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Process for catalytically carrying out multiphase reactions, in particular hydroformylations

5 The present invention relates to a process for carrying out multiphase reactions in a tubular reactor, in particular for preparing aldehydes by reacting olefinically unsaturated compounds with hydrogen and carbon monoxide in the presence of a catalyst.

10 Aldehydes are used in the synthesis of many organic compounds. Their direct secondary products are alcohols and carboxylic acids which are used industrially. The alcohols prepared from the aldehydes are used, inter alia, as solvents and as a precursor for the preparation
15 of plasticizers and detergents.

It is known to prepare aldehydes and alcohols by reacting olefins with carbon monoxide and hydrogen. The reaction
20 is catalyzed by hydrido metal carbonyls, preferably those of metals of group 8 of the Periodic Table of the Elements. In addition to cobalt, which is used industrially to a broad extent as catalyst metal, recently rhodium has achieved increasing importance. In
25 contrast to cobalt, rhodium permits the reaction to be carried out at relatively low pressure. The hydrogenation of the olefins to give saturated hydrocarbons is markedly less when rhodium catalysts are used than when cobalt catalysts are used.

30 In the case of the processes carried out industrially, the rhodium catalyst is formed during the process from a catalyst precursor, synthesis gas and, if appropriate, other ligands having a modifying action. In the case of
35 use of modified catalysts, the modifying ligands can be present in the reaction mixture in excess. Ligands which have proved particularly expedient are tertiary phosphines or phosphites. Their use enables the reaction pressure to be decreased to values below 300 bar.

40 However, in the case of this process, problems arise in separating off the reaction products and recovering the catalysts which are homogeneously dissolved in the reaction product. Generally, for this purpose, the reaction product is distilled off from the reaction
45 mixture. In practice, this route, because of the thermal sensitivity of the catalyst or the products formed, can only be taken in the event of the hydroformylation of lower olefins having up to about 5 carbon atoms in the molecule.

50 On an industrial scale, C₄ and C₅ aldehydes are prepared, for example in accordance with DE 3234701 or DE 2715685.

In the latter process, the catalyst is dissolved in the organic phase which consists of product and high-boilers (resulting from the product). Olefin and synthesis gas are introduced into this mixture. The product is
5 discharged from the reaction together with the synthesis gas, and in a more recent variant taken off as liquid. Since the catalyst slowly decays in its output, a portion must continuously be discharged together with high-boilers and replaced by an equivalent amount. Because of
10 the high cost of rhodium, recovering the rhodium from the discharge stream is essential. The workup process is complex and thus burdens the process.

According to DE 3234701, this disadvantage is overcome, for example, by the catalyst being dissolved in water.
15 The water solubility of the rhodium catalyst used is achieved by using trisulfonated triarylphosphines as ligands. Olefin and synthesis gas are passed into the aqueous phase. The product resulting from the reaction
20 forms a second liquid phase. The liquid phases are separated outside the reactor and the catalyst phase separated off is recycled to the reactor.

Technically, the two said processes are multiphase
25 reactions.

Multiphase reactions are taken to mean below reactions which proceed with the participation of two or more immiscible, or only partially miscible, fluid phases.
30 This concerns, for example, reactions between a gas phase and a liquid phase (gl), between two liquid phases which are immiscible or have a miscibility gap (ll) and reactions in which both two liquid immiscible, or only partially miscible, phases and one gas phase participate
35 (gll).

However, in addition, the use of other fluid phases, e.g. supercritical phases, is also conceivable. A supercritical phase of this type can occur alternatively
40 to said phases, but also additionally.

Examples of industrially important gas-liquid reactions (gl) are, in addition to the hydroformylation of liquid olefins in the presence of a catalyst dissolved in
45 organic phase, the reaction of acetylene with carboxylic acids or hydrogenations with homogeneously dissolved catalysts or oxidations with air or oxygen.

Said cases share the problem of mass transfer, since the
50 reaction partners are present in different phases. In the case of hydroformylation in the 3-phase system, the process procedure is particularly difficult, since the starting materials are present in three separate phases.

Not only olefin but also synthesis gas must be transported into the aqueous catalyst phase in order to come into contact there with the catalyst. Finally, backtransport out of the aqueous phase must take place.

- 5 Since the transport processes are frequently slower than the actual reaction, such reactions are determined by the rate of mass transfer, and one speaks of a transport-inhibited reaction.

Multiphase reactions are associated with a series of
10 problems which makes them considerably more difficult to carry out industrially than is the case with simple homogeneous reactions. Some typical problems are mentioned below:

- 15 In all cases, the substances must be brought into contact with one another as intimately as possible in order to minimize the problem of mass transfer: a mass transfer area a_s as large as possible must be generated between the phases. On the other hand, the phases must be able to be
20 easily separated again after reaction is completed. Too intensive a mixing can lead to problems here. When two liquid phases are present, emulsion formation can occur, and in the case of gas-liquid processes foaming can occur. In the 3-phase process mentioned, all problems can
25 even occur simultaneously.

