

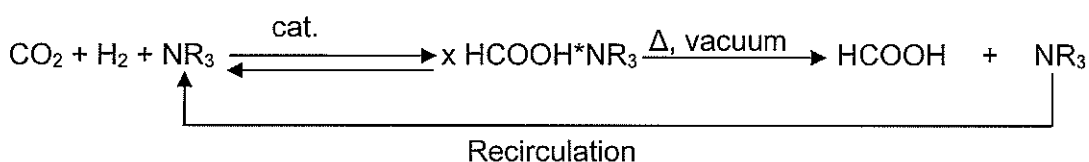
Process for preparing formic acid by reaction of carbon dioxide with hydrogen

Description

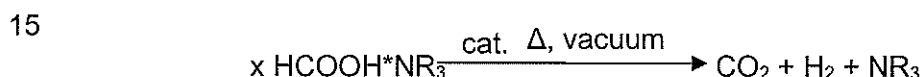
- 5 The invention relates to a process for preparing formic acid by reaction of carbon dioxide with hydrogen in a hydrogenation reactor in the presence of a catalyst comprising an element of group 8, 9 or 10 of the Periodic Table, a tertiary amine and a polar solvent to form formic acid/amine adducts as intermediates which are subsequently thermally dissociated.
- 10 Adducts of formic acid and tertiary amines can be thermally dissociated into free formic acid and tertiary amine and therefore serve as intermediates in the preparation of formic acid.
- 15 Formic acid is an important and versatile product. It is used, for example, for acidification in the production of animal feeds, as preservative, as disinfectant, as auxiliary in the textile and leather industry, as a mixture with its salts for deicing aircraft and runways and also as synthetic building block in the chemical industry.
- 20 The abovementioned adducts of formic acid and tertiary amines can be prepared in various ways, for example (i) by direct reaction of tertiary amine with formic acid, (ii) by hydrolysis of methyl formate to form formic acid in the presence of the tertiary amine or (iii) by catalytic hydration of carbon monoxide or hydrogenation of carbon dioxide to form formic acid in the presence of the tertiary amine. The latter process of catalytic
- 25 hydrogenation of carbon dioxide has the particular advantage that carbon dioxide is available in large quantities and is flexible in terms of source.
- An industrially promising process appears to be, in particular, the catalytic hydrogenation of carbon dioxide in the presence of amines (W. Leitner, *Angewandte Chemie* 1995, 107, pages 2391 to 2405; P. G. Jessop, T. Ikariya, R. Noyori, *Chemical Reviews* 1995, 95, pages 259 to 272). The adducts of formic acid and amines formed here can be thermally dissociated into formic acid and the amine used, which can be recirculated to the hydrogenation.
- 30
- 35 The catalyst necessary for the reaction comprises one or more elements from group 8, 9 or 10 of the Periodic Table, i.e. Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and/or Pt. The catalyst preferably comprises Ru, Rh, Pd, Os, Ir and/or Pt, particularly preferably Ru, Rh and/or Pd and very particularly preferably Ru.

To make an economical process possible, the catalyst used has to be separated off ideally completely from the product stream and recirculated to the reaction, for two reasons:

- 5 (1) large losses of the expensive catalyst would incur considerable additional costs and would be prohibitive for economical operation of the process.
- (2) in the thermal dissociation of the formic acid/amine adducts, very little catalyst should be present since in the absence of a CO₂ and/or H₂ pressure this also catalyzes the reverse reaction and thus leads to losses of the
10 formic acid formed.



Formation of formic acid by CO₂ hydrogenation (x = 0.4 – 3)



Decomposition of formic acid/amine adducts in the presence of a catalyst (x = 0.4 – 3)

- 20 The transition metal-catalyzed decomposition of formic acid has been described comprehensively, especially recently: C. Fellay, N. Yan, P.J. Dyson, G. Laurenczy *Chem. Eur. J.* **2009**, *15*, 3752-3760; C. Fellay, P.J. Dyson, G. Laurenczy *Angew. Chem.* **2008**, *120*, 4030-4032; B. Loges, A. Boddien, H. Junge, M. Beller *Angew. Chem.* **2008**, *120*, 4026-4029; F. Joó *ChemSusChem* **2008**, *1*, 805-808; S. Enthaler
- 25 *ChemSusChem* **2008**, *1*, 801-804; S. Fukuzumi, T. Kobayashi, T. Suenobu *ChemSusChem* **2008**, *1*, 827-834; A. Boddien, B. Loges, H. Junge, M. Beller *ChemSusChem* **2008**, *1*, 751-758.

- 30 The catalysts used here are in principle also suitable in principle for the hydrogenation of CO₂ to formic acid (P.G. Jessop, T. Ikariya, R. Noyori *Chem. Rev.* **1995**, *95*, 259-272; P.G. Jessop, F. Joó, C.C. Tai *Coord. Chem. Rev.* **2004**, *248*, 2425-2442; P.G. Jessop, *Homogeneous Hydrogenation of Carbon Dioxide*, in: *The Handbook of Homogeneous Hydrogenation*, Hrsg.: J.G. de Vries, C.J. Elsevier, Volume 1, **2007**, Wiley-VCH, pp. 489-511). Thus, the hydrogenation catalysts have to be separated off

before the thermal dissociation in order to prevent the undesirable decomposition of formic acid.

WO 2008/116,799 discloses a process for the hydrogenation of carbon dioxide in the presence of a catalyst which comprises a transition metal of transition group VIII (groups 8, 9, 10) and is suspended or homogeneously dissolved in a solution, a tertiary amine having at least one hydroxyl group and a polar solvent to form an adduct of formic acid and the tertiary amine. The hydroxyl group(s) in the tertiary amine enable an increased carbon dioxide solubility compared to the triethylamine which is usually used to be achieved. As preferred homogeneous catalysts, mention may be made of RuH_2L_4 having monodentate phosphorus-based ligands L and $\text{RuH}_2(\text{LL})_2$ having bidentate phosphorus-based ligands LL and particularly preferably $\text{RuH}_2[\text{P}(\text{C}_6\text{H}_5)_3]_4$. As polar solvents, mention may be made of alcohols, ethers, sulfolanes, dimethyl sulfoxide and amides whose boiling point at atmospheric pressure is at least 5°C above that of formic acid. The tertiary amines which are preferably to be used also have a boiling point above that of formic acid. Since no phase separation takes place, the work-up of the entire reaction product mixture is carried out by distillation, optionally after prior removal of the catalyst, in which the adduct of formic acid and the tertiary amine which is formed is thermally dissociated and the formic acid liberated is isolated as overhead product. The bottom product comprising tertiary amine, polar solvent and optionally catalyst is recirculated to the hydrogenation stage.

A disadvantage of this process is the introduction of the entire liquid reaction product mixture into the apparatus for thermal dissociation and distillation, optionally after prior specific removal of the homogeneous catalyst by means of a separate process step, for example an extraction, adsorption or ultrafiltration step. The apparatus for the thermal dissociation and distillation consequently has to be made larger and more complex both in terms of the higher liquid throughput and the more specific separation properties, which is reflected, inter alia, in the capital costs (for example via engineering input, material, space requirement). In addition, the higher liquid throughput also results in a higher energy usage.

However, the fundamental work on the catalytic hydrogenation of carbon dioxide to form formic acid was carried out as early as the 1970s and 1980s. The processes of BP Chemicals Ltd filed as the patents EP 0 095 321 A, EP 0 151 510 A and EP 0 181 078 A may be considered to result therefrom. All three documents describe the hydrogenation of carbon dioxide in the presence of a homogeneous catalyst comprising a transition metal of transition group VIII (groups 8, 9, 10), a tertiary amine and a polar solvent to form an adduct of formic acid and the tertiary amine. As preferred homogeneous catalysts, EP 0 095 321 A and EP 0 181 078 A in each case make mention of ruthenium-based carbonyl-, halide- and/or triphenylphosphine-

comprising complex catalysts and EP 0 151 510 A mentions rhodium-phosphine complexes. Preferred tertiary amines are C₁-C₁₀-trialkylamines, in particular the short-chain C₁-C₄-trialkylamines, and also cyclic and/or bridged amines such as 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,4-diazabicyclo[2.2.2]octane, pyridine or picolines. The hydrogenation is carried out at a carbon dioxide partial pressure of up to 6 MPa (60 bar), a hydrogen partial pressure of up to 25 MPa (250 bar) and a temperature from about room temperature to 200°C.

EP 0 095 321 A and EP 0 151 510 A teach the use of an alcohol as polar solvent. However, since primary alcohols tend to form formic esters (organic formates), secondary alcohols, in particular isopropanol, are preferred. In addition, the presence of water is described as advantageous. According to the examples in EP 0 095 321 A, the reaction product mixture is worked up by directly subsequent two-stage distillation in which the low boilers alcohol, water, tertiary amine are separated off in the first stage and the adduct of formic acid and the tertiary amine is separated off at the top under vacuum conditions in the second stage. EP 0 151 510 A likewise teaches a work-up by distillation, but with reference to EP 0 126 524 A with subsequent replacement of the tertiary amine in the adduct which has been separated off by distillation by a weaker, less volatile nitrogen base before thermal cleavage of the adduct in order to aid or make possible the subsequent thermal dissociation to produce free formic acid.

EP 0 181 078 A teaches the targeted choice of the polar solvent on the basis of three essential criteria which have to be fulfilled at the same time:

- (i) the homogeneous catalyst has to be soluble in the polar solvent;
- (ii) the polar solvent must not have an adverse effect on the hydrogenation; and
- (iii) the adduct of formic acid and the tertiary amine which is formed should be able to be readily separated off from the polar solvent.

As particularly suitable polar solvents, mention is made of various glycols and phenylpropanols.

According to the teaching of EP 0 181 078 A, the work-up of the reaction product mixture is carried out by firstly separating off the gaseous components (in particular unreacted starting materials hydrogen and carbon dioxide) at the top of an evaporator and separating off the homogeneous catalyst dissolved in the polar solvent at the bottom and recirculating them to the hydrogenation stage. The adduct of formic acid and the tertiary amine is subsequently separated off from the remaining liquid phase comprising the adduct of formic acid and the tertiary amine, free tertiary amine and possibly water and the remaining part of the liquid phase comprising the free tertiary amine and possibly water is recirculated to the hydrogenation stage. The separation

can be effected by distillation or phase separation of the two-phase system (decantation).

A further significant teaching of EP 0 181 078 A is the subsequent, absolutely necessary replacement of the tertiary amine in the adduct which has been separated off by a weaker, less volatile nitrogen base before the adduct is thermally dissociated in order to aid or make possible the subsequent thermal dissociation to produce free formic acid. As particularly suitable weaker nitrogen bases, mention is made of imidazole derivatives such as 1-n-butylimidazole.

A disadvantage of the process of EP 0 181 078 A is the very complicated, four-stage work-up of the reaction product mixture by

- (i) separating off the gaseous components and also the homogeneous catalyst and the polar solvent in an evaporator and recirculating them to the hydrogenation stage;
- (ii) separating off the adduct of formic acid and the tertiary amine in a distillation column or a phase separator and recirculating the remaining liquid stream to the hydrogenation stage;
- (iii) replacing the tertiary amine in the adduct of formic acid and the tertiary amine by a weaker, less volatile nitrogen base in a reaction vessel having a superposed distillation column and recirculating the tertiary amine liberated to the hydrogenation stage; and
- (iv) thermally dissociating the adduct of formic acid and the weaker nitrogen base and recirculating the weaker nitrogen base liberated to the base replacement stage.

A further, important disadvantage of the process of EP 0 181 078 A and also of the processes of EP 0 095 321 A and EP 0 151 510 A is the fact that the adduct of formic acid and the tertiary amine partly redissociates into carbon dioxide and hydrogen in the presence of the homogeneous catalyst during the work-up in the evaporator. As a solution to this problem, EP 0 329 337 A proposes the addition of a decomposition inhibitor which reversibly inhibits the homogeneous catalyst. As preferred decomposition inhibitors, mention is made of carbon monoxide and oxidants. However, disadvantages of this are the introduction of further substances into the overall process and the necessity of reactivating the inhibited homogeneous catalyst before it is used further.

