

Preparation of carboxylic acids by carbonylation of olefins

The present invention relates to a process for preparing
5 carboxylic acids or their esters by reacting an olefin with
carbon monoxide in the presence of water and a halogen-free
catalyst system comprising a mixture of rhodium or a rhodium
compound, a nitrogen-containing compound, an alkali metal
carboxylate or alkaline earth metal carboxylate and a glycol
10 ether at from 30 to 150°C and a pressure of from 30 to 150 bar.

In Industrielle Organische Chemie, 1994, 4th edition, Verlag
Chemie, pp. 153-154, Weissermel et al. describe the carbonylation
of olefins by the Reppe process, for example the preparation of
15 propionic acid from ethylene, carbon monoxide and water in the
presence of catalysts. The catalyst used is nickel propionate
which is converted into nickel carbonyl under the reaction
conditions. A high ethylene conversion is only achieved at high
pressures (200-240 bar). These reaction conditions require the
20 costly construction of suitable reactors and - due to the
corrosive nature of the product under the reaction conditions -
special and expensive materials of construction.

Carbonylations of olefins can be carried out at pressures of
25 about 100 bar using noble metal catalysts. Thus, EP-A 495 547
teaches the use of catalysts which comprise a palladium source
and bidentate phosphine ligands. However, such catalysts are
frequently deactivated by precipitation of metallic palladium
after a short reaction time; in particular, the phosphine ligands
30 used are not stable under the desired reaction conditions.

DE-A 2 263 442 describes the carbonylation of olefins over
halogen-free rhodium- or iridium-containing catalysts in the
presence of phenol derivatives or thiophenol derivatives or
35 fluorinated carboxylic acids, thiocarboxylic acids or sulfonic
acids. However, the catalytic activity is unsatisfactory.

WO 98/37049 discloses the carbonylation of olefins at 30-100 bar
and 100-270°C over a halogen-free, nickel-containing catalyst
40 system which further comprises an additional metal and also a
tertiary or quaternary nitrogen, arsenic or phosphorus compound
or a nitrogen-containing heterocyclic compound. The catalyst
system is so active even at low water concentrations that it is
possible to prepare carboxylic acids which have a water content
45 of less than 1% even in the reactor output. Disadvantages are the
instability of the quaternary ammonium compounds at the high
temperatures necessary and also the high volatility and toxicity

of the nickel tetracarbonyl formed during reaction, which make costly purification of the waste gas necessary.

EP-A 759 420 describes a process for preparing carboxylic acids by carbonylation of olefins at 30 - 200°C and 30 - 200 bar over a halogen-free catalyst system comprising a rhodium compound and at least one heterocyclic compound, which process can be carried out in a glycol ether solvent. However, the catalyst system has low activity at low water concentrations and, under these conditions, gives the carboxylic acids with low selectivity.

It is an object of the present invention to provide a process for the carbonylation of olefins which avoids the abovementioned disadvantages and gives carboxylic acids with good selectivity and activity even at low water concentrations.

We have found that this object is achieved by a new and improved process for preparing carboxylic acids from olefins and carbon monoxide in the presence of water and a halogen-free catalyst system comprising a mixture of

- a) rhodium or a rhodium compound,
- b) at least one nitrogen-containing heterocyclic compound,
- c) at least one alkali metal salt or alkaline earth metal salt of an aliphatic C₂-C₂₀-carboxylic acid and
- d) at least one glycol ether of the formula I

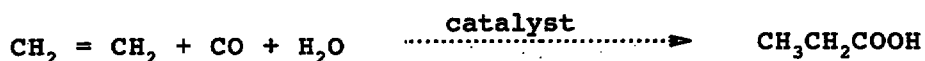
where R¹ and R² are independently C₁-C₂₀-alkyl or R³CO where R³ is hydrogen or C₁-C₂₀-alkyl, or R¹ and R² together form a C₁-C₂₀-alkylene chain, and n is from 1 to 30.