In addition to a high mass transfer surface area a_s , as high as possible a mass transfer coefficient k_1 should be achieved in all multiphase reactions. Overall, what is
30 termed the KLA value, i.e. the product of k_1 and a_s in the mass transfer equation

$$j = k_1 * a_s * (C^* - C)$$

35 where

- j [mol/s] is the molar flow rate of the reacting component passing through the phase interface,
 k_1 [m/s] is the mass transfer coefficient,
40 a_s [m²] is the phase interface area in the reactor,
 C^* [mol/m³] is the maximum solubility of the starting material in the second phase and
 C [mol/m³] is the actual concentration of the starting material, which in turn is coupled to
45 the reaction rate,
should be a maximum.

Another problem in the case of multiphase reactions is heat dissipation with exothermic reactions. If the
50 reaction rate is successfully increased by improving the mass transfer, obviously, more heat must be dissipated, which can lead to an unwanted temperature increase up to reaction runaway.

These problems of the multiphase reaction can be solved technically, e.g. by using a stirred-tank reactor.

- 5 For the hydroformylation of olefins, the use of a stirrer under elevated pressure is disadvantageous, since in this case a fault-susceptible shaft seal must be provided. In addition, in this process, a plurality of stirrers must be used in order to achieve adequate phase mixing.
- 10 The high heat of reaction produced in hydroformylations can generally only be controlled by using heat exchangers mounted in the interior of the reactor.
- 15 The use of a stirred tank always leads to backmixing, which decreases the effective concentration of the reactants, which leads to lowering the space-time yield. This disadvantage must be paid for by the capital expenditure on expensive reaction space.
- 20 During the hydroformylation of olefins, the space-time yield decreases sharply anyway with increasing number of carbon atoms in the olefin. The correlation between molecular size and reaction rate is known (B. Cornils, W. Herrmann, Aqueous-Phase Organometallic Catalysis, Concepts and Application, Verlag Wiley-VCH, pp. 308-310).
- 25 Thus, for example, the ratio of hydroformylation reaction rates of 1-pentene to 1-hexene is 2.6/1. A conversion of higher olefins therefore becomes increasingly uneconomic.
- 30 In view of the above considerations, there is a requirement for a process which avoids abovementioned disadvantages and, in addition, can be implemented industrially in a simple manner.
- 35 The object of the present invention is thus the development of a process for carrying out multiphase reactions which is suitable especially for preparing aldehydes by means of catalytic hydroformylation of olefins.

40 Technically, the novel process should comply with the following requirements of a multiphase process:

- 45 ♦ generation of high and stable mass transfer between the participating phases
- ♦ simple to carry out, as far as possible with conventional industrial apparatuses
- ♦ simple and safe heat dissipation
- ♦ high operation reliability
- 50 ♦ simple and secure scaling up

With respect to the preparation of aldehydes to be carried out, in addition the following are especially

important:

- ♦ high selectivity, avoidance in particular of high-boiling byproducts
- 5 ♦ no, or only slight, catalyst discharge
- ♦ high space-time yield, small reactors
- ♦ high product purity

10 By means of the process according to the invention, a surprisingly simple process has been found for carrying out multiphase reactions which can be carried out in a tubular reactor - if appropriate filled with random packing elements or internals - and is suitable for the hydroformylation of olefins using synthesis gas with high
15 space-time yields and selectivities.

The invention therefore relates to a process for carrying out multiphase reactions catalytically in a tubular reactor, with the catalyst being in the continuous phase
20 and at least one starting material being present in a disperse phase and the load factor B of the reactor being equal to or greater than 0.8.

In a special embodiment of the present invention, olefins
25 are hydroformylated, i.e. reacted with synthesis gas to form aldehydes, via the multiphase reaction.

The tubular reactor used in the process of the invention can comprise random packing elements or internals. Random
30 packing elements in the context of the present invention are, for example: Raschig rings, saddles, Pall rings, tellerettes, wire mesh rings, wire mesh cloth. Examples of internals are filter plates, flow breakers, column trays, perforated plates or other mixing apparatuses.
35 However, internals in the context of the present invention which are also conceivable are a plurality of narrow tubes connected in parallel, a multitube reactor thus resulting. Particular preference is given to structured mixer packings or demister packings.

40 Of critical importance in the process of the invention is maintaining or exceeding a minimum cross sectional loading of the tubular reactor. In the case of upwards mode operation of the reactor (flow direction from bottom
45 to top), the flooding point should be exceeded. The reactor is thus operated above the point at which bubble columns are customarily operated. In the case of downwards mode operations (flow direction from top to bottom), the cross sectional loading must be set in such
50 a manner that the reactor is completely flooded. Operation is therefore carried out above the point at which one can still speak of a trickle bed phase.