EP 0 357 243 A, too, addresses the disadvantage of the partial redissociation of the adduct of formic acid and the tertiary amine in the process of EP 0 181 078 A by joint work-up of the reaction product mixture in the evaporator. The process proposed in EP 0 357 243 A teaches the use of a homogeneous catalyst comprising a transition

metal of transition group VIII (groups 8, 9, 10), a tertiary amine and two different solvents, namely a nonpolar, inert solvent and a polar, inert solvent, which form two immiscible liquid phases in the catalytic hydrogenation of carbon dioxide to form an adduct of formic acid and tertiary amine. As nonpolar solvents, mention is made of aliphatic and aromatic hydrocarbons but also of phosphines having aliphatic and/or aromatic hydrocarbon radicals. Polar solvents mentioned are water, glycerol, alcohols, polyols, sulfolanes and mixtures thereof, with water being preferred. The homogeneous catalyst dissolves in the nonpolar solvent and the adduct of formic acid and tertiary amine dissolves in the polar solvent. After the reaction is complete, the two liquid phases are separated, for example by decantation, and the nonpolar phase comprising the homogeneous catalyst and the nonpolar solvent is recirculated to the hydrogenation stage. The polar phase comprising the adduct of formic acid and tertiary amine and the polar solvent is then subjected to an absolutely necessary replacement of the tertiary amine in the adduct by a weaker, less volatile nitrogen base before thermal dissociation of the adduct in order to aid or make possible the subsequent thermal dissociation to produce free formic acid. In a manner analogous to EP 0 181 078 A, imidazole derivatives such as 1-n-butylimidazole are also mentioned here as particularly suitable weaker nitrogen bases.

- A disadvantage of the process of EP 0 357 243 A is the very complicated, three-stage work-up of the reaction product mixture by
- (i) separating the two liquid phases and recirculating the phase comprising the homogeneous catalyst and the nonpolar solvent to the hydrogenation stage;
 - (ii) replacing the tertiary amine in the adduct of formic acid and the tertiary amine of the other phase by a weaker, less volatile nitrogen base in a reaction vessel with superposed distillation column and recirculating the tertiary amine liberated to the hydrogenation stage; and
 - (iii) thermally dissociating the adduct of formic acid and the weaker nitrogen base and recirculating the weaker nitrogen base liberated to the base replacement stage.

A further disadvantage of the process of EP 0 357 243 A is the use of two solvents and thus introduction of a further substance into the overall process.

As an alternative, EP 0 357 243 A also discloses the possibility of using only one solvent. In this case, the addition of the polar solvent in which the adduct of formic acid and the tertiary amine would otherwise dissolve is omitted. The sole solvent used here is the nonpolar solvent which dissolves the homogeneous catalyst. However, this alternative also has the disadvantage of the very complicated, three-stage work-up as described above.

DE 44 31 233 A likewise describes the hydrogenation of carbon dioxide in the presence of a catalyst comprising a transition metal of transition group VIII (groups 8, 9, 10), a tertiary amine and a polar solvent and water to form an adduct of formic acid and the tertiary amine, in which, however, the catalyst is present in heterogeneous form and the active component is applied to an inert support. Preferred tertiary amines are C₁-C₈-trialkylamines, polyamines having from 2 to 5 amino groups, aromatic nitrogen heterocycles such as pyridine or N-methylimidazole and also cyclic and/or bridged amines such as N-methylpiperidine, 1,8-diazabicyclo[5.4.0]undec-7-ene or 1,4-diazabicyclo[2.2.2]octane. As suitable polar solvents, mention is made of the low-boiling C₁-C₄-monoalcohols, and, in a manner analogous to EP 0 095 321 A, secondary alcohols are preferred. The hydrogenation is carried out at a total pressure of from 4 to 20 MPa (from 40 to 200 bar) and a temperature of from 50 to 200°C. For the work-up of the adduct of formic acid and tertiary amine which is formed, DE 44 31 233 A teaches the use of known methods with explicit reference to the work-up with replacement of the tertiary amine in the adduct of formic acid and the tertiary amine by a weaker, less volatile nitrogen base as disclosed in EP 0 357 243 A. In a manner analogous to the process of EP 0 357 243 A, the process of DE 44 31 233 A also has the disadvantage of the very complicated, three-stage work-up of the reaction product mixture.

It was an object of the present invention to provide a process for preparing formic acid by hydrogenation of carbon dioxide, which does not have the abovementioned disadvantages of the prior art or suffers from them only to a significantly reduced extent and which leads to concentrated formic acid in a high yield and high purity. Furthermore, the process should be able to be carried out in a simple manner or at least a simpler manner than is described in the prior art, in particular by means of a simpler process concept for working up the output from the hydrogenation reactor, simpler process stages, a reduced number of process stages or simpler apparatuses. In addition, the process should also be able to be carried out with the lowest possible consumption of energy. In particular, an efficient solution to the problem of recycling the catalyst, which has to date been solved only unsatisfactorily, should be provided while at the same time ensuring a high activity of the hydrogenation catalyst.

The work-up of the output from the hydrogenation reactor should, in particular, be carried out using exclusively the materials present in the process, without additional auxiliaries, and these should be able to be completely or largely completely recycled in the process.

The object is achieved by a process for preparing formic acid by reaction of carbon dioxide with hydrogen in a hydrogenation reactor in the presence of

- a catalyst comprising an element of group 8, 9 or 10 of the Periodic Table,
- a tertiary amine comprising at least 12 carbon atoms per molecule and
- a polar solvent comprising one or more monoalcohols selected from among methanol, ethanol, propanols and butanols,

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to form formic acid/amine adducts as intermediates which are subsequently thermally dissociated,

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where a tertiary amine which has a boiling point at least 5°C higher than that of formic acid is used and

a reaction mixture comprising the polar solvent, the formic acid/amine adducts, the tertiary amine and the catalyst carried from the reactor is formed in the reaction in the hydrogenation reactor,

wherein

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the work-up of the output from the hydrogenation reactor (I) is carried out by the following process steps:

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1) addition of water to the output from the hydrogenation reactor to give two liquid phases,

2) separation of the two liquid phases in a phase separation vessel, recirculation of the upper phase from the phase separation vessel to the hydrogenation reactor and passing-on of the lower phase from the phase separation vessel to an extraction apparatus in which

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3) residues of catalyst are extracted with the same tertiary amine which was used in the hydrogenation, the catalyst-laden tertiary amine is recycled to the hydrogenation reactor and the catalyst-free stream of polar solvent loaded with the formic acid/amine adducts is passed on to a distillation unit in which

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4) a fractional distillation is carried out to give a first fraction which comprises predominantly the polar solvent and is recycled to the hydrogenation reactor, a second fraction which comprises predominantly water and is recycled to the output from the hydrogenation reactor or is discarded and also a fraction,

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5) is separated in a phase separation vessel into an upper phase comprising predominantly the tertiary amine and a lower phase comprising predominantly the formic acid/amine adducts, where

- 6) the lower phase from the phase separation vessel is fed to a thermal dissociation unit and dissociated therein into a stream which comprises the tertiary amine and is recirculated to the phase separation vessel and pure formic acid and
- 5 a stream comprising the tertiary amine is conveyed from the phase separation vessel into the extraction apparatus as selective solvent for the catalyst.

In process step (6), in an embodiment only a substream of the stream comprising the tertiary amine being conveyed from the phase separation vessel into the extraction apparatus as selective solvent for the catalyst and the remaining proportion of the stream comprising the tertiary amine being conveyed directly into the hydrogenation reactor.

The catalyst to be used in the hydrogenation of carbon dioxide in the process of the invention is preferably a homogeneous catalyst. It comprises an element of group 8, 9 or 10 of the Periodic Table, i.e. Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and/or Pt. The catalyst preferably comprises Ru, Rh, Pd, Os, Ir and/or Pt, particularly preferably Ru, Rh and/or Pd, and very particularly preferably Ru.

The abovementioned elements are homogeneously dissolved in the form of complex-like compounds in the reaction mixture. The homogeneous catalyst should be selected so that it is enriched together with the tertiary amine in the same liquid phase (B). For the present purposes, "enriched" means a partition coefficient of the homogeneous catalyst

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$$P = \frac{\text{[concentration of homogeneous catalyst in liquid phase (B)]}}{\text{[concentration of homogeneous catalyst in liquid phase (A)]}}$$

of > 1. The choice of the homogeneous catalyst is generally made by means of a simple test in which the partition coefficient of the desired homogeneous catalyst under the planned process conditions is determined experimentally.

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Liquid phase (A) is here the lower phase from the phase separation vessel in process step 1).

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Owing to their good solubility in tertiary amines, preference is given to using a metal-organic complex comprising an element of group 8, 9 or 10 of the Periodic Table and at least one phosphine group having at least one unbranched or branched, acyclic or cyclic, aliphatic radical having from 1 to 12 carbon atoms, where individual carbon atoms can also be substituted by >P-, as homogeneous catalysts in the process of the invention. Branched cyclic aliphatic radicals thus also include radicals such as

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-CH₂-C₆H₁₁. Suitable radicals are, for example, methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl, 1-(2-methyl)propyl, 2-(2-methyl)propyl, 1-pentyl, 1-hexyl, 1-heptyl, 1-octyl, 1-nonyl, 1-decyl, 1-undecyl, 1-dodecyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl, methylcyclopentyl, methylcyclohexyl, 1-(2-methyl)pentyl 1-(2-ethyl)hexyl, 1-(2-propyl)heptyl and norbonyl. The unbranched or branched, acyclic or cyclic, aliphatic radical preferably comprises at least 1 and preferably not more than 10 carbon atoms. In the case of an exclusively cyclic radical in the abovementioned sense, the number of carbon atoms is from 3 to 12 and preferably at least 4 and also preferably not more than 8. Preferred radicals are ethyl, 1-butyl, sec-butyl, 1-octyl and cyclohexyl.

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The phosphine group can comprise one, two or three of the abovementioned unbranched or branched, acyclic or cyclic, aliphatic radicals. These can be identical or different. The phosphine group preferably comprises three of the abovementioned unbranched or branched, acyclic or cyclic, aliphatic radicals and particular preference is given to all three radicals being identical. Preferred phosphines are P(n-C_nH_{2n+1})₃ where n is from 1 to 10, particularly preferably tri-n-butylphosphine, tri-n-octylphosphine and 1,2-bis(dicyclohexylphosphino)ethane.

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As mentioned above, individual carbon atoms can also be substituted by >P- in the abovementioned unbranched or branched, acyclic or cyclic, aliphatic radicals. Polydentate, for example bidentate or tridentate, phosphine ligands are thus also comprised. These preferably comprise the group $\begin{array}{c} >P-CH_2CH_2-P< \\ | \\ >P-CH_2CH_2-P-CH_2CH_2-P< \end{array}$ or

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If the phosphine group comprises radicals other than the abovementioned unbranched or branched, acyclic or cyclic, aliphatic radicals, these generally correspond to those which are otherwise customarily used in phosphine ligands for metal-organic complex catalysts. Examples which may be mentioned are phenyl, tolyl and xylyl.

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The metal-organic complex can comprise one or more, for example two, three or four, of the abovementioned phosphine groups having at least one unbranched or branched, acyclic or cyclic, aliphatic radical. The remaining ligands of the metal-organic complex can have various natures. Examples which may be mentioned are hydride, fluoride, chloride, bromide, iodide, formate, acetate, propionate, carboxylate, acetylacetonate, carbonyl, DMSO, hydroxide, trialkylamine, alkoxide.

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The homogeneous catalysts can either be used directly in their active form or be generated only under reaction conditions from customary standard complexes such as [M(p-cymene)Cl₂]₂, [M(benzene)Cl₂]_n, [M(COD)(allyl)], [MCl₃ x H₂O],

[M(acetylacetonate)₃], [M(DMSO)₄Cl₂] where M is an element of group 8, 9 or 10 of the Periodic Table by addition of the corresponding phosphine ligand or ligands.

Homogeneous catalysts which are preferred in the process of the invention are
 5 [Ru(PⁿBu₃)₄(H)₂], [Ru(Pⁿoctyl₃)₄(H)₂], [Ru(PⁿBu₃)₂(1,2-bis(dicyclohexylphosphino)-ethane)(H)₂], [Ru(Pⁿoctyl₃)₂(1,2-bis(dicyclohexylphosphino)ethane)(H)₂], [Ru(PEt₃)₄(H)₂.
 By means of these, TOF (turnover frequency) values of greater than 1000 h⁻¹ can be achieved in the hydrogenation of carbon dioxide.

