized and freed of the cobalt catalyst by treatment with acetic acid and air at $80^\circ C$. According to the GC analysis carried out, the reaction mixture has the following composition: 10.5%
15 by weight of C_8 -olefins, 2.5% by weight of C_8 -paraffins, 54.8% by weight of C_9 -aldehyde, 22.6% by weight of C_9 -alcohol, 4.5% by weight of C_9 -formates and 5.1% by weight of high boilers. Accordingly, a dibutene conversion of 87.0% at a desired product selectivity of
20 90.6% was obtained, corresponding to a desired product yield of 78.8% based on the dibutene used. Desired products are considered to be C_9 -aldehydes, C_9 -alcohols and C_9 -formates.

25 Example 5:

For comparison with Example 4, the Co water carbonylated in Example 2, which had an increased Co activity of 38%, was used as catalyst for the hydroformylation of dibutene to give C_9 -aldehyde. For this
30 purpose, the active cobalt carbonyls were firstly extracted with stirring from the Co water into the starting material dibutene (1000 g of dibutene, 250 g of Co water) in a 2 l high-pressure autoclave, as described in Example 4. After separating off the
35 aqueous phase, the dibutene laden with cobalt catalyst was hydroformylated for 5 hours at $185^\circ C$ and 270 bar. After cooling to room temperature, the reaction mixture was depressurized and freed of the cobalt catalyst by treatment with acetic acid and air at $80^\circ C$. GC analysis

of the reaction mixture after cobalt removal indicates the following composition: 6.2% by weight of C₈-olefins, 3.3% by weight of C₈-paraffins, 55.1% by weight of C₉-aldehyde, 25.4% by weight of C₉-alcohol, 5 4.5% by weight of C₉-formates and 5.5% by weight of high boilers. Accordingly, a dibutene conversion of 92.3% at a desired product selectivity of 89.5% was obtained, corresponding to a desired product yield of 82.6% based on the dibutene used. Desired products are 10 considered to be C₉-aldehydes, C₉-alcohols and C₉-formates.

It can be seen that a reduction in the formic acid contents of the Co water leads to a significant 15 improvement in the desired product yields and thus the space-time yield of the reaction.



Claims:

1. A process for preparing aldehydes having from 4 to 25 carbon atoms by hydroformylation of the corresponding olefins in the presence of a cobalt catalyst, wherein the formic acid formed in the hydroformylation or in the subsequent catalyst work-up is decomposed catalytically.
2. The process as claimed in claim 1, wherein the reaction mixture formed in the hydroformylation is separated in the presence of an aqueous phase by oxidative treatment and subsequent phase separation into an organic product phase and an aqueous phase comprising cobalt salts and formic acid and all or part of the aqueous phase is used for the catalytic decomposition of formic acid.
3. The process as claimed in claim 1 or 2, wherein the decomposition of the formic acid is carried out in an aqueous phase and all or part of this is subsequently returned to the hydroformylation process.
4. The process as claimed in any of claims 1 to 3, wherein catalysts comprising metals of groups Ib, VIIa and VIII of the Periodic Table of the Elements are used in elemental or oxidic form, in each case as a mixture or as a mixed oxide, for the catalytic decomposition of formic acid.
5. The process as claimed in claim 4, wherein the catalysts comprise Al_2O_3 , SiO_2 , MgO , zeolites or activated carbon as support material.
6. The process as claimed in any of claims 1 to 5, wherein the catalytic decomposition of formic acid is carried out continuously.



7. The process as claimed in any of claims 1 to 6, wherein the catalytic decomposition of formic acid is carried out at a temperature of from 100 to 300°C and a pressure of from 1 to 350 bar.
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8. The process as claimed in any of claims 1 to 7, wherein the catalytic decomposition of the formic acid proceeds to an extent of at least 50%.
- 10 9. The process as claimed in any of claims 1 to 8, wherein the catalytic decomposition of formic acid is carried out in the presence of synthesis gas, hydrogen, nitrogen or carbon monoxide.
- 15 10. The process as claimed in any of claims 1 to 9, wherein the catalytic decomposition of formic acid is carried out in the presence of synthesis gas to form the cobalt catalyst used in the hydroformylation of the respective olefins.
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11. The process as claimed in any of claims 1 to 10, wherein the catalytic decomposition of formic acid is carried out at a pressure of from 150 to 330 bar.
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12. The process as claimed in claim 10 or 11, wherein the catalytic decomposition of formic acid is carried out at a temperature of from 140 to 220°C.
- 30 13. The process as claimed in any of claims 1 to 12, wherein the catalytic decomposition of formic acid is carried out in the presence of organic solvents.
- 35 14. The process as claimed in claim 13, wherein the organic solvents comprise hydrocarbons which are liquid under the reaction conditions of the hydroformylation and/or the respective olefins.



15. The process as claimed in claim 13, wherein the organic solvents comprise the aldehydes and/or alcohols obtained from the hydroformylation.
- 5 16. The process as claimed in any of claims 10 to 15, wherein the cobalt catalyst formed in the catalytic decomposition of formic acid is recirculated to the hydroformylation reaction.
- 10 17. The use of the aldehydes prepared as claimed in any of claims 1 to 16 for the preparation of alcohols by hydrogenation.