To establish more precisely the minimum loading of the reactor which is to be maintained, the load factor B of the tubular reactor is calculated as a dimensionless pressure drop of

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$$B = PD/PS,$$

where PD [Pa/m] is a pressure drop per unit length over the reactor under operating conditions and PS [Pa/m] is an operand having the dimension of a pressure per unit length, defined as ratio of mass flow rate M [kg/s] of all components in the reactor to the volumetric flow rate V [m³/s] of all components under operating conditions multiplied by g 9.81 m/s², i.e. $PS = (M/V) \cdot g$.

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Clearly PS should be the static pressure per meter of a multiphase mixture in a vertically upright tube if all phases were to flow with the same velocity. PS is a pure operand which results from the flow rates fed to the reactor and which can be specified independently of the flow direction of the reactor, the flow velocity of all phases or the flooding state of the reactor.

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The pressure drop PD [Pa/m] is used as an operand in order to specify the process conditions and can be calculated according to the customary methods for single- or multiphase flows. Customary processes for calculating the pressure drop PD in tubes, internals or dumped packing beds etc. can be looked up for example, in VDI-Wärmeatlas [VDI Atlas of Heat] 7th expanded edition, VDI-Verlag GmbH, Düsseldorf 1994, sections Lal to Lgb7, and in the standard work Heinz Brauer, Grundlagen der Einphasen- und Mehrphasenströmungen [Fundamentals of Single-phase and Multiphase Flows], Verlag Sauerländer, Aarau and Frankfurt am Main, 1971.

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The pressure drop in the case of single-phase flow through an empty tube is given by

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$$PD = C_w \cdot \rho / 2 \cdot w^2 / D$$

where

ρ [kg/m³] is the density of the flowing medium under operating conditions,

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w [m/s] is the flow velocity (volumetric flow rate/cross sectional area),

D [m] is the tube diameter and

C_w [-] is the drag coefficient of the tube through which flow passes.

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In the case of flow through random packing elements, arranged packings or internals, the velocity w must be replaced by the effective velocity (w/i) and the tube

diameter D by the hydraulic channel diameter d_H of the random packing elements or internals, so that the following applies:

5
$$PD = Cw \cdot \rho / 2 \cdot (w/\epsilon)^2 \cdot 1/d_H$$

where

- d_H [m] is the hydraulic channel diameter
1 ϵ [-] is the void content
10 Cw [-] is the drag coefficient of the packed apparatus with flow

The packing-specific data d_H and ϵ are frequently a component of the delivery specifications of packings.
15 Data are specified for a number of packings in the abovementioned VDI-Wärmeatlas.

The void content ϵ can also be determined experimentally by, for example, gaging the capacity in liters of the reactor before and after charging with the packings. The
20 hydraulic channel diameter in turn can, if it is unknown, be calculated from the specific surface area F [m^2/m^3] of the random packing elements or internals (generally known or experimentally determinable) according to the simple
25 relationship

$$d_H = 4\epsilon/F.$$

The drag coefficient of tubes, internals and random
30 packing elements is generally described as a function of the Reynolds number Re , which gives information on the flow state under the chosen conditions. In the case of random packing elements, internals etc., the relationship below is virtually always applicable:

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$$Cw = K_1/Re^n + K_2/Re^m$$

where frequently $n = 1$, $m = 0$ (approach according to S. Ergun, Chem. Engng. Progr. 48, (1948), 89), or $n = 1$,
40 $m = 0.1$ (approach according to Brauer et al.). K_1 , K_2 are packing-specific constants which are known from the delivery data or from the literature (examples can be found in the VDI-Wärmeatlas and in Brauer et al.). However, they can also be determined experimentally by
45 operating the tubular reactor containing random packing elements with a liquid under different velocities and determining Cw as a function of Re from the known data and the measured pressure drop.

50 The dimensionless Reynolds number Re finally is defined as

$$Re = w \cdot (\rho/\eta) \cdot D \text{ for empty tubes and}$$

$Re = (w/i) * (\rho/\eta) * d_H$ for tubes containing internals or random packing elements. η [Pa*s] denotes in each case the viscosity and ρ [kg/m³] denotes the density of the flowing medium.

5 The pressure drop in the case of two-phase flows (here gas-liquid for synthesis gas/catalyst solution) increases superproportionately. Generally, according to Lockhart-Martinelli (in Brauer et al.), the pressure drop
10 of the two-phase flow P_{1g} is based on the pressure drop of one of the two phases, for example on the pressure drop of the pure flowing liquid phase P_l , and related to the ratio of the pressure drop of the two phases P_l and P_g thought of as flowing alone.