10 When homogeneous catalysts are used, the amount of the specified metal component in the metal-organic complex which is used is generally from 0.1 to 5000 ppm by weight, preferably from 1 to 800 ppm by weight and particularly preferably from 5 to 800 ppm by weight, in each case based on the total liquid reaction mixture in the hydrogenation reactor.

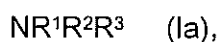
15 The partition coefficient of the homogeneous catalyst based on the amount of ruthenium in the amine phase and the product phase comprising the formic acid/amine adduct is in the range of P greater than 0.5, preferably greater than 1.0 and particularly preferably greater than 4, after the hydrogenation.

20 The tertiary amine to be used in the hydrogenation of carbon dioxide in the process of the invention has a boiling point which is at least 5°C higher than that of formic acid. Here, as is customary, the boiling point of compounds have to be based on the same pressure in each case when the relative position of boiling points is indicated. The
 25 tertiary amine is selected or matched to the polar solvent so that the tertiary amine is present in enriched form in the upper phase in the hydrogenation reactor. For the present purposes, "in enriched form" means a proportion by weight of > 50% of the free, i.e. not bound in the form of the formic acid/amine adduct, tertiary amine in the upper phase, based on the total amount of free, tertiary amine in the two liquid phases.
 30 The proportion by weight is preferably > 90%. The tertiary amine is generally selected by means of a simple test in which the solubility of the desired tertiary amine in the two liquid phases under the planned process conditions is determined experimentally. The upper phase can additionally comprise amounts of the polar solvent and of a nonpolar inert solvent.

35 The tertiary amine to be used preferably has a boiling point which is at least 10°C higher, particularly preferably at least 50°C higher and very particularly preferably at least 100°C higher, than that of formic acid. A restriction in terms of an upper limit to the boiling point is not necessary since a very low vapor pressure of the tertiary amine
 40 is in principle an advantage for the process of the invention. In general, the boiling point

of the tertiary amine at a pressure of 1013 hPa abs, if necessary at a pressure extrapolated by known methods from vacuum to 1013 hPa abs, is below 500°C.

The tertiary amine which is preferably to be used in the process of the invention is an
 5 amine, comprising at least 12 carbon atoms per molecule, of the general formula (Ia)



where the radicals R^1 to R^3 are identical or different and are each, independently of one
 10 another, an unbranched or branched, acyclic or cyclic, aliphatic, araliphatic or aromatic radical having in each case from 1 to 16 carbon atoms, preferably from 1 to 12 carbon atoms, where individual carbon atoms can also be substituted, independently of one another, by a hetero group selected from the group consisting of -O- and >N- or two or
 15 all three radicals can also be joined to one another to form a chain comprising at least four atoms in each case.

Examples of suitable amines are:

- Tri-n-butylamine, tri-n-pentylamine, tri-n-hexylamine, tri-n-heptylamine, tri-n-octylamine, tri-n-nonylamine, tri-n-decylamine, tri-n-undecylamine, tri-n-dodecylamine, tri-n-tridecylamine, tri-n-tetradecylamine, tri-n-pentadecylamine, tri-n-hexadecylamine, tri(2-ethylhexyl)amine.
- Dimethyldodecylamine, dimethyldodecylamine, dimethyltetradecylamine, ethyldi(2-propyl)amine (bp_{1013 hPa} = 127°C), dioctylmethylamine, dihexylmethylamine.
- Tricyclopentylamine, tricyclohexylamine, tricycloheptylamine, tricyclooctylamine and derivatives thereof which are substituted by one or more methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl or 2-methyl-2-propyl groups.
- Dimethylcyclohexylamine, methyldicyclohexylamine, diethylcyclohexylamine, ethyldicyclohexylamine, dimethylcyclopentylamine, methyldicyclopentylamine.
- Triphenylamine, methyldiphenylamine, ethyldiphenylamine, propyldiphenylamine, butyldiphenylamine, 2-ethylhexyldiphenylamine, dimethylphenylamine, diethylphenylamine, dipropylphenylamine, dibutylphenylamine, bis(2-ethylhexyl)phenylamine, tribenzylamine, methyldibenzylamine, ethyldibenzylamine and derivatives thereof which are substituted by one or more methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl or 2-methyl-2-propyl groups.

- N-C₁-C₁₂-alkylpiperidines, N,N-di-C₁-C₁₂-alkylpiperazines, N-C₁-C₁₂-alkylpyrrolidines, N-C₁-C₁₂-alkylimidazoles and derivatives thereof which are substituted by one or more methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl or 2-methyl-2-propyl groups.

- 5 • 1,8-Diazabicyclo[5.4.0]undec-7-ene ("DBU"), 1,4-diazabicyclo[2.2.2]octane ("DABCO"), N-methyl-8-azabicyclo[3.2.1]octane ("tropane"), N-methyl-9-azabicyclo[3.3.1]nonane ("granatane"), 1-azabicyclo[2.2.2]octane ("quinuclidine").

10 It is naturally also possible to use mixtures of any amount of various tertiary amines in the process of the invention.

In the process of the invention, particular preference is given to using an amine of the general formula (Ia) in which the radicals R¹ to R³ are selected independently from the group consisting of C₁-C₁₂-alkyl, C₅-C₈-cycloalkyl, benzyl and phenyl as tertiary amine.

15 Particular preference is given to using a saturated amine, i.e. only comprising single bonds, of the general formula (Ia) as tertiary amine in the process of the invention.

20 Very particular preference is given to using an amine of the general formula (Ia) in which the radicals R¹ to R³ are selected independently from the group consisting of C₅-C₈-alkyl, in particular tri-n-pentylamine, tri-n-hexylamine, tri-n-heptylamine, tri-n-octylamine, dimethylcyclohexylamine, methyldicyclohexylamine, dioctylmethylamine and dimethyldodecylamine, as tertiary amine in the process of the invention.

25 In particular, an amine of the general formula (Ia) in which the radicals R¹ to R³ are selected independently from among C₅- and C₆-alkyl is used as tertiary amine.

The tertiary amine is preferably present in liquid form in all process stages of the process of the invention. However, this is not absolutely necessary. It would also be sufficient for the tertiary amine to be at least dissolved in suitable solvents. Suitable solvents are in principle those which are chemically inert in respect of the hydrogenation of carbon dioxide and the thermal dissociation of the adduct and in which the tertiary amine and, if a homogeneous catalyst is used, also the latter readily dissolve but do not readily dissolve the polar solvent and the formic acid/amine adduct.

35 Possibilities are therefore in principle chemically inert, nonpolar solvents such as aliphatic, aromatic or araliphatic hydrocarbons, for example octane and higher alkanes, toluene, xylenes.

The polar solvent to be used in the hydrogenation of carbon dioxide in the process of the invention has a boiling point which is at least 5°C lower than the temperature required for the dissociation of the formic acid/amine adducts at the same pressure.

40

The polar solvent is to be selected or matched to the tertiary amine so that the polar solvent is present in enriched form in the lower phase. For the present purposes, "in enriched form" means a proportion by weight of > 50% of the polar solvent in the lower phase based on the total amount of polar solvent in the two liquid phases. The proportion by weight is preferably > 70%. The polar solvent is generally selected by means of a simple test in which the solubility of the desired polar solvent in the two liquid phases under the planned process conditions is determined experimentally.

The polar solvent can be a pure polar solvent or a mixture of various polar solvents, as long as the abovementioned conditions in respect of boiling point and phase behavior which the solvent has to meet are satisfied.

The polar solvent to be used preferably has a boiling point which is at least 10°C lower, particularly preferably at least 50°C lower, than the temperature required for dissociation of the formic acid/amine adducts at the same pressure. In the case of solvent mixtures, the boiling points of the solvent mixture used or an azeotrope or heteroazeotrope are at least 10°C lower, particularly preferably at least 50°C lower, than the temperature required for dissociation of the formic acid/amine adducts at the same pressure.

Classes of substances which are suitable as polar solvents are preferably alcohols and the formic esters thereof and water. The alcohols have a boiling point which is at least 10°C lower, particularly preferably at least 50°C lower, than the temperature required for dissociation of the formic acid/amine adducts at the same pressure in order to keep the esterification of the alcohols by formic acid very low.

As suitable alcohols, mention may be made of alcohols in the case of which the trialkylammonium formates preferentially dissolve in a mixture of the alcohol with water and this product phase has a miscibility gap with the free trialkylamine. Suitable alcohols are, for example, methanol, ethanol, 2-methoxyethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol. The ratio of alcohol to water has to be selected so that together with the trialkylammonium formate and the trialkylamine a two-phase mixture in which the major part of the trialkylammonium formate, the water and the polar solvent are present in the lower phase is formed, which is generally determined by means of a simple test in which the solubility of the desired polar solvent mixture in the two liquid phases under the planned process conditions is determined experimentally.

The molar ratio of the polar solvent or solvent mixture to be used in the process of the invention to the tertiary amine used is generally from 0.5 to 30 and preferably from 1 to 20.

According to the invention, the work-up of the output from the hydrogenation reactor is carried out with, in a first process step, water being added to the output from the hydrogenation reactor.

5

The addition of water after hydrogenation is complete has the effect that the partition coefficients of the catalyst are improved by the addition of water so that they accumulate in the amine phase and thus allow efficient recirculation of the catalyst without the hydrogenation activity thereof being reduced. The hydrogenation output can, depending on the polar solvent used and the concentration of formic acid-amine adducts, consist of two phases, with the formic acid-amine adducts in the product phase (the lower phase) then being enriched as a result of the addition of water. In the case of single-phase hydrogenation outputs when using polar solvents according to the invention, the phase separation to form the product phase (the lower phase) and the amine phase (the upper phase) is induced by the addition of water. Water is preferably added until a water content in the product phase of from 0.1 to 50% by weight, based on the total weight of the lower phase from the phase separation vessel II, has been reached, particularly preferably from 2 to 30% by weight, based on the total weight of the lower phase from the phase separation vessel II. The water to be introduced can originate from the distillation unit IV in which the major part of the polar solvent and also the water are separated off from the product stream (7) and/or can be water which is freshly introduced into the process. The water can be added either after depressurization of the output from the hydrogenation reactor to atmospheric pressure or before the output from the hydrogenation reactor is depressurized.

25

The carbon dioxide to be used in the hydrogenation of carbon dioxide can be used in solid, liquid or gaseous form. It is also possible to use industrially available gas mixtures comprising carbon dioxide as long as these are largely free of carbon monoxide, i.e. a proportion by volume of < 1% of CO. The hydrogen to be used in the hydrogenation of carbon dioxide is generally gaseous. Carbon dioxide and hydrogen can also comprise inert gases such as nitrogen or noble gases. However, the content of these is advantageously below 10 mol% based on the total amount of carbon dioxide and hydrogen in the hydrogenation reactor. Although larger amounts may likewise be tolerable, they generally require the use of a higher pressure in the reactor which in turn makes further compression energy necessary and increases the outlay for apparatus.

35

The hydrogenation of carbon dioxide is preferably carried out in the liquid phase at a temperature of from 20 to 200°C and a total pressure of from 0.2 to 30 MPa abs. The temperature is preferably at least 30°C and particularly preferably at least 40°C and also preferably not more than 150°C, particularly preferably not more than 120°C and

40

very particularly preferably not more than 80°C. The total pressure is preferably at least 1 MPa abs and particularly preferably at least 5 MPa abs and also preferably not more than 15 MPa abs.

- 5 The partial pressure of carbon dioxide is generally at least 0.5 MPa and preferably at least 2 MPa and also generally not more than 8 MPa. The partial pressure of hydrogen is generally at least 0.5 MPa and preferably at least 1 MPa and also generally not more than 25 MPa and preferably not more than 10 MPa.

- 10 The molar ratio of hydrogen to carbon dioxide in the feed to the hydrogenation reactor is preferably from 0.1 to 10 and particularly preferably from 1 to 3.

The molar ratio of carbon dioxide to tertiary amine in the feed to the hydrogenation reactor is generally from 0.1 to 10 and preferably from 0.5 to 3.