The process of the present invention enables the activity and the selectivity to be considerably improved compared to the catalyst system described in EP 759 420, particularly at low pressures of up to 100 bar and low water concentrations. In addition, the catalyst system used according to the present invention is stable under the reaction conditions. Deposition or decomposition of catalyst components, which is particularly disadvantageous in industrial processes, does not occur. Even at low water concentrations of from 0.5 to 2 mol of water per mol of olefin, the catalyst system used in the process of the present invention is so active that it makes it possible to prepare carboxylic acids which have a water content of from 0 to 5%, preferably below 1%, even in the reactor output, which considerably

simplifies the work-up of the reaction product.

This is particularly surprising since US-A 3 917 677 and EP-A 55 875 report the disadvantageous influence of alkali metal salts of aliphatic carboxylic acids such as sodium acetate on halogen-free carbonylation catalysts. Thus, Example 7 of US A 3,917,677 indicates that the activity of a halogen-free rhodium/phosphine catalyst in the alkoxycarbonylation of olefins decreases greatly in the presence of sodium acetate. Example 9 of EP-A 55 875 reports the loss of all activity of a halogen-free palladium catalyst system in the presence of sodium acetate.

Using the conversion of ethylene into propionic acid as an example, the following reaction equation illustrates the process of the present invention:



Suitable starting materials for the process of the present invention are aliphatic and cycloaliphatic alkenes having preferably from 2 to 20, particularly preferably from 2 to 7, carbon atoms. Examples are ethylene, propylene, iso-butene, 1-butene, 2-butene and the isomers of pentene and hexene as well as cyclohexene, among which ethylene is preferred.

The abovementioned starting materials are reacted with water and carbon monoxide (CO) with the latter being able to be used in pure form or diluted with inert gases such as nitrogen or argon. The molar ratios of the starting compounds olefin and water can vary within wide limits, but at least an equimolar amount of water is generally used. However, preference is given to using from 0.5 to 2 mol, particularly preferably from 0.9 to 1.5 mol, of water per mol of olefin in order to obtain carboxylic acids having a water content of from 0 to 5%, particularly preferably from 0 to 1%, in the reactor output.

The molar ratio of olefin to carbon monoxide can also vary greatly, in general from 5:1 to 1:5, with a molar ratio of from 0.5:1 to 1.5:1 mol of olefin per mol of carbon monoxide being preferred.

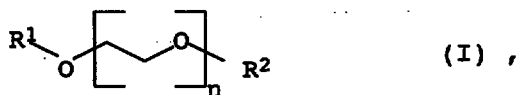
In the process of the present invention, the halogen-free catalyst system comprises a mixture of

- a) rhodium or a rhodium compound,

- b) at least one nitrogen-containing heterocyclic compound,
 c) at least one alkali metal salt or alkaline earth metal salt of an aliphatic C₂-C₂₀-carboxylic acid and

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- d) at least one glycol ether of the formula I



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where R¹ and R² are independently C₁-C₂₀-alkyl or R³CO where R³ is hydrogen or C₁-C₂₀-alkyl, or R¹ and R² together form a C₁-C₂₀-alkylene chain, and n is from 1 to 30.

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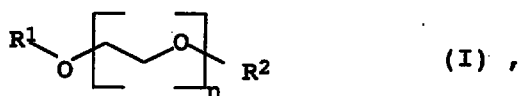
The catalyst system of the present invention is preferably free of nickel and nickel compounds and is also preferably free of phosphines.

- 20 In order to enable the formation of the catalytically active rhodium-containing components, soluble rhodium compounds such as acetates, propionates, acetylacetonates, oxides, hydroxides or carbonates are advantageously added to the reaction mixture. Further suitable rhodium compounds are carbonyl compounds, in
 25 particular dicarbonylrhodium acetylacetonate, bis(dicarbonylrhodium propionate), bis(dicarbonylrhodium acetate), Rh₄(CO)₁₂, Rh₆(CO)₁₆, salts of the anion [Rh₁₂(CO)₃₀]²⁻ or metal compounds stabilized by donor ligands such as nitrogen bases or by olefins. Depending on the solubilities, rhodium is
 30 present either in dissolved form or in suspension in the reaction mixture. The formation of the active catalyst component a) can be accelerated by introduction of hydrogen into the reaction mixture. The activation (prec carbonylation) of this catalyst component can also be carried out in a separate reaction space by
 35 reaction with CO and water or with CO and hydrogen at from 50 to 150°C and pressures of from 50 to 150 bar. Rhodium or the rhodium compounds of the catalyst component a) can also be used on organic or inorganic inert supports, for example activated carbon, graphite, aluminum oxide, zirconium oxide and silicon
 40 oxide. The rhodium content of the reaction solution (calculated as metal) is generally from 0.001 to 1% by weight, preferably from 0.01 to 0.5% by weight.