15 To calculate pressure drops in two-phase flows, frequently dimensionless pressures are used according to $N^2 = P_{1g}/P_l$ and $X^2 = P_g/P_l$. The further correlation $N^2 = \text{function}(X^2)$ is frequently studied. Examples can be
20 found in the following literature references:

Y. Sato, T. Hirose, F. Takahashi, M. Toda: "Pressure Loss and Liquid Hold Up in Packed Bed Reactor with Cocurrent Gas-Liquid Down Flow"; J. Chem. Eng. of Japan, Vol. 6
25 (No. 2), 1973, 147-152;

D. Sweeney: "A Correlation for Pressure Drop in Two-Phase Concurrent Flow in Packed Beds"; AIChE-Journal, Vol. 13, 7/1967, 663-669;

V.W. Weekman, J.E. Myers: "Fluid-Flow Characteristics of Concurrent Gas-Liquid Flow in Packed Beds";
30 AIChE-Journal, Vol. 10 (No. 6), 11/1964, 951-957;

R.P. Larkins, R.P. White, D.W. Jeffrey: "Two-Phase Concurrent Flow in Packed Beds"; AIChE-Journal, Vol. 7 (No. 2) 6/1961, 231-239 or

35 N. Midoux, M. Favier, J.-C. Charpentier: "Flow Pattern, Pressure Loss and Liquid Holdup Data in Gas-Liquid Down-Flow Packed Beds with Foaming and Nonfoaming Liquids"; J. Chem. Eng. of Japan, Vol. 9 (No. 5), 1976, 350-356.

40 Frequently, the relationship proposed by Midoux, which has been checked for many gas-liquid systems, is used for the calculation. In the case of nonfoaming systems, this is, for example

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$$N^2 = 1 + 1/X + 1.14/X^{0.54}.$$

This relationship named after Lockhart-Martinelli is shown graphically in many works, detailed treatments
50 thereof can be found in many textbooks of process engineering and publications, as well as in Brauer et al.

The pressure drop of the two-phase flow P_{g1} results from the experimentally determined pressure drop or pressure drop estimated as described above of the pure flowing liquid phase P_1 then by

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$$P_{g1} = N^2 * P_1$$

In the special case of the preparation of aldehydes by hydroformylation of olefins, the calculation of the pressure drop becomes still more complex. In addition to the synthesis gas phase and a liquid catalyst phase, the presence of organic liquid phase must be taken into account. This problem can be taken into account by determining a further dimensionless pressure

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15 $N^2_{org} = P_{g11}/P_{lg}$, so that the pressure drop must be determined as below:

$$P_{g11} = N^2 * N^2_{org} * P_1$$

20 Generally, with a reactor length L [m] the following applies

$$PD = P_{g1}/L \text{ or } PD = P_{g11}/L$$

25 The pressure drop of a multiphase flow can thus be calculated via conventional means of chemical process engineering. The same applies to the above-defined dimensionless pressure drop B , i.e. the loading factor of the multiphase reactor.

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The size of the dimensionless loading factor B is a necessary basic condition of the process of the invention; B should be greater than or equal to 0.8, preferably greater than or equal to 0.9, or particularly

35 preferably greater than or equal to 1.

In the range B is greater than or equal to 0.8, a reactor operated from top to bottom begins to flood. Reference may be expressly made to the fact that when these

40 conditions are complied with, the advantages of the process of the invention are also achieved if the reactor is operated from bottom to top or in another direction.

Higher cross sectional loadings of the reactor ($B \gg 1$), recognizable by an increasing pressure differential over the reactor, are possible at any time and even desirable provided that the increasing space-time yields justify the energy consumption which increases to the same extent. An upper limit is therefore only given by

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50 practical considerations such as energy consumption or difficulties in the separation of the phases when the reaction is complete.

It can thus be seen that in addition to the volumetric flow rates of the individual phases or the superficial velocities derived therefrom $w = V/(\pi D^2/4)$ the dimensions of the reactor (length L, diameter D) and, in particular, the data of the packings used (hydraulic diameter d_H , void content ϵ) play an important role. Via the correct choice of these parameters, the process can be adapted without difficulty to the most varied requirements; it is only of importance to comply with the requirement $B \geq 0.8$, preferably $B \geq 0.9$ and particularly preferably $B \geq 1$.

In the case of a slow reaction, for example, the hydraulic diameter of the random packing elements is chosen to be small or their specific surface area is chosen to be high, so that the required conditions for B are already achieved at low flow velocities. In this manner sufficient residence times are achieved over the length of a reactor which is dimensioned expediently industrially. In the case of very rapid reactions, a reverse procedure is advisable.