15

As hydrogenation reactors, it is in principle possible to use all reactors which are suitable in principle for gas/liquid reactions at the given temperature and the given pressure. Suitable standard reactors for liquid-liquid reaction systems are indicated, for example, in K.D. Henkel, "Reactor Types and Their Industrial Applications", in Ullmann's Encyclopedia of Industrial Chemistry, 2005, Wiley-VCH Verlag GmbH & Co. KGaA, DOI: 10.1002/14356007.b04_087, chapter 3.3 "Reactors for gas-liquid reactions". Examples which may be mentioned are stirred tank reactors, tube reactors or bubble column reactors.

20

- 25 The hydrogenation of carbon dioxide in the process of the invention can be carried out batchwise or continuously. In the case of batch operation, the reactor is charged with the desired liquid and optionally solid starting materials and auxiliaries and carbon dioxide and hydrogen are subsequently introduced to the desired pressure at the desired temperature. After the reaction is complete, the reactor is generally depressurized and the two liquid phases which are formed are separated from one another. In the continuous mode of operation, the starting materials and auxiliaries including the carbon dioxide and hydrogen are introduced continuously. Accordingly, the liquid phase is continuously discharged from the reactor so that the average liquid level in the reactor remains constant. Preference is given to the continuous hydrogenation of carbon dioxide.
- 30
- 35

The average residence time in the hydrogenation reactor is generally from 10 minutes to 5 hours.

The formic acid/amine adducts formed in the hydrogenation of carbon dioxide in the presence of the catalyst to be used, the polar solvent and the tertiary amine generally have the general formula (IIa)



where the radicals R^1 to R^3 correspond to the radicals described for the tertiary amine (Ia) and x_i is from 0.4 to 5, preferably from 0.7 to 1.6. The respective average values of the amine-formic acid ratios in the product phases in the respective process steps, i.e. the factor x_i , can be determined, for example, by determining the formic acid content by titration with an alcoholic KOH solution against phenolphthalein and the amine content can be determined by gas chromatography. The composition of the formic acid/amine adducts, i.e. the factor x_i , can change during the various process steps. Thus, for example, adducts having a relatively high formic acid content with $x_2 > x_1$ and $x_2 = 1$ to 4 are generally formed after removal of the polar solvent, with the excess, free amine being able to form a second phase.

Two liquid phases are formed in the hydrogenation of carbon dioxide by the process of the invention. The lower phase is enriched with the formic acid/amine adducts and the polar solvent. With regard to the formic acid/amine adducts, "enriched" means a partition coefficient of the formic acid/amine adducts

$$P = \frac{\text{[concentration of formic acid/amine adduct (II) in liquid phase (A)]}}{\text{[concentration of formic acid/amine adduct (II) in liquid phase (B)]}}$$

of > 1 . The partition coefficient is preferably ≥ 2 and particularly preferably ≥ 5 . The upper phase is enriched with the tertiary amine. If a homogeneous catalyst is used, this is likewise present in enriched form in the upper phase.

The liquid phases (A) and (B) have the meaning defined above.

The two liquid phases formed are, in the process of the invention, separated from one another and the upper phase is recirculated to the hydrogenation reactor. Recirculation of a further liquid phase comprising unreacted carbon dioxide present in addition to the two abovementioned liquid phases and also of a gas phase comprising unreacted carbon dioxide and/or unreacted hydrogen to the hydrogenation reactor may also be advantageous. It may also be desirable, for example to discharge undesirable by-products or impurities, to discharge part of the upper phase and/or part of the carbon dioxide or liquid or gaseous phases comprising carbon dioxide and hydrogen from the process.

The two liquid phases are generally separated by gravimetric phase separation. As phase separation vessels, it is possible to use, for example, standard apparatuses and standard methods which are described, for example, in E. Müller et al., "Liquid-Liquid Extraction", in Ullmann's Encyclopedia of Industrial Chemistry, 2005, Wiley-VCH Verlag GmbH & Co. KGaA, DOI:10.1002/14356007.b03_06, chapter 3 "Apparatus". In general, the liquid phase enriched with the formic acid/amine adducts and the polar solvent is heavier and forms the lower phase.

The phase separation can be effected, for example, by depressurization, preferably to about or close to atmospheric pressure, and cooling of the liquid reaction mixture, for example to about or close to ambient temperature. However, there is a risk that at least part of the gas dissolved in the liquid phases at the higher reaction pressure, in particular carbon dioxide, will degas during the depressurization and have to be compressed separately as a gas stream and recirculated to the hydrogenation reactor. Likewise, the lower phase has to be brought separately to the reaction pressure before recirculation to the hydrogenation reactor. Here, a suitable compressor designed according to the pressure difference to be overcome or a pump, which also consumes additional energy in operation and also involves higher apparatus costs, has to be provided for each of the gas and liquid phases to be recirculated.

In the context of the present invention, it has been found that in the case of the present system, i.e. a lower phase enriched with the formic acid/amine adducts and the polar solvent and an upper phase enriched with the tertiary amine and in the case of the use of a homogeneous catalyst also with this, the two liquid phases can separate very well from one another even at a significantly elevated pressure. For this reason, the solvent in the process of the invention is preferably selected so that the separation of the lower phase enriched in the formic acid/amine adducts and the polar solvent from the upper phase in which with the tertiary amine and also the recirculation of the upper phase to the hydrogenation reactor can take place at a pressure of from 1 to 30 MPa abs. Depending on the total pressure in the hydrogenation reactor, the pressure is preferably not more than 15 MPa abs. It is even possible to separate the two liquid phases from one another without prior depressurization and recirculate the upper phase to the hydrogenation reactor without an appreciable pressure increase. In this case, and also in the case of an only slight depressurization, it is possible to entirely dispense with recirculation of any gas phase. Whether this omission is possible for the respective specific system should be determined beforehand in the case of doubt by simple experimental examples.

The process of the invention can therefore preferably be carried out in such a way that the pressure and the temperature in the hydrogenation reactor and in the phase separation vessel are the same or approximately the same; for the present purposes,

the same means a pressure difference of up to +/-5 bar or a temperature difference of up to +/-5°C.

- 5 In an embodiment the phase separation is particularly preferably carried out at a pressure of at least 50%, very particularly preferably at least 90% and in particular at least 95%, of the reaction pressure. The pressure in the phase separation is particularly preferably not more than 105% and very particularly preferably not more than 100% of the reaction pressure.
- 10 It has surprisingly also been found that in the case of the present system the two liquid phases can separate very readily from one another even at an elevated temperature corresponding to the reaction temperature. In this case, no cooling is necessary for the phase separation and no subsequent heating of the upper phase to be recirculated is required, which likewise saves energy.
- 15 The major part of the polar solvent of the lower phase which has been separated off is separated off thermally from the formic acid/amine adducts in a distillation unit, with the polar solvent removed by distillation being recirculated to the hydrogenation reactor. The pure formic acid/amine adducts and free amine are obtained at the bottom of the
- 20 distillation unit, since when the polar solvent is removed formic acid/amine adducts having a relatively low amine content are formed, as a result of which a two-phase bottoms mixture comprising an amine phase and a formic acid/amine adduct phase is formed.
- 25 The thermal removal of the polar solvent or mixture, see above, is preferably carried out at a temperature at the bottom at which, at the given pressure, no free formic acid is formed from the formic acid/amine adduct having the higher (x1) or lower (x2) amine content. In general, the temperature at the bottom of the thermal separation unit is at least 20°C, preferably at least 50°C and particularly preferably at least 70°C, and
- 30 generally not more than 210°C, preferably not more than 190°C. The pressure is generally at least 1 hPa abs, preferably at least 50 hPa abs and particularly preferably at least 100 hPa abs, and generally not more than 1 MPa abs and preferably 0.1 MPa abs.
- 35 The thermal removal of the polar solvent or mixture is carried out either in an evaporator or in a distillation unit comprising vaporizer and column filled with ordered packing, random packing elements and/or trays. The solvent can be condensed after the thermal separation, with the enthalpy of condensation liberated once again being able to be utilized for, for example, preheating the solvent coming with amine/formic
- 40 acid adduct mixture coming from the extraction to evaporation temperature.

As an alternative, only parts of the solvent mixture can be separated off. This applies in particular in the case of solvent components which can be separated off via a side stream in the later formic acid distillation. (Keyword: aqueous formic acid).

- 5 The formic acid/amine adducts which are obtained after the thermal removal of the polar solvent or mixture or parts of the solvent are then dissociated thermally into free formic acid and free tertiary amine in a distillation unit, with the free formic acid formed being removed by distillation and the free tertiary amine comprised in the bottoms from the distillation unit being recirculated to the hydrogenation reactor. Here, the free amine
10 obtained as second phase in the thermal removal of the polar solvent can be separated off beforehand in a phase separation vessel, in a joint phase separation vessel be fed together with the bottom product from the thermal dissociation unit to the formic acid removal or as two-phase mixture directly to the dissociation unit (see general embodiments). The formic acid liberated can be taken off, for example, (i) at the top, (ii)
15 at the top and as side offtake stream or (iii) only as side offtake stream. If formic acid is taken off at the top, a formic acid purity of up to 99.99% by weight is possible. When formic acid is taken off as side offtake stream, aqueous formic acid is obtained, with a mixture comprising about 85% by weight of formic acid being of particular importance here in industrial practice. Depending on the water content of the feed to the distillation
20 unit, the majority of the formic acid is taken off as overhead product or as side product. If necessary, it is even possible to take off formic acid only as side product, in which case the required amount of water may be deliberately added. The thermal dissociation of the formic acid/amine adduct is generally carried out under the process parameters known from the prior art in respect of pressure, temperature and configuration of the
25 apparatus. Thus, for example, reference may be made to the descriptions in EP 0 181 078 A or WO 2006/021,411. The distillation unit to be used generally comprises a distillation column which generally comprises random packing elements, ordered packings and/or trays.
- 30 In general, the temperature at the bottom of the distillation column is at least 130°C, preferably at least 140°C and particularly preferably at least 150°C, and generally not more than 210°C, preferably not more than 190°C and particularly preferably not more than 185°C. The pressure is generally at least 1 hPa abs, preferably at least 50 hPa abs and particularly preferably at least 100 hPa abs, and generally not more than
35 500 hPa abs, preferably not more than 300 hPa abs and particularly preferably not more than 250 hPa abs.

A water-comprising stream of formic acid is optionally taken off as side product. In the case of addition of water, for example to promote the hydrogenation or the catalyst
40 extraction, this is even particularly advantageous.

The solution of the adduct of tertiary amine and formic acid is extracted with streams of free tertiary amine coming from the appropriate phase separation vessels and recirculated to the hydrogenation reactor. This occurs in order to separate residual amounts of hydrogenation catalyst from the product stream. Without this extraction, hydrogenation catalyst could get into the apparatus for the thermal dissociation of the adduct of tertiary amine and formic acid, catalyze the decomposition of formic acid and thus reduce the yield of formic acid. Residual amounts of hydrogen and carbon dioxide are disposed of as offgas.

- 10 The extraction is carried out at temperatures of from 30 to 100°C and pressures of from 1 to 80 bar. The extraction can also be carried out under hydrogen pressure.

The extraction of the hydrogenation catalyst can be carried out in any suitable apparatus known to those skilled in the art, preferably in countercurrent extraction columns, mixer-settler cascades or combinations of mixer-settlers with columns.

The product stream from the extraction apparatus, which comprises a solution of the formic acid/amine adduct in the respective solvent or solvent mixture, is fed into the thermal dissociation unit in order to separate the polar solvent or solvent mixture from the formic acid/amine adduct. The phase comprising tertiary amine and hydrogenation catalyst from the extraction apparatus is recirculated to the hydrogenation stage.

Apart from the catalyst, amounts of individual components of the polar solvent from the liquid phase to be extracted are sometimes dissolved in the extractant, viz. the amine stream. This is not a disadvantage for the process since the amount of solvent already extracted does not have to be fed to the solvent removal and may thus save vaporization energy and apparatus costs.

It can be advantageous to integrate an apparatus for the adsorption of traces of hydrogenation catalyst between the extraction apparatus and the thermal separation apparatus. Numerous adsorbents are suitable for the adsorption. Examples are polyacrylic acid and salts thereof, sulfonated polystyrenes and salts thereof, activated carbons, montmorillonites, bentonites, silica gels and also zeolites.