- Suitable nitrogen-containing heterocyclic compounds b) are
 45 pyridine, pyridines bearing from one to three C₁-C₃₀-alkyl, aryl or arylalkyl groups as substituents, quinoline and isoquinoline, pyrimidine, pyridazine, pyrazine, pyrazole, imidazole, thiazole

and oxazole. Preference is given to unsubstituted pyridine or pyridines which are monosubstituted by C₁-C₃₀-alkyl, aryl or arylalkyl, for example 4-ethylpyridine, 4-tridecylpyridine, 4-tert-butylpyridine, 4-(phenylpropyl)pyridine, 4-phenylpyridine or 4-benzylpyridine, and 4,4'-trimethylenedipyridine. The amount of nitrogen-containing heterocyclic compound present in the reaction solution is generally from 1 to 50% by weight, preferably from 5 to 30% by weight.

- 10 As alkali metal salt or alkaline earth metal salt c), preference is given to using the lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium or barium, particularly preferably sodium or potassium, salts of aliphatic C₂-C₂₀-carboxylic acid, preferably an aliphatic C₂-C₁₀-carboxylic acid such as acetic acid, propionic acid or butyric acid. Very particular preference is given to using an alkali metal or alkaline earth metal salt of the carboxylic acid which is to be prepared. Accordingly, the preparation of propionic acid is preferably carried out using propionates, particularly preferably sodium or potassium propionate. The amount of alkali metal or alkaline earth metal salt of the C₂-C₂₀-carboxylic acid present in the reaction solution is generally from 1 to 50% by weight, preferably from 5 to 30% by weight. It is also possible to prepare the alkali metal salt or alkaline earth metal salt c) in situ from the appropriate precursors, for example from alkali metal or alkaline earth metal hydroxides, hydrogencarbonates, carbonates or oxides, by reaction with the corresponding carboxylic acid.
- 30 The further catalyst component d) used is at least one glycol ether of the formula I



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- where R¹ and R² are independently C₁-C₂₀-alkyl, or R³CO where R³ is hydrogen or C₁-C₂₀-alkyl, or R¹ and R² together form a C₁-C₂₀-alkylene chain, and n is from 1 to 30. The compounds in which R¹ and R² are independently C₁-C₁₀-alkyl, in particular ethyl, propyl, pentyl or butyl, and n is 2, 3 or 4, for example diethylene glycol diethyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether and triethylene glycol diethyl ether, are preferred. The amount of glycol ether of the formula I present in the reaction solution is generally from 1 to 70% by weight, preferably from 5 to 50% by weight.

The molar ratio of the second catalyst component b) to the rhodium (calculated as metal) present in the first component a) of the catalyst system is from 10:1 to 10,000:1, preferably from 50:1 to 1500:1. The molar ratio of the third catalyst component
5 c), namely the alkali metal salt or alkaline earth metal salt of the C_x-C_y -carboxylic acid, to the rhodium (calculated as metal) is generally from 10:1 to 10,000:1, preferably from 50:1 to 1500:1. The molar ratio of the catalyst component d) to the rhodium (calculated as metal) present in the first component a) of the
10 catalyst system is from 20:1 to 10,000:1, preferably from 100:1 to 3000:1.

As solvents used in the process of the present invention, preference is given to the starting materials and products which
15 are liquid under the reaction conditions and the liquid catalyst components. However, an additional solvent may be used. Depending on the composition, the reaction mixture can form a single phase or be made up of two phases. The reaction is generally carried out at from 30 to 150°C, preferably from 90 to 120°C, and
20 pressures of from 30 to 150 bar, preferably from 40 to 100 bar.

The starting compounds olefin, water and the catalyst system can be mixed, if desired in a solvent, in a reactor prior to the reaction. They can then be heated to the reaction temperature,
25 and the reaction pressure is set by injection of carbon monoxide or, when using short-chain olefins, by injection of a mixture of this olefin and carbon monoxide.