A further criterion when carrying out the process of the invention is the ratio of the mass flow rate of the liquid catalyst-containing phase M_1 to the mass flow rate of the disperse phase or phases M_2 . In the case of hydroformylation, the mass flow rate of the catalyst phase M_1 is substantially greater than the mass flow rate of the disperse phases, i.e. the organic olefin phase M_{2a} and the synthesis gas phase M_{2b} . In the process of the invention the mass ratio M_1/M_2 of the continuous phase (M_1) to the disperse phases (M_2) can be greater than 2, for example $M_1/M_2 > 10$ applies. Flow conditions where $M_1/M_2 > 100$ are absolutely possible and are frequently even advantageous. Under the condition $M_1/M_2 > 2$, the catalyst phase is the continuous phase, while the disperse phases are divided into fine bubbles or into fine droplets. In the process of the invention it is possible that at least one starting material is dispersed by the energy introduced into the tubular reactor by the continuous phase. This leads to a distribution of at least one starting material in bubbles or droplets within the continuous catalyst phase.

This can also be estimated via conventional engineering means. Suitable approaches for this are those having dimension parameters such as

$$d_s/d_H = k \cdot Re_{g1(g11)}^{m*} We_{g1(g11)}^n$$

where

d_s is the diameter of the droplets or bubbles according to Sauter (in Brauer et al.)
 d_H is the hydraulic random packing element diameter,

- $Re_{gl(gll)}$ is the Reynolds number of the multiphase flow = $w_{gl(gll)} * (\rho_l \eta_l) * (d_H / \tau)$,
 $We_{gl(gll)}$ is the Weber number of the multiphase flow = $w_{gl(gll)}^2 * (\rho_l \sigma_{gl}) * (d_H / \tau^2)$,
5 k, m, n are empirical constants (known or to be determined by experiments),
 w is the superficial velocities [m/s] = $V / (\pi D^2 / 4)$,
 V is the volumetric flow rate under operating conditions [m³/s],
10 ρ is the density under operating conditions [kg/m³],
 η is the viscosity under operating conditions [Pa*s] and
 γ is the interfacial tension under operating conditions [N/m]
15 and the indices are l (liquid phase), g (gas phase), gl (gas/liquid two-phase flow) and gll (gas/liquid/liquid three-phase flow).

In the case of structured packings such as Sulzer SMV or narrow tubes as internals, it is plausible that a calculated or droplet diameter d_s greater than the channel diameter is not rational. However, this does not apply to permeable packings and random packing elements, for example wire mesh rings or wire mesh cloth (so-called demister packings or mist eliminators). In the process of the invention, calculated droplet diameters can be used which are at least equal to less than the hydraulic channel diameter:

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$$d_s / d_H \leq 1, \text{ preferably } < 0.9.$$

From the calculated droplet diameter, finally, a mass transfer surface area may be calculated from

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$$A_s = 6 \phi_g d_s [m^2 / m^3].$$

For the phase content ϕ_g of the disperse phase (in the case of hydroformylation synthesis gas and organic phase are dispersed), the following can be set

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$$\phi_g \sim w_g / w_{gl}$$

using the superficial velocities of the phases.

45 The residence time τ of the phases flowing through the reactor may be calculated approximately from $\tau \sim L^* \tau / w_{lg}$. The residence time τ in the process of the invention is generally far less than one hour and can be in the range of minutes or even below. Nevertheless, in the case of this completely unusual mode of operation - high catalyst throughput in the reactor, comparatively very low content of starting material in the reaction mass, causing in turn very short residence time - in many multiphase

reactions, surprisingly high space-time yields are achieved. Alternatively, markedly lower temperatures than usual can be employed for the same space-time yields, since the increase in reaction rate which, for example,
5 can be accompanied by minimization of secondary reactions and thus improved selectivity, permits this economically.

The process of the invention can be adapted highly flexibly to the most varied requirements. For special
10 requirements, the following embodiments of the process of the invention are suitable:

If the application requires a very long mixing zone or if static zones are required, for example for taking off
15 substance streams, a cascade arrangement of tubular reactors having internals or random packing elements is advisable.

A cascade of tubular reactors or the alternative disposition of packed and empty tube sections is advisable
20 if an especially low pressure drop is desirable.

In addition, the parallel disposition of tubular reactors or the use of a multitube reactor, in which case the
25 tubes can adopt the function of the internals, is conceivable. Furthermore, reactors having a multiple feed of gas over the reactor length can be provided if the gas consumption is so high that unfavorable phase ratios of gas to liquid result when the two phases are combined
30 upstream of the reactor.

The special conditions of the process of the invention permit further embodiments of the process. Thus the
35 high necessary circulation of the catalyst phase or of the continuous phase can be exploited in addition to the operation of a jet nozzle which is disposed as liquid jet gas compressor upstream of the actual tubular reactor. This can be used for thorough pre-mixing of the two phases and for compressing the gas
40 phase which makes possible the mode of operation at relatively high inlet pressures in the reactor. Finally, if, vice versa, instead of the compression of the gas the suction action is exploited, a recirculation of gas with simultaneous premixing of the phases
45 is even possible. The energy introduced into the tubular reactor via the catalyst-containing continuous phase can thus be used for dispersing the starting material phase or at least one starting material.