If the amount of hydrogenation catalyst in the product stream from the phase separation vessel B is less than 1 ppm, in particular less than 0.1 ppm, the adsorption apparatus is sufficient for separating off and recovering the hydrogenation catalyst. The extraction stage can then be omitted and the tertiary amine can be recirculated together with the organic solvent to the hydrogenation stage.

Compared to the integrated processes which have previously been described in EP 181 078 B1 and EP 357 243 B1, the process of the invention has a series of advantages: the same tertiary amine is used for binding of the formic acid in the hydrogenation and thermal dissociation of the formic acid/amine adducts. This amine, which is obtained in free form in the thermal dissociation, is then used for extraction of catalyst residues from the product phase in order to recirculate traces of the catalyst together with the amine to the reaction vessel. It has a higher stability than the previously described N-alkylimidazoles. There are virtually no losses of noble metals. The catalyst is prevented from getting into the thermal dissociation unit and catalyzing the decomposition of formic acid therein. It is a great advantage that the catalyst is separated off in its active form and can be recirculated. High formic acid yields and a high product purity are achieved. Extractions and phase separations replace two distillations. This enables energy and capital costs to be reduced.

The process of the invention makes it possible to obtain concentrated formic acid in high yield and high purity by hydrogenation of carbon dioxide. It is, in particular, carried out in a particularly simple way which, compared to the prior art, has a simpler process concept, simpler process steps, a smaller number of process steps and also requires simpler apparatuses. Thus, for example, when a homogeneous catalyst is used and the tertiary amine and the polar solvent are chosen appropriately, the catalyst is separated from formic acid/amine adducts by phase separation and recirculated without further work-up steps to the hydrogenation reactor. The phase separation can also be carried out under superatmospheric pressure. Due to the prompt separation of the catalyst from the formic acid/amine adducts formed, a back reaction involving decomposition into carbon dioxide and hydrogen is suppressed. In addition, losses of catalyst and thus losses of noble metal are minimized by the holding back or removal of the catalyst due to the formation of two liquid phases. Furthermore, catalyst remaining in the product stream can be recirculated virtually completely to the hydrogenation reactor as a result of the extraction with free amine from the thermal dissociation units, which further minimizes the losses of noble metal and is a very great advantage for an economical process. In addition, decomposition of the formic acid in the thermal dissociation units is largely suppressed without the catalyst having to be deactivated. Furthermore, the process of the invention does not require any complicated, separate base exchange, so that the formic acid/amine adducts formed in the hydrogenation reactor can be used directly for the thermal dissociation. The use of a low-boiling polar solvent allows the solvent to be separated off thermally in a stage preceding the thermal dissociation to give formic acid under mild conditions, as a result of which esterification of alcohols used and decomposition of the formic acid is minimized, a lower energy input is required and a higher purity of the formic acid can be achieved. As a result of the simpler process concept, the production plant required for carrying out the process of the invention is more compact in the sense of a lower

space requirement and the use of fewer apparatuses compared to the prior art. It has lower capital costs and a lower energy consumption.

The invention will be illustrated below with the aid of examples and a drawing.

5

Examples A-1 to A-16 (according to the invention)
(hydrogenation and phase separation, addition of water
after the reaction)

10 A 250 ml autoclave made of Hastelloy C and provided with a magnetic stirrer bar was charged under inert conditions with tertiary amine, polar solvent and homogeneous catalyst. The autoclave was subsequently closed and CO₂ was injected at room temperature. H₂ was then injected and the reactor was heated while stirring (700 rpm).
15 After the desired reaction time, the autoclave was cooled and the reaction mixture was depressurized. Unless indicated otherwise, a two-phase product mixture was obtained after the addition of water, with the upper phase being enriched in the still free tertiary amine and the homogeneous catalyst and the lower phase being enriched in the polar solvent, water and the formic acid/amine adducts formed. The total content of formic acid in the formic acid/amine adduct was determined by potentiometric titration with
20 0.1 N KOH in MeOH using a "Mettler Toledo DL50" titrator. The turnover frequency (= TOF; for the definition of the TOF see: J.F. Hartwig, *Organotransition Metal Chemistry*, 1st edition, **2010**, University Science Books, *Sausalito/California*, p. 545) and the reaction rate was calculated. The ruthenium content was determined by atomic absorption spectroscopy. The composition of the two phases was determined by gas
25 chromatography and proton NMR spectroscopy. The parameters and results of the individual experiments are shown in Tables 1.1 to 1.5.

In the embodiments in experiments A-1 to A-16, the Ru partition coefficients k_{Ru} after the reaction are unfavorable. The product phase, viz. stream 3, was therefore
30 subsequently admixed with water to form a two-phase mixture, with the upper phase comprising mainly amine and the alcohol and the lower phase comprising the formic acid-amine adducts, the alcohol and water and with improved Ru partition coefficients between these two phases being established as a result of the addition of water. In the embodiments in the comparative experiments for A3, A7 and A15 (experiments A-17 to
35 A-19 in Table 1.6), the entire amount of water was added during the reaction. It can clearly be seen that, in the case of the solvents and catalysts used here, the addition of this amount of water during the hydrogenation leads to poorer ruthenium partition coefficients after the reaction and/or lower reaction rates.

Table 1.1

	Example A-1	50 g of the lower phase from Example A-2 are admixed with 6.1 g of water. This results in formation of two phases.	Example A-2	50 g of the lower phase from Example A-2 are admixed with 8.3 g of water. This results in formation of two phases.
Tertiary amine	75 g of trihexylamine		75 g of tripentylamine	
Polar solvent (used)	25 g of methanol		25 g of methanol	
Catalyst	0.18 g of $[\text{Ru}(\text{P}^n\text{Bu}_3)_4(\text{H})_2]$		0.18 g of $[\text{Ru}(\text{P}^n\text{Bu}_3)_4(\text{H})_2]$	
Injection of CO_2	19.9 g to 1.8 MPa abs		19.7 g to 1.9 MPa abs	
Injection of H_2	To 9.8 MPa abs		To 9.9 MPa abs	
Heating	To 50°C		To 50°C	
Pressure change	To 9.4 MPa abs		To 9.4 MPa abs	
Reaction time	1 hour		1 hour	
Peculiarity	-		-	
Upper phase	15.9 g 12.4% of methanol 87.6% of trihexylamine	18.8 g 2.8% of methanol 97.2% of trihexylamine	38.5 g 4.9% of methanol 95.1% of tripentylamine	10.4 g 1.1% of methanol 98.9% of tripentylamine
Lower phase	87.3 g 5.9% of formic acid 26.4% of methanol 67.7% of trihexylamine	36.2 g 7.3% of formic acid 16.9% of water 35.0% of methanol 40.8% of trihexylamine	64.1 g 8.1% of formic acid 36.1% of methanol 55.8% of tripentylamine	46.7 g 8.0% of formic acid 17.8% of water 38.5% of methanol 35.7% of tripentylamine
k_{Ru} (c_{Ru} in upper phase/ c_{Ru} in lower phase)	0.3	4.0	0.7	2.7
TOF	560 h^{-1}	-	562 h^{-1}	-
Reaction rate	1.09 $\text{mol kg}^{-1} \text{h}^{-1}$	-	1.09 $\text{mol kg}^{-1} \text{h}^{-1}$	-

Table 1.2

	Example A-3	50 g of the lower phase from Example A-3 are admixed with 5.7 g of water. This results in formation of two phases.	Example A-4	50 g of the lower phase from Example A-4 are admixed with 7.8 g of water. This results in formation of two phases.
Tertiary amine	75 g of trihexylamine		75 g of tripentylamine	
Polar solvent (used)	24 g of methanol 1 g of water		24 g of methanol 1 g of methanol	
Catalyst	0.18 g of $[\text{Ru}(\text{P}^n\text{Bu}_3)_4(\text{H})_2]$		0.18 g of $[\text{Ru}(\text{P}^n\text{Bu}_3)_4(\text{H})_2]$	
Injection of CO_2	20.1 g to 2.1 MPa abs		20.1 g to 2.2 MPa abs	
Injection of H_2	To 10.1 MPa abs		To 10.2 MPa abs	
Heating	To 50°C		To 50°C	
Pressure change	To 9.6 MPa abs		To 10.3 MPa abs.	
Reaction time	1 hour		1 hour	
Peculiarity	-		-	
Upper phase	27.4 g 9.0% of methanol 91.0% of trihexylamine	12.3 g 2.8% of methanol 97.2% of trihexylamine	43.9 g 3.4% of methanol 96.6% of tripentylamine	7.3 g 1.3% of methanol 98.7% of tripentylamine
Lower phase	76.3 g 7.1% of formic acid 1.3% of water 28.2% of methanol 63.4% of trihexylamine	41.7 g 7.8% of formic acid 15.2% of water 33.0% of methanol 44.0% of trihexylamine	59.2 g 8.7% of formic acid 38.0% of methanol 1.7% of water 51.6% of tripentylamine	49.1 g 8.3% of formic acid 17.6% of water 38.5% of methanol 35.6% of tripentylamine
k_{Ru} (c_{Ru} in upper phase/ c_{Ru} in lower phase)	0.6	3.3	1.1	1.7
TOF	591 h^{-1}	-	551 h^{-1}	-
Reaction rate	1.09 $\text{mol kg}^{-1} \text{h}^{-1}$	-	1.08 $\text{mol kg}^{-1} \text{h}^{-1}$	-

Table 1.3

	Example A-5	Example A-6	Example A-7	Example A-8
Tertiary amine	75 g of tripentylamine	75 g of trihexylamine	75 g of tripentylamine	75 g of tripentylamine
Polar solvent (used)	25 g of methanol	25 g of methanol	25 g of methanol	25 g of methanol
Catalyst	0.16 g of [Ru(PnOct3)4(H)2]	0.16 g of [Ru(PnOct3)4(H)2]	0.16 g of [Ru(PnOct3)4(H)2]	0.33 g of [Ru(PnOct3)4(H)2]
Injection of CO ₂	30.0 g to 2.5 MPa abs	20.0 g to 1.7 MPa abs	19.9 g to 2.1 MPa abs	20.0 g to 2.0 MPa abs
Injection of H ₂	To 8.0 MPa abs	To 9.7 MPa abs	To 10.0 MPa abs	To 10.0 MPa abs
Heating	To 50°C	To 50°C	To 50°C	To 50°C
Pressure change	To 10.5 MPa abs	To 10.4 MPa abs	To 10.6 MPa abs	To 10.8 MPa abs
Reaction time	1 hour	1 hour	1 hour	1 hour
Peculiarity	Addition of 2 g of water after the reaction	Addition of 2 g of water after the reaction	Addition of 5 g of water after the reaction	Addition of 3 g of water after the reaction
Upper phase	55.9 g 4.9% of methanol 95.1% of tripentylamine	43.9 g 9.7% of methanol 92.3% of trihexylamine	55.5 g 3.1% of methanol 96.9% of tripentylamine	40.5 g VH10-44
Lower phase	44.6 g 6.4% of formic acid 4.5% of water 50.0% of methanol 39.1% of tripentylamine	49.9 g 5.7% of formic acid 41.5% of methanol 4.0% of water 48.8% of trihexylamine	45.5 g 6.1% of formic acid 51.2% of methanol 11.0% of water 31.7% of tripentylamine	61.5 g 7.0% of formic acid 35.9% of methanol 4.9% of water 52.2% of trihexylamine
k _{Ru} (c _{Ru} in upper phase/ c _{Ru} in lower phase)	4.2	6.8	10.9	41.0
TOF	602 h ⁻¹	602 h ⁻¹	586 h ⁻¹	447 h ⁻¹
Reaction rate	0.62 mol kg ⁻¹ h ⁻¹	0.62 mol kg ⁻¹ h ⁻¹	0.60 mol kg ⁻¹ h ⁻¹	0.91 mol kg ⁻¹ h ⁻¹