The reaction is generally complete after from 0.5 to 3 hours. It
30 can be carried out continuously or batchwise in reactors such as tanks, bubble columns, tube reactors or loop reactors.

To isolate the process products, the reactor output is, in a preferred embodiment, depressurized. The liquid phase of the
35 reactor output, which comprises the process product together with soluble or suspended catalyst, is worked up by distillation so as to isolate the process product, if appropriate after a subsequent fine distillation. The catalyst-containing distillation bottoms are returned to the reaction. Likewise, any catalyst constituents
40 separated off prior to the distillation and also volatile catalyst constituents separated off as low boilers or as a sidestream in a distillation can be returned after appropriate work-up.

45 The process of the present invention allows the preparation of the process products in high space-time yields with high selectivity at low water concentrations, low temperatures and

moderate pressures while avoiding volatile, toxic transition metal compounds as catalyst components. Deposition or decomposition of catalyst components, which is particularly disadvantageous in the industrial implementation of processes, does not occur. The process of the present invention makes it possible to prepare carboxylic acids having water contents of <1% even in the reactor output and thus makes it possible to effect considerable cost savings in the preparation and the work-up.

10 Examples

Examples 1 to 6: Batchwise experiments on the preparation of propionic acid

- 15 A 270 ml autoclave provided with magnetic stirrer bar was charged with the amount of propionic acid, water and novel catalyst system indicated in Table 1. Subsequently, the initial pressure indicated in Table 1 was set using, unless otherwise indicated in Table 1, a gas mixture of 50% by volume of CO and 50% by volume
20 of ethylene, and the reaction mixture was heated to the temperature indicated in Table 1. After the reaction temperature had been reached, the reaction pressure as specified in Table 1 was set by means of the CO/ethene gas mixture and was maintained by injection of further amounts of the CO/ethene gas mixture.
25 After 1 hour, the autoclave was cooled to room temperature and vented, and the reaction product was analyzed by gas chromatography.

- The experimental results of Examples 1 to 6 according to the
30 present invention are summarized in Table 1. The space-time yield (STY_{PA}) is calculated as the amount of propionic acid produced divided by the volume of the reaction solution used (100 ml). The propionic acid selectivity (S_{PA}) is based on ethylene as starting compound. The conversion of the water is shown as C_{H_2O} in Table 1.
35 The catalyst activity is reported as turnover frequency (TOF). The rhodium compound (catalyst component (a)) used was dicarbonylrhodium acetylacetonate ($Rh(acac)(CO)_2$) in all examples. In the table, diglyme = diethylene glycol dimethyl ether, PA = propionic acid and DEGBDE [sic] = diethylene glycol di-n-butyl
40 ether. The catalyst component c) used was potassium propionate, abbreviated as KO_2CEt in Table 1.

Comparative Examples A to E

- 45 The comparative experiments A to E were carried out as described above for Examples 1 to 6, but the catalyst components (c) and (d) were left out in Experiments A and B. Experiment C was

carried out without catalyst component (d) and Experiments D and E were carried out without catalyst component (c). The results of the comparative experiments are summarized in Table 1. The comparative experiments show that lower space-time yields and selectivities are obtained in the absence of one or both catalyst components (c) and (d) than are achieved in Examples 1 to 6 according to the present invention.

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Table 1

No.	PA [g]	H ₂ O [g]	Pyridi- ne [g]	Rh [mmol]	Cat.(c) [mmol]	Cat.(d) [g]	p [bar]	T [°C]	STYPA [g/l/h]	SpA [%]	[H ₂ O]output [%m/m]	CH ₂ O [%]	TOF molPA/ (molRh·h)
A1)	80	10	10	0.43	-	-	100	100	89	86	6.0	34	280
B2)	85	5	10	0.43	-	-	100	100	51	81	2.4	50	237
C1)	77	5	10	0.43	250 KO ₂ CET	-	100	100	< 5	not able to be deter- mined	5.1	< 1 %	not able to be determi- ned
D2)	45	5	10	0.43	-	50 diglyme	100	100	98	90	1.8	60	472
E2)	45	5	10	0.43	-	50 DEGDBE	100	100	12	55	3	33	60
11)	47	5	10	0.43	125 KO ₂ CET	34 diglyme	100	100	195	94	< 0.1	> 99	994
21)	55	5	10	0.43	105 KO ₂ CET	28 diglyme	100	100	131	95	0.6	80	640
33)	47	5	10	0.86	125 KO ₂ CET	34 diglyme	55	100	184	92	0.4	91	469
42)	45	5	10	0.43	125 KO ₂ CET	50 DEGDBE	100	100	156	93	< 0.1	> 99	905