50 The heat dissipation in the case of highly exothermic reactions, for example in the case of hydroformylation, is also non-critical in the process of the invention. The high throughput of the catalyst circulation acts as

a heat carrier, so that even in the case of the adiabatic mode of operation of the reactor, only small temperature differences occur and a homogeneous temperature distribution in the reactor results without temperature peaks. The heat generated may then be conveniently dissipated by a conventional heat exchanger disposed anywhere in the external catalyst circuit, or exploited for energy production. For improved heat dissipation, under some circumstances, it may be expedient to run the catalyst circulation rate still higher (that is at higher B value) than is necessary according to the experimental results, since a lower temperature gradient over the reactor can be set via the catalyst circulation rate.

The process of the invention, in comparison with the prior art, offers considerable advantages, those which may be mentioned are as follows:

- At comparatively low temperatures, high space-time yields can be achieved. Formation of byproducts is extremely low, values of 1-2% by weight and below are possible. The catalyst is treated mildly, the deactivation is very low and a continuous discharge is avoided.

In the case of preparation of aldehydes by hydroformylation of olefins, further advantages result with the use of the process of the invention:

- Owing to the increased reaction rate, this process can also be used economically for hydroformylating higher olefins having more than 10 carbon atoms. In the case of gaseous olefins, the starting material portion remaining after a partial reaction can be recirculated by simple recycling by means of a jet nozzle.

- A special embodiment of the present invention, a process for hydroformylating olefins by synthesis gas in a multiphase system, may be described in more detail. The continuous phase used is the catalyst phase and it is pumped through a tubular reactor by means of a pump.

- Suitable solvents for preparing the catalyst solution and phase are all those solvents which comply with the following conditions:
The solvent is sparingly soluble in the product phase. The product dissolves only sparingly in the catalyst phase which consists of catalyst and solvent. The solvent has a sufficiently high solubility for the catalyst used.

The solvent can comprise as additive phase-transfer reagents, surface-active reagents or amphiphilic reagents or surfactants. The preferred solvent used is water.

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The hydroformylation catalysts used can be metals of subgroup 8 of the Periodic Table of the Elements (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt). These metals or compounds of these metals should be soluble in the catalyst phase, but
10 not the product phase, under the reaction conditions. If aqueous catalyst solutions are used, this necessitates water-soluble metal compounds. The preferred catalyst used is rhodium or water-soluble rhodium compounds. Suitable rhodium salts are for example rhodium(III)
15 sulfate, rhodium(III) nitrate, rhodium(III) carboxylates such as rhodium acetate, rhodium propionate, rhodium butyrate or rhodium 2-ethylhexanoate.

The type of ligands depends on the metal used and solvent
20 of the catalyst solution. These complexes must be catalytically active and not lose their catalytic activity in long-term operation. A condition of this is that the ligands do not alter, for example by reaction with the solvent.

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The ligands used for the catalytically active metals can be triarylphosphines. Suitable phosphines have one or two phosphorus atoms which have three aryl radicals per phosphorus atom, the aryl radicals being identical or
30 different and representing a phenyl, naphthyl, biphenyl, phenylnaphthyl or binaphthyl radical, in particular phenyl, biphenyl or binaphthyl radical. The aryl radicals can be bonded directly to the phosphorus atoms or via a $-(CH_2)_x$ group, where x is an integer from 1 to 4, preferably from 1 to 2, particularly preferably 1. For
35 water-soluble catalyst systems, a ligand should preferably contain three $-(SO_3)M$ radicals, where M is identical or different and is H, an alkali metal ion, an ammonium ion, a quaternary ammonium ion, (by calculation
40 half) an alkaline earth metal ion or zinc ion.

The $-SO_3M$ radicals are customarily substituents on the aryl radicals and give the triarylphosphines the required water solubility. A preferred sulfonated triarylphosphine
45 containing one phosphorus atom is trisodium tri-(m-sulfophenyl)phosphine.

In addition to the sulfonato units $-(SO_3M)$, other polar groups, for example carboxylato units, can also be used.

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The aqueous phase can be used directly in the hydroformylation or it can be subjected in advance to a preformation of the catalyst under reaction conditions in

order then to use it in preformed form. The aqueous catalyst solution may be prepared in a relatively simple manner, however, by dissolving a water-soluble metal salt and the water-soluble ligands in water and complexing them.

The metal salt concentration necessary in the process of the invention can be set over a broad range. The highest value is predetermined by the solubility. The reaction rate also depends on the metal salt concentration. Generally, at higher metal salt concentrations, higher reaction rates are achieved. On the other hand, higher metal salt concentrations mean higher costs. Therefore, depending on reactivity of the starting material and the other reaction conditions, an optimum can be chosen. The rhodium content in the catalyst phase is customarily 20 ppm to 2000 ppm, preferably 100 to 1000 ppm.

In the catalyst system used, the molar ratio between metal and ligands can be varied in order to achieve the optimum for each individual reaction. This ratio is between 1/5 and 1/200, in particular between 1/10 and 1/60.

The pH of the catalyst solution can be optimized for the hydroformylation of each olefin with respect to selectivity of aldehyde formation. It is between 2 and 8, preferably between 3.0 and 5.5.

Starting material which can be used for the hydroformylation are olefinic compounds having 2-25 carbon atoms, preferably 2-12 carbon atoms. The olefinic compounds can contain one or more carbon-carbon double bonds, each of which may be disposed terminally or internally. Preference is given to olefinic compounds having a terminal carbon-carbon double bond. An olefin of uniform structure can be used in the process. Olefin mixtures can also be used. The mixture can consist of isomeric olefins of the same number of carbon atoms or olefins of a differing number of carbon atoms or of a mixture which comprises both isomeric olefins and olefins of a differing number of carbon atoms. In addition, the olefins or olefin mixtures can comprise under reaction conditions inert substances such as aliphatic hydrocarbons.

In the process of the invention olefins from the most varied sources can be used. For example, olefins from cracking processes, dehydrogenations or from the Fischer-Tropsch synthesis may be mentioned. Likewise, suitable starting materials are olefins or olefin mixtures which have been formed by dimerization, oligomerization, codimerization, cooligomerization or metathesis of olefins. The olefins used can (under standard conditions) be gaseous, liquid or solid. Solid olefins are used as solutions. The solvents

used are inert liquids which are scarcely soluble in the catalyst phase. Particular preference is given to solvents which have a higher boiling point than the product to be prepared, since by this means separation off by distillation and recirculation are facilitated.

Preferably, α -olefinic compounds are used in the process of the invention. Examples of suitable α -olefinic compounds are 1-alkenes, alkyl alkenoates, alkylene alkenoates, alkenyl alkyl ethers and alkenols, for example propene, butene, pentene, butadiene, pentadiene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-hexadecene, 2-ethyl-1-hexene, 1,4-hexadiene, 1,7-octadiene, 3-cyclohexyl-1-butene, styrene, 4-vinylcyclohexene, allyl acetate, vinyl formate, vinyl acetate, vinyl propionate, allyl methyl ether, vinyl methyl ether, vinyl ethyl ether, allyl alcohol, 3-phenyl-1-propene, hex-1-en-4-ol, oct-1-en-4-ol, 3-butenyl acetate, allyl propionate, allyl butyrate, n-propyl 7-octenoate, 7-octenoic acid, 5-hexenamide, 1-methoxy-2,7-octadiene, 3-methoxy-1,7-octadiene, in particular propene, 1-butene, technically available mixtures which essentially comprise 1-butene, 2-butene and isobutene, and/or 1-pentene.

Products of the hydroformylation of olefins are aldehydes and if appropriate alcohols which are longer by one carbon atom. The aldehydes prepared by the process of the invention can be used for preparing alcohols by hydrogenation. The resultant alcohols are in turn precursors for plasticizers, for example as phthalic diesters or detergents.

In addition, the aldehydes prepared by the process of the invention are used in aldol condensations and in the preparation of carboxylic acids by oxidation.

Hydroformylation agents used are mixtures of hydrogen and carbon monoxide (synthesis gas) or other mixtures of hydrogen, carbon monoxide and substances inert under reaction conditions.

When liquid olefins or solid olefins in solution are used it is expedient to use the hydroformylation agent in excess so that as complete a degree of conversion as possible is achieved. This decreases the workup expenditure. When gaseous olefins are used it can, in contrast, be expedient to use a deficiency of hydroformylation reagent, since the excess gaseous olefin separates from the liquid product and can be recirculated back to the process.

The molar ratio of olefin to hydrogen and olefin to carbon monoxide can be greater than, less than or equal to 1.

The process of the invention, in the case of hydroformylation when a gaseous olefin is used, is firstly a two-phase reaction, with a liquid product phase forming during the reaction and thus a three-phase system being
5 formed. When a liquid olefin is used, a three-phase system is present from the beginning.

The process of the invention can be carried out in one or more tubular reactors having internals corresponding to the
10 preceding description.

In the process of the invention, the catalyst phase is the continuous phase; a mass ratio between catalyst phase and the disperse phase or phases in the range from 2/1 to
15 3500/1, preferably in the range 40/1 to 2500/1, is therefore expedient.

If the process of the invention is used for the hydroformylation of olefins, the mass ratio between catalyst
20 phase and olefinic phase at the reactor inlet can be in the range 5000/1 to 4/1, preferably in the range 2000/1 to 50/1. The mass ratio between catalyst phase and the hydroformylation agent (generally synthesis gas) is 4/1 to 10,000/1, preferably 200/1 to 4000/1.

25 The reactants can be fed preheated, i.e. in the range of the reaction temperature, or can be fed cold. Owing to the high phase ratio with the catalyst phase, the preheating may also be performed via the process heat.

30 If the process of the invention is used for the hydroformylation of olefins, the reaction is performed in a temperature range from 20°C to 250°C, preferably in the range from 90°C to 150°C; in this case the overall pressure
35 is between 10 bar and 300 bar, preferably between 20 bar and 150 bar.

Flow can pass through the reaction tube cocurrently from top to bottom or vice versa. For safety reasons, preference is
40 given to charging from the top.

The heat of reaction can be dissipated via various heat exchangers. The heat exchangers in this case need not be in the vicinity of the reaction space, but can also be
45 optionally outside the reactor. The individual heat fluxes are dependent on the specific heat of reaction and on the desired temperature in the reactor and in the workup apparatuses.

50 The heat of reaction dissipated can thus be simply utilized, for example in the process itself, for heating a distillation device or for generating steam.

The mixture leaving the reactor can be degassed in the event of use of gaseous olefins or in the event of an incomplete conversion in a gas-liquid separation vessel. The gas-liquid separation can be performed at the same pressure as
5 prevails at the reactor outlet. This is particularly advantageous when at least a portion of the expansion gas is recirculated to the reactor. Otherwise, expansion can also be performed at lower pressure (down to 1 bar).

10 The gas stream separated off can be wholly or partly recirculated to the reactor.

This recirculation can be achieved in a known manner, for example by a jet or mixing nozzle which is mounted upstream
15 of the reactor in the catalyst circulating stream, or by a circulating gas compressor. From energetic considerations, preferably a jet or mixing nozzle which is mounted upstream of the reactor in the catalyst circulating stream is used.

20 The remaining amount of gas, or optionally all of the gas can be introduced cooled or uncooled into an exhaust gas utilization system. When a cooler is used, the gas condensate arising in the cooler can be passed via a line to the gas-liquid separation vessel.

25 The degassed liquid mixture is mechanically separated in a liquid-liquid separation vessel into the catalyst phase and the product phase. This can be performed in settling vessels of various types of centrifuges. For reasons of cost, preference is given to settling vessels.

30 Although the residence times in the separation apparatus are not fundamentally critical, they are advantageously kept short. This has the following advantages: the separation apparatus is small and the capital costs thereof are
35 correspondingly low. With short residence times virtually no side reactions occur in the separation vessel. So that the phase separation proceeds rapidly, the density differences between the two phases must be sufficiently high and their viscosities must be low. All four parameters
40 are a function of temperature and can readily be determined by preliminary experiments.

Furthermore, the density and viscosity of the catalyst solution can be varied by selecting the solvent and
45 catalyst concentration. As a further possibility, the density and viscosity of the product phase can be altered by adding a solvent.

The phase separation can be performed in a broad temperature range. In this case the separation temperature can also be
50 higher than the temperature of the reaction discharge at the reactor outlet. For energetic reasons, however, it is not expedient to use a temperature higher than the liquid temperature in the gas separator. The lowest possible

temperature to be considered is the setting point of one of the two liquid phases. With respect to short separation times, however, excessively low temperature should not be chosen, as mentioned above.

5

The product stream is fractionated by known processes, e.g. by distillation.

The catalyst solution separated off is, if appropriate after
10 ejection of a small partial quantity and corresponding replacement by fresh catalyst solution, recycled to the reactor.

The examples below are intended to describe the invention
15 without restricting its broadness of application which is given by the patent claims.

Hydroformylation of olefins

The hydroformylation of olefins took place in an
20 experimental apparatus which is shown diagrammatically in Fig. 1. Herein, the aqueous catalyst is circulated by pumping by a pump 1. Olefin 3 and synthesis gas 4 are added to the catalyst phase 2. The multiphase mixture 5 is pumped through the tubular reactor 6 which is provided with static
25 mixer elements. The resulting mixture 7, consisting of product, unreacted starting material and the catalyst, is degassed in the gas separator 8. The gas 9, consisting of synthesis gas, if appropriate gaseous olefin and enriched inert substances is for the most part fed again to the
30 reactor 6 via a gas recycle line 10 using a mixture nozzle or jet nozzle 11. A small portion of the gas stream 9 is ejected via line 12. By suitable cooling 13 and return, olefin losses can be minimized. The ejection 14 is reduced to enriched inert substances and small amounts