Table 1.4

	Example A-9	Example A-10	Example A-11	Example A-12
Tertiary amine	75 g of trihexylamine	75 g of trihexylamine	75 g of trihexylamine	75 g of trihexylamine
Polar solvent (used)	25 g of methanol	25 g of methanol	25 g of methanol	25 g of methanol
Catalyst	0.16 g of $[\text{Ru}(\text{PnOctyl})_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexyl- phosphino)ethane	0.16 g of $[\text{Ru}(\text{PnOctyl})_3)_4(\text{H})_2]$,	0.16 g of $[\text{Ru}(\text{PnOctyl})_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexyl- phosphino)ethane	0.32 g of $[\text{Ru}(\text{PnOctyl})_3)_4(\text{H})_2]$, 0.17 g of 1,2-bis(dicyclohexyl- phosphino)ethane, 0.15 g of PnOctyl_3
Injection of CO_2	To 2.0 MPa abs	To 1.9 MPa abs	To 1.8 MPa abs	To 2.0 MPa abs
Injection of H_2	To 10.0 MPa abs	To 9.9 MPa abs	To 9.8 MPa abs	To 12.0 MPa abs
Heating	70°C	70°C	40°C	50°C
Pressure change	To 10.4 MPa abs	To 11.1 MPa abs	To 10.0 MPa abs	To 12.4 MPa abs
Reaction time	1 hour	1 hour	1 hour	1 hour
Peculiarity	Addition of 5 g of water after the reaction	Addition of 5 g of water after the reaction	Addition of 5 g of water after the reaction	Addition of 5 g of water after the reaction
Upper phase	4.25 g	55.2 g	50.5 g	25.9 g
Lower phase	58.4 g	43.4 g	49.0 g	78.0 g
	7.3% of formic acid	5.4% of formic acid	6.2% of formic acid	8.5% of formic acid
k_{Ru} (c_{Ru} in upper phase/ c_{Ru} in lower phase)	16.3	100	2.2	19.4
TOF	904 h^{-1}	492 h^{-1}	650 h^{-1}	696
Reaction rate	0.92 $\text{mol kg}^{-1} \text{h}^{-1}$	0.52 $\text{mol kg}^{-1} \text{h}^{-1}$	0.62 $\text{mol kg}^{-1} \text{h}^{-1}$	1.38 $\text{mol kg}^{-1} \text{h}^{-1}$

Table 1.5

	Example A-13	Example A-14	Example A-15	Example A-16
Tertiary amine	75 g of trihexylamine	75 g of trihexylamine	75 g of trihexylamine	75 g of trihexylamine
Polar solvent (used)	25 g of methanol	25 g of methanol	25 g of methanol	25 g of ethanol
Catalyst	0.11 g of [Ru(COD)Cl ₂] ₂ , 0.17 g of 1,2-bis(dicyclohexylphosphino)ethane, 0.15 g of PnOct ₃	0.32 g of [Ru(PnOctyl ₃) ₄ (H) ₂], 0.08 g of 1,2-bis(diphenylphosphino)ethane	0.32 g of [Ru(PnOctyl ₃) ₄ (H) ₂], 0.08 g of 1,2-bis(dicyclohexylphosphino)ethane	0.18 g of [Ru(P ⁿ Oct ₃) ₄ (H) ₂],
Injection of CO ₂	To 1.6 MPa abs	To 1.6 MPa abs	To 1.7 MPa abs	20.0 g to 2.2 MPa abs
Injection of H ₂	To 12.0 MPa abs	To 9.6 MPa abs	To 9.7 MPa abs	To 10.2 MPa abs
Heating	50°C	50°C	50°C	To 50°C
Pressure change	To 12.1 MPa abs	To 8.6 MPa abs	To 9.5 MPa abs	To 11.1 MPa abs
Reaction time	1 hour	2 hours	2 hours	1 hour
Peculiarity	Addition of 5 g of water after the reaction	Addition of 5 g of water after the reaction	Addition of 5 g of water after the reaction	Single-phase reaction output; addition of 5 g of water after the reaction, resulting in formation of two phases
Upper phase	16.6 g	36.2 g	26.7 g	66.3 g 8.8% of ethanol 0.8% of water 90.4% of trihexylamine
Lower phase	88.1 g 9.0% of formic acid	66.1 g 7.3% of formic acid	74.0 g 8.3% of formic acid	29.6 g 2.7% of formic acid 20.9% of water 64.4% of ethanol 12% of trihexylamine
k _{Ru} (c _{Ru} in upper phase/ c _{Ru} in lower phase)	12.0	1.4	14	22.5
TOF	435 h ⁻¹	258 h ⁻¹	335 h ⁻¹	152 h ⁻¹
Reaction rate	1.64 mol kg ⁻¹ h ⁻¹	1.02 mol kg ⁻¹ h ⁻¹	1.33 mol kg ⁻¹ h ⁻¹	0.18 mol kg ⁻¹ h ⁻¹

Table 1.6: Comparative experiments - addition of water in the reaction

	Example A-17 (comparative experiment for A3)	Example A-18 (comparative experiment for A15)	Example A-19 (comparative experiment for A7)
Tertiary amine	75 g of trihexylamine	75 g of trihexylamine	75 g of tripentylamine
Polar solvent (used)	24 g of methanol 6.7 g of water	25 g of methanol 5.0 g of water	25 g of methanol 5.0 g of water
Catalyst	0.18 g of $[\text{Ru}(\text{P}^n\text{Bu}_3)_4(\text{H})_2]$	0.32 g of $[\text{Ru}(\text{P}^n\text{Octyl}_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexylphosphino)ethane	0.16 g of $[\text{Ru}(\text{P}^n\text{Octyl}_3)_4(\text{H})_2]$
Injection of CO_2	20.0 g to 3.5 MPa abs	20.0 g to 2.5 MPa abs	20.0 g to 2.1 MPa abs
Injection of H_2	To 11.5 MPa abs	To 10.6 MPa abs	To 10.1 MPa abs
Heating	To 50°C	To 50°C	To 50°C
Pressure change	To 11.0 MPa abs	To 11.0 MPa abs	To 11.3 MPa abs
Reaction time	1 hour	1 hour	1 hour
Peculiarity	Water is added before the reaction	Water is added before the reaction	Water is added before the reaction
Upper phase	44.1 g	64.3 g	66.6 g
Lower phase	65.9 g 7.5% of formic acid	41.7 g 4.7% of formic acid	37.6 g 2.4% of formic acid
k_{Ru} (c_{Ru} in upper phase/ c_{Ru} in lower phase)	1.8	1.3	32.5
TOF	551 h^{-1}	394 h^{-1}	187 h^{-1}
Reaction rate	0.98 $\text{mol kg}^{-1} \text{h}^{-1}$	0.4 $\text{mol kg}^{-1} \text{h}^{-1}$	0.19 $\text{mol kg}^{-1} \text{h}^{-1}$

Examples B1-B4 (extraction of the catalyst)

5 A 100 ml autoclave made of Hastelloy C and provided with a blade stirrer was charged under inert conditions with the trialkylamine, polar solvent and the catalyst. The autoclave was subsequently closed and CO₂ was injected at room temperature. H₂ was then injected and the reactor was heated while stirring (1000 rpm). After the reaction time, the autoclave was cooled and the reaction mixture was depressurized. After the reaction, water was added to the reaction product mixture and the mixture was stirred
10 for 10 minutes at room temperature. A two-phase product mixture was obtained, with the upper phase being enriched in the still free tertiary amine and the homogeneous catalyst and the lower phase being enriched in the polar solvent and the formic acid/amine adduct formed. The lower phase was separated off and admixed three times under inert conditions with the same amount (mass of amine corresponds to the
15 mass of the lower phase) of free trialkylamine (stirring for 10 minutes at room temperature and subsequently separating the phases). The total content of formic acid in the formic acid/amine adduct was determined by potentiometric titration with 0.1 N KOH in MeOH using a "Mettler Toledo DL50" titrator. The ruthenium content was determined by AAS. The parameters and results of the individual experiments are
20 shown in Table 1.7.

Examples B-1 to B-4 show that the ruthenium in the product phase can be depleted to values as low as less than one ppm by varying the catalyst and the amount of water added in the formation of formic acid.
25

Table 1.7

	Example B-1	Example B-2	Example B-3	Example B-4
Tertiary amine	37.5 g of trihexylamine	37.5 g of trihexylamine	37.5 g of trihexylamine	37.5 g of trihexylamine
Polar solvent (used)	12.0 g of methanol	12.0 g of methanol	12.0 g of methanol	12.0 g of methanol 0.5 g of water
Catalyst	0.16 g of [Ru(<i>Pn</i> Octyl ₃) ₄ (H) ₂]	0.16 g of [Ru(<i>Pn</i> Octyl ₃) ₄ (H) ₂]	0.16 g of [Ru(<i>Pn</i> Octyl ₃) ₄ (H) ₂]	0.1 g of [Ru(<i>Pn</i> Butyl ₃) ₄ (H) ₂]
Injection of CO ₂	To 1.7 MPa abs	To 1.6 MPa abs	To 1.8 MPa abs	To 1.7 MPa abs
Injection of H ₂	To 8.0 MPa abs	To 8.0 MPa	To 8.0 MPa	To 8.0 MPa
Heating	50°C	50°C	50°C	50°C
Reaction time	1.5 hours	1.5 hours	16 hours	1.5 hours
Addition of water after the reaction	2.5 g	4.7 g	2.5 g	0.8 g
Upper phase	26.3 g	27.4 g	23.2 g	17.5 g
Lower phase	24.7 g 6.6% of formic acid	25.5 g 5.9% of formic acid	28.1 g 6.8% of formic acid	28.9 g 7.4% of formic acid
c _{Ru} in upper phase after reaction and addition of water	350 ppm	280 ppm	370 ppm	200 ppm
c _{Ru} in lower phase after extraction	4 ppm	2 ppm	< 1 ppm	43 ppm

Example C1-9 (reuse of the catalyst and catalyst extraction)

A 100 ml autoclave made of Hastelloy C and provided with a blade stirrer was charged under inert conditions with trialkylamine, polar solvent and the catalyst. The autoclave was subsequently closed and CO₂ was injected at room temperature. H₂ was then injected and the reactor was heated while stirring (1000 rpm). After the reaction time, the autoclave was cooled and the reaction mixture was depressurized. After the reaction, water was added to the reaction output and the mixture was stirred at room temperature for 10 minutes. A two-phase product mixture was obtained, with the upper phase being enriched in the still free tertiary amine and the homogeneous catalyst and the lower phase being enriched in the polar solvent and the formic acid/amine adduct formed. The phases were subsequently separated and the formic acid content of the lower phase and also the ruthenium content of both phases were determined by the methods described below. The upper phase comprising ruthenium catalyst was then made up to 37.5 g with fresh amine and reused for the CO₂ hydrogenation with the same solvent under the same reaction conditions as before. After the reaction was complete and water had been added, the lower phase was separated off and admixed three times under inert conditions with the same amount (mass of amine corresponds to the mass of the lower phase) of fresh trialkylamine (stirred for 10 minutes at room temperature and phases subsequently separated) to extract the catalyst. The total content of formic acid in the formic acid/amine adduct was determined by potentiometric titration with 0.1 N KOH in MeOH using a "Mettler Toledo DL50" titrator. The ruthenium content was determined by AAS. The parameters and results of the individual experiments are shown in Tables 1.8 to 1.13.

Examples C-1 to C-9 show that variation of the catalyst, the amount of water added (both before and after the reaction) and the reaction conditions make it possible for the active catalyst to be reused for the CO₂ hydrogenation and the ruthenium in the product phase can be reduced to 2 ppm by means of only a single extraction.