No.	PA [g]	H ₂ O [g]	Pyridi- ne [g]	Rh [mmol]	Cat.(c) [mmol]	Cat.(d) [g]	p [bar]	T [°C]	STY _{PA} [g/l/h]	SPA [%]	[H ₂ O] output [%m/m]	CH ₂ O [%]	TOF mol _{PA} / (mol _{Rh} ·h)
53)	45	5	10	0.43	125 KO ₂ CET	50 DEGDBE	55	100	189	96	0.7	82	1055
63)	46	10	10	0.43	125 KO ₂ CET	34 diglyme	55	110	300	95	1.84	77	1660

1) Initial pressure 30 bar CO/ethene gas mixture

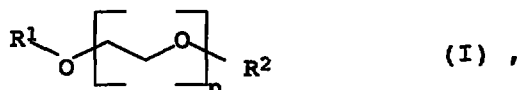
2) Initial pressure 9.5 bar CO

3) Initial pressure 4.5 bar CO



We claim:

1. A process for preparing carboxylic acids from olefins and carbon monoxide in the presence of water, in which a halogen-free catalyst system comprising a mixture of
 - a) rhodium or a rhodium compound,
 - b) at least one nitrogen-containing heterocyclic compound
 - c) at least one alkali metal salt or alkaline earth metal salt of an aliphatic C₂-C₂₀-carboxylic acid and
 - d) at least one glycol ether of the formula I



where R¹ and R² are independently C₁-C₂₀-alkyl, or R³CO where R³ is hydrogen or C₁-C₂₀-alkyl, or R¹ and R² together form a C₁-C₂₀-alkylene chain, and n is from 1 to 30,

is used.

2. A process for preparing carboxylic acids as claimed in claim 1, wherein the components of the catalyst system are present in a molar ratio of a):b):c):d) of from 1:10:10:20 to 1:10,000:10,000:10,000.
3. A process for preparing carboxylic acids as claimed in claim 1 or 2, wherein the catalyst component b) is selected from the group consisting of pyridine, pyridines bearing from one to three C₁-C₃₀-alkyl, aryl or arylalkyl groups as substituents, quinoline and isoquinoline, pyrimidine, pyridazine, pyrazine, pyrazole, imidazole, thiazole and oxazole.
4. A process for preparing carboxylic acids as claimed in any of claims 1 to 3, wherein the catalyst component c) is a sodium or potassium salt of an aliphatic C₂-C₂₀-carboxylic acid.
5. A process for preparing carboxylic acids as claimed in claim 1 or 2, wherein the catalyst component d) used is a glycol ether of the formula I, in which R¹ and R² are identical or





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different and are each C_1 - C_{20} -alkyl and n is 2, 3 or 4.

6. A process for preparing carboxylic acids as claimed in any of claims 1 to 5, wherein the reaction solution comprises 0.5 - 2 mol of water per mol of olefin.
7. A process for preparing carboxylic acids as claimed in any of claims 1 to 6, wherein the reaction is carried out at from 30 to 150°C and pressures of from 30 to 150 bar.
8. A process for preparing carboxylic acids as claimed in any of claims 1 to 7, wherein carbon monoxide and the olefin are used in a molar ratio of from 5:1 to 1:5.
9. A process for preparing carboxylic acids or their esters as claimed in any of claims 1 to 7, wherein the olefin used is ethylene.
10. A halogen-free catalyst system as defined in at least one of claims 1 to 4 which is suitable for carrying out processes for preparing carboxylic acids or their esters as defined in at least one of claims 1 to 9.
11. The use of a catalyst system as defined in at least one of claims 1 to 5 for preparing carboxylic acids from olefins and carbon monoxide in the presence of water.

This Sheet Has Been Replaced