Table 1.8

	Example C-1a (first hydrogenation)	Example C-1b (reuse of the catalyst and extraction)	Example C-2a (first hydrogenation)	Example C-2b (reuse of the catalyst and extraction)
Tertiary amine	37.5 g of trihexylamine	Upper phase from C-1a made up to 37.5 g with fresh trihexylamine	37.5 g of trihexylamine	Upper phase from C-2a made up to 37.5 g with fresh trihexylamine
Polar solvent (used)	12.0 g of methanol 0.5 g of water	12.0 g of methanol	12.0 g of methanol 0.3 g of water	12.0 g of methanol 0.25 g of water
Catalyst	0.16 g of $[\text{Ru}(\text{P}n\text{Octyl}_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexylphosphino)ethane	Upper phase from C-1a	0.16 g of $[\text{Ru}(\text{P}n\text{Octyl}_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexylphosphino)ethane	Upper phase from C-2a
Injection of CO_2	To 1.6 MPa abs	To 1.5 MPa abs	To 1.6 MPa abs	To 1.7 MPa abs
Injection of H_2	To 8.0 MPa abs	To 8.0 MPa	To 8.0 MPa abs	To 8.0 MPa abs
Heating	70°C	70°C	70°C	70°C
Reaction time	1.5 hours	1.5 hours	1.5 hours	1.5 hours
Addition of water after the reaction	0.5 g	1.0 g	1.0 g	1.0 g
Upper phase	19.3 g	24.7 g	20.9 g	25.9 g
Lower phase	30.8 g 6.0% of formic acid	25.4 g 5.9% of formic acid	29.9 g 6.6% of formic acid	24.8 g 6.4% of formic acid
c_{Ru} in upper phase after reaction and addition of water	250 ppm	170 ppm	200 ppm	140 ppm
c_{Ru} in lower phase after reaction and addition of water	120 ppm	-	130 ppm	-
c_{Ru} in lower phase after extraction	-	9 ppm	-	10 ppm

Table 1.9

	Example C-3a (first hydrogenation)	Example C-3b (reuse of the catalyst and extraction)	Example C-4a (first hydrogenation)	Example C-4b (reuse of the catalyst and extraction)
Tertiary amine	37.5 g of trihexylamine	Upper phase from C-3a made up to 37.5 g with fresh trihexylamine	37.5 g of trihexylamine	Upper phase from C-4a made up to 37.5 g with fresh trihexylamine
Polar solvent (used)	12.0 g of methanol	12.0 g of methanol	12.0 g of methanol 0.5 g of water	12.0 g of methanol 0.5 g of water
Catalyst	0.16 g of $[\text{Ru}(\text{PnOctyl}_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexylphosphino)ethane	Upper phase from C-3a	0.16 g of $[\text{Ru}(\text{PnOctyl}_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexylphosphino)ethane	Upper phase from C-4a
Injection of CO_2	To 1.8 MPa abs	To 1.6 MPa abs	To 1.8 MPa abs	To 1.7 MPa abs
Injection of H_2	To 8.0 MPa abs	To 8.0 MPa	To 8.0 MPa abs	To 8.0 MPa abs
Heating	70°C	70°C	70°C	70°C
Reaction time	16 hours	1.5 hours	16 hours	1.5 hours
Addition of water after the reaction	1.0 g	1.0 g	1.0 g	1.0 g
Upper phase	19.9 g	24.7 g	19.7 g	24.0 g
Lower phase	30.8 g 6.8% of formic acid	24.4 g 6.0% of formic acid	31.1 g 7.1% of formic acid	26.8 g 6.4% of formic acid
C_{Ru} in upper phase after reaction and addition of water	205 ppm	135 ppm	250 ppm	175 ppm
C_{Ru} in lower phase after reaction and addition of water	145 ppm	-	125 ppm	-
C_{Ru} in lower phase after extraction	-	4 ppm	-	4 ppm

Table 1.10

	Example C-5a (first hydrogenation)	Example C-5b (reuse of the catalyst and extraction)	Example C-6a (first hydrogenation)	Example C-6b (reuse of the catalyst and extraction)
Tertiary amine	37.5 g of trihexylamine	Upper phase from C-5a made up to 37.5 g with fresh trihexylamine	37.5 g of trihexylamine	Upper phase from C-6a made up to 37.5 g with fresh trihexylamine
Polar solvent (used)	12.0 g of methanol	12.0 g of methanol	12.0 g of methanol	
Catalyst	0.16 g of $[\text{Ru}(\text{PnOctyl}_3)_4(\text{H})_2]$	Upper phase from C-5a	0.16 g of $[\text{Ru}(\text{PnOctyl}_3)_4(\text{H})_2]$	Upper phase from C-6a
Injection of CO_2	To 1.7 MPa abs	To 1.6 MPa abs	To 1.7 MPa abs	To 1.7 MPa abs
Injection of H_2	To 8.0 MPa abs	To 8.0 MPa	To 8.0 MPa abs	To 8.0 MPa abs
Heating	50°C	50°C	50°C	50°C
Reaction time	1.5 hours	1.5 hours	1.5 hours	1.5 hours
Addition of water after the reaction	1.0 g	1.0 g	2.5 g	1.0 g
Upper phase	22.1 g	27.1 g	23.8 g	28.6 g
Lower phase	27.8 g 6.7% of formic acid	22.1 g 4.5% of formic acid	26.9 g 6.2% of formic acid	20.6 g 4.8% of formic acid
C_{Ru} in upper phase after reaction and addition of water	420 ppm	310 ppm	400 ppm	310 ppm
C_{Ru} in lower phase after reaction and addition of water	14 ppm	-	4 ppm	-
C_{Ru} in lower phase after extraction	-	2 ppm	-	2 ppm

Table 1.11

	Example C-7a (first hydrogenation)	Example C-7b (reuse of the catalyst and extraction)
Tertiary amine	37.5 g of trihexylamine	Upper phase from C-7a made up to 37.5 g with fresh trihexylamine
Polar solvent (used)	12.0 g of methanol 0.25 g of water	12.0 g of methanol 0.25 g of water
Catalyst	0.16 g of $[\text{Ru}(\text{PnOctyl}_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexylphosphino)ethane	Upper phase from C-7a
Injection of CO_2	To 1.5 MPa abs	To 1.6 MPa abs
Injection of H_2	To 8.0 MPa abs	To 8.0 MPa
Heating	50°C	50°C
Reaction time	1.5 hours	1.5 hours
Addition of water after the reaction	1.0 g	1.0 g
Upper phase	17.5 g	19.7 g
Lower phase	33.0 g 7.3% of formic acid	30.6 g 7.1% of formic acid
C_{Ru} in upper phase after reaction and addition of water	370 ppm	260 ppm
C_{Ru} in lower phase after reaction and addition of water	34 ppm	-
C_{Ru} in lower phase after extraction	-	16 ppm

Table 1.12

	Example C-8a (first hydrogenation)	Example C-8b (reuse of the catalyst and extraction)	Example C-8c (reuse of the catalyst and extraction)
Tertiary amine	37.5 g of trihexylamine	Upper phase from C-8a made up to 37.5 g with fresh trihexylamine	Upper phase from C-8b made up to 37.5 g with fresh trihexylamine
Polar solvent (used)	12.0 g of methanol	12.0 g of methanol	12.0 g of methanol
Catalyst	0.16 g of $[\text{Ru}(\text{P}n\text{Octyl}_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexylphosphino)ethane	Upper phase from C-8a	Upper phase from C-8b
Injection of CO_2	To 1.7 MPa abs	To 1.8 MPa abs	To 1.6 MPa abs
Injection of H_2	To 8.0 MPa abs	To 8.0 MPa	To 8.0 MPa
Heating	70°C	70°C	70°C
Reaction time	16 hours	1.5 hours	1.5 hours
Addition of water after the reaction	1.0 g	1.0 g	1.0 g
Upper phase	20.4 g	27.3 g	23.7 g
Lower phase	29.8 g 6.7% of formic acid	22.3 g 5.7% of formic acid	25.3 g 4.9% of formic acid
C_{Ru} in upper phase after reaction and addition of water	215 ppm	150 ppm	110 ppm
C_{Ru} in lower phase after reaction and addition of water	145 ppm	14 ppm	-
C_{Ru} in lower phase after extraction	-	-	3 ppm

Table 1.13

	Example C-9a (first hydrogenation)	Example C-9b (reuse of the catalyst and extraction)	Example C-9c (reuse of the catalyst and extraction)
Tertiary amine	37.5 g of trihexylamine	Upper phase from C-9a made up to 37.5 g with fresh trihexylamine	Upper phase from C-9b made up to 37.5 g with fresh trihexylamine
Polar solvent (used)	12.0 g of methanol 0.5 g of water	12.0 g of methanol	12.0 g of methanol
Catalyst	0.16 g of $[\text{Ru}(\text{P}n\text{Octyl}_3)_4(\text{H})_2]$, 0.08 g of 1,2-bis(dicyclohexylphosphino)ethane	Upper phase from C-9a	Upper phase from C-9b
Injection of CO_2	To 1.5 MPa abs	To 1.6 MPa abs	To 1.6 MPa abs
Injection of H_2	To 8.0 MPa abs	To 8.0 MPa	To 8.0 MPa
Heating	70°C	70°C	70°C
Reaction time	16 hours	1.5 hours	1.5 hours
Addition of water after the reaction	1.0 g	1.0 g	1.0 g
Upper phase	19.7 g	27.8 g	25.6 g
Lower phase	31.6 g 7.0% of formic acid	22.6 g 6.1% of formic acid	24.4 g 6.1% of formic acid
C_{Ru} in upper phase after reaction and addition of water	235 ppm	155 ppm	125 ppm
C_{Ru} in lower phase after reaction and addition of water	110 ppm	11 ppm	-
C_{Ru} in lower phase after extraction	-	-	3 ppm

Examples D1-D4 (thermal separation of the polar solvent from the trialkylamine/solvent/formic acid mixtures present as product phase after the extraction)

5 Alcohol and water are distilled off from the product phase (comprises the formic acid/amine adduct) under reduced pressure by means of a rotary evaporator. A two-phase mixture (trialkylamine phase and formic acid/amine adduct phase) is formed as bottoms, the two phases are separated and the formic acid content of the lower phase is determined by potentiometric titration with 0.1 N KOH in MeOH using a "Mettler Toledo DL50" titrator. The amine content and alcohol content are determined by gas
10 chromatography. The parameters and results of the individual experiments are shown in Table 1.14.

Examples D-1 to D-4 show that, in the process of the invention, various polar solvents can be separated off from the product phase under mild conditions to form a lower
15 phase which is relatively rich in formic acid and an upper phase which comprises predominantly tertiary amine.

Table 1.14

	Example D-1	Example D-2	Example D-3	Example D-4
Feed mixture (% by weight)	18.7 g 7.2% of formic acid 26.4% of 1-propanol 15.5% of water 48.3% of trihexylamine	19.3 g 5.8% of formic acid 22.8% of 2-propanol 4.1% of water 67.2% of trihexylamine	81.8 g 7.3% of formic acid 41.3% of methanol 15.4% of water 35.9% of tripentylamine	88.6 g 9.2% of formic acid 31.4% of ethanol 11.3% of water 48.1% of tripentylamine
Formic acid: amine feed mixture	1 : 1.2	1 : 2.0	1 : 1	1 : 1.1
Pressure	20 mbar	20 mbar	200 mbar	200 mbar
Temperature	50°C	50°C	100°C	110°C
Formic acid content of lower phase after distillation (% by weight)	16.4%	18.0%	23.7%	22.7%
Formic acid: amine in lower phase after distillation (molar ratio)	1 : 0.76	1 : 0.78	1 : 0.6	1 : 0.56
Recovery of formic acid after distillation	95.3%	93.7%	90.4%	95.2%

Examples E1 and E2 (thermal separation of the polar solvent from the trialkylamine/solvent/formic acid mixtures and dissociation of the formic acid/amine adduct)

5 Alcohol and water are distilled off from the product phase (comprises the formic acid/amine adduct) under reduced pressure by means of a rotary evaporator. A two-phase mixture (trialkylamine phase and formic acid/amine adduct phase) is formed as bottoms and the two phases are separated. The composition of the distillates (comprising the major part of the methanol and of the water), of the upper phase
10 (comprising the free trialkylamine) and of the lower phase (comprising the formic acid/amine adduct) was determined by gas chromatography and by potentiometric titration of the formic acid against 0.1 N KOH in MeOH using a "Mettler Toledo DL50" titrator. The formic acid is then thermally dissociated from the trialkylamine in the lower phase from the first step in a vacuum distillation apparatus comprising a 10 cm Vigreux
15 column. After the formic acid has been completely split off, a single-phase bottom product comprising the pure trialkylamine is obtained and can be used for extraction of the catalyst and recirculation to the hydrogenation. The formic acid and residual water are present in the distillate. The composition of the bottoms and of the distillate was determined by gas chromatography and by potentiometric titration of the formic acid
20 against 0.1 N KOH in MeOH using a "Mettler Toledo DL50" titrator. The parameters and results of the individual experiments are shown in Table 1.15.

Examples E-1 and E2 show that, in the process of the invention, various polar solvents can be separated off from the product phase under mild conditions, with a lower phase
25 which is relatively rich in formic acid and an upper phase comprising predominantly tertiary amine being formed. The formic acid can then be dissociated from the trialkylamine in this lower phase which is relatively rich in formic acid at elevated temperatures giving the free trialkylamine. The formic acid obtained in this way still comprises a little water, but this can be separated off from the formic acid by means of
30 a column having a relatively high separation power. The trialkylamine obtained both in the removal of the solvent and in the thermal dissociation can be used for removing the catalyst from the product stream.

Table 1.15

	Example D-1a (removal of the polar solvent)	Example D-1b (dissociation of the formic acid/amine adduct)	Example D-2a (removal of the polar solvent)	Example D-2b (dissociation of the formic acid/amine adduct)
Feed mixture (% by weight)	199.8 g 8.9% of formic acid 28.4% of methanol 5.6% of water 57.1% of trihexylamine	Lower phase from D1-a	199.8 g 7.8% of formic acid 33.0% of methanol 15.1% of water 44.0% of trihexylamine	Lower phase from D2-a
Formic acid: amine in feed mixture	1 : 1.1	1 : 0.64	1 : 1	1 : 0.89
Pressure	200 mbar	90 mbar	200 mbar	90 mbar
Temperature	120°C	153°C	120°C	153°C
Lower phase in the bottoms after distillation (% by weight)	79.8 g 22.1% of formic acid 1.5% of water 76.4% of trihexylamine	63.6 g 100% of trihexylamine	69.4 g 14.9% of formic acid 6.9% of water 78.2% of trihexylamine	55.5 g 99.7% of trihexylamine 0.3% of water
Upper phase in the bottoms after distillation	50.5 g 100% of trihexylamine	Single-phase	32.7 g 99.7% of trihexylamine 0.3% of water	Single-phase
Distillate	66.6 g 0.3% of formic acid 81.2% of methanol 18.5% of water	14.9 g 92.1% of formic acid 7.9% of water	93.1 g 70.1% of methanol 29.9% of water	12.9 g 85.0% of formic acid 15% of water

The drawings specifically show:

figure 1 a block diagram of a preferred embodiment of the process of the invention,
 5 figures 2A,
 2B and 2C in each case different, preferred variants for the fractionated separation of
 polar solvent and water,

10 figure 3 a block diagram of a further preferred embodiment of the process of the
 invention.

In the embodiment as per figure 1, carbon dioxide, stream 1, and hydrogen, stream 2,
 are fed into the hydrogenation reactor I. In the reactor, the two streams are reacted in
 15 the presence of a catalyst comprising an element of group 8, 9 or 10 of the Periodic
 Table, a tertiary amine and a polar solvent to give a formic acid/amine adduct.

The output from the hydrogenation reactor I (stream 3), which can consist of one or two
 phases, is admixed with the stream 16 comprising predominantly water from the
 20 distillation vessel IV.

It is also possible to introduce the stream 16 comprising predominantly water directly
 into the phase separation vessel II. A lower phase enriched in formic acid-amine
 adducts and the polar solvent and an upper phase enriched in the tertiary amine and, if
 25 a homogeneous catalyst is used, also enriched in that are present in the phase
 separation vessel II. The upper phase 4 is recirculated to the hydrogenation reactor I.
 The lower phase 5 is fed to an extraction apparatus III in which catalyst residues are
 extracted with the tertiary amine from the phase separation vessel V (stream 13). The
 tertiary amine together with the catalyst residues (stream 6) from the extraction unit III
 30 is recirculated to the hydrogenation reactor I. The product phase 7 from the extraction
 unit III is fed to the thermal separation unit IV in order to separate off the polar solvent
 and the water thermally from the formic acid-amine adducts. The stream 7 can be
 passed beforehand over an adsorbent bed in order to remove last traces of catalyst
 from this stream. The polar solvent which is separated off thermally in the distillation
 35 unit IV is recirculated as stream 8 to the hydrogenation reactor I, the water is
 recirculated as stream 16 to the output from the hydrogenation reactor (stream 3) and
 the two-phase mixture from the bottom of the distillation unit IV, which comprises the
 formic acid-amine adducts and the tertiary amine, is fed to the phase separation vessel
 V. The formic acid-amine adducts are separated off in the phase separation vessel V
 40 and fed as stream 10 to the distillation unit VI in which they are thermally dissociated
 into free formic acid and tertiary amine. The free formic acid is taken off as overhead
 product, stream 12, and the two-phase bottoms from the distillation unit VI, which

comprise tertiary amine and undissociated formic acid/amine adducts, stream 11, is fed back to the phase separation vessel V. The tertiary amine which is separated off in the phase separation vessel V is fed as stream 13 to the extraction unit III in order to extract catalyst residues, or part of stream 13 can be recirculated directly to the hydrogenation reactor I if not all the trialkylamine is required for the extraction.

Figures 2A, 2B and 2C schematically show different variants of the thermal removal of water and polar solvent.

Figure 2A shows the removal of the two streams, i.e. the stream 8 comprising predominantly polar solvent and the stream 16 comprising predominantly water, in a single distillation column which can be a column with a side offtake or a dividing wall column.

Figure 2B schematically shows an embodiment with a 2-column variant (columns IVa and IVb), where the lower-boiling component, generally the polar solvent, is separated off in the first column, IVa, and the intermediate-boiling component, generally the water, is separated off as stream 16 in the second column, IVb, into which a feed stream 7a depleted in the polar solvent is fed.

Figure 2C shows a further embodiment for the removal of water and the polar solvent, where the phase 9 comprising the formic acid/amine adducts and the tertiary amine is firstly separated off in a first distillation column IVc and a stream 7b is subsequently fractionated in a second distillation column IVd to give a stream 8 comprising predominantly polar solvent and a stream 16 comprising predominantly water.

Figure 3 shows the block diagram of a further preferred embodiment of the process of the invention, where, unlike the embodiment depicted in figure 1, the fraction comprising predominantly water, viz. stream 16, is discharged from the distillation unit IV and supplied to the output from the hydrogenation reactor I, stream 3, fresh water, stream 17.

In addition, the embodiment shown schematically in figure 3 differs from the variant shown in figure 1 in that a further phase separation vessel, VII, is provided and is supplied with the product stream 9 from the distillation unit IV, which comprises the formic acid/amine adducts and the tertiary amine, and in which the tertiary amine is separated off as stream 15 and recycled as stream 15 to the extraction unit III, or part of stream 15 is recirculated directly to the hydrogenation reactor I if not all the trialkylamine is required for the extraction.

The stream comprising formic acid/amine adducts is subsequently fed to the distillation unit VI in which the adducts are dissociated into free formic acid, stream 12. The two-phase bottoms from the distillation unit VI, which comprise tertiary amine and undissociated formic acid/amine adducts, are fed to the phase separation vessel V in which a stream 13 comprising the tertiary amine is separated off, and the stream 13 is recycled to the distillation unit III in order to extract catalyst residues. Undissociated formic acid/amine adducts, stream 10, are recycled to the distillation unit VI.

Claims

1. A process for preparing formic acid by reaction of carbon dioxide (1) with hydrogen (2) in a hydrogenation reactor (I) in the presence of

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- a catalyst comprising an element of group 8, 9 or 10 of the Periodic Table,
- a tertiary amine comprising at least 12 carbon atoms per molecule and
- a polar solvent comprising one or more monoalcohols selected from among methanol, ethanol, propanols and butanols,

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to form formic acid/amine adducts as intermediates which are subsequently thermally dissociated,

where a tertiary amine which has a boiling point at least 5°C higher than that of formic acid is used and

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a reaction mixture comprising the polar solvent, the formic acid/amine adducts, the tertiary amine and the catalyst carried from the reactor is formed in the reaction in the hydrogenation reactor (I),

wherein

the work-up of the output (3) from the hydrogenation reactor (I) is carried out by the following process steps:

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- 1) addition of water to the output (3) from the hydrogenation reactor to give two liquid phases,

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- 2) separation of the two liquid phases in a phase separation vessel (II), recirculation of the upper phase (4) from the phase separation vessel (II) to the hydrogenation reactor (I) and passing-on of the lower phase (5) from the phase separation vessel (II) to an extraction apparatus (III) in which

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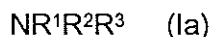
- 3) residues of catalyst are extracted with the same tertiary amine which was used in the hydrogenation, the catalyst-laden tertiary amine (6) is recycled to the hydrogenation reactor (I) and the catalyst-free stream of polar solvent (7) loaded with the formic acid/amine adducts is passed on to a distillation unit (IV) in which

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- 4) a fractional distillation is carried out to give a first fraction (8) which comprises predominantly the polar solvent and is recycled to the hydrogenation reactor (I), a second fraction (16) which comprises predominantly water and is recycled to the output (3) from the hydrogenation reactor (I) or is discarded and also a fraction (9),

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- 5) is separated in a phase separation vessel (V) into an upper phase comprising predominantly the tertiary amine and a lower phase comprising predominantly the formic acid/amine adducts, where
- 5 6) the lower phase from the phase separation vessel (IV) is fed to a thermal dissociation unit (VI) and dissociated therein into a stream (11) which comprises the tertiary amine and is recirculated to the phase separation vessel (V) and pure formic acid (12) and
- 10 a stream (13) comprising the tertiary amine is conveyed from the phase separation vessel (V) into the extraction apparatus (III) as selective solvent for the catalyst.
2. The process according to claim 1, wherein, in process step (6), only a substream of the stream (13) comprising the tertiary amine is conveyed from the phase separation vessel (V) into the extraction apparatus (III) as selective solvent for the catalyst and the remaining proportion of the stream (13) comprising the tertiary amine is conveyed into the hydrogenation reactor (I).
- 15
3. The process according to claim 1 or 2, wherein an amine of the general formula (Ia)
- 20



25 where the radicals R^1 to R^3 are identical or different and are each, independently of one another, an unbranched or branched, acyclic or cyclic, aliphatic, araliphatic or aromatic radical having in each case from 1 to 6 carbon atoms, where individual carbon atoms can also be substituted, independently of one another, by a hetero group selected from the group consisting of -O- and >N- or two or all three radicals can also be joined to one another to form a chain comprising at least four atoms in each case, is used as tertiary amine, with the proviso that the tertiary amine comprises at least 12 carbon atoms per molecule.

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4. The process according to claim 3, wherein an amine of the general formula (Ia) in which the radicals R^1 to R^3 are selected independently from the group consisting of C_1 - C_{12} -alkyl, C_5 - C_8 -cycloalkyl, benzyl and phenyl is used as tertiary amine.
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5. The process according to claim 3, wherein a saturated amine of the general formula (Ia) is used as tertiary amine.

6. The process according to claim 3, wherein an amine of the general formula (Ia) in which the radicals R^1 to R^3 are selected independently from C_5 and C_6 -alkyl is used as tertiary amine.
- 5 7. The process according to any of claims 1 to 6, wherein methanol and/or ethanol are used as polar solvent.
8. The process according to any of claims 1 to 7, wherein the amount of water added in process step 1) is such that the water content in the lower phase (5) from the
10 phase separation vessel (II), based on the total weight of the lower phase (5) from the phase separation vessel (II), is from 0.1 to 50% by weight, preferably from 2 to 30% by weight.
9. The process according to any of claims 1 to 8, wherein the catalyst is a
15 homogeneous catalyst.
10. The process according to claim 9, wherein the homogeneous catalyst is a metal-organic complex comprising an element of group 8, 9 or 10 of the Periodic Table and at least one phosphine group having at least one unbranched or branched,
20 acyclic or cyclic aliphatic radical having from 1 to 12 carbon atoms, with individual carbon atoms also being able to be substituted by $>P-$.
11. The process according to any of claims 1 to 10, wherein the reaction in the hydrogenation reactor (I) is carried out at a temperature in the range from 20 to
25 200°C and a pressure in the range from 0.2 to 30 MPa abs.
12. The process according to claim 11, wherein the pressure in the hydrogenation reactor (I) and in the phase separation vessel (II) is the same or approximately the same.
- 30 13. The process according to claim 11, wherein the temperature in the hydrogenation reactor (I) and in the phase separation vessel (II) is the same or approximately the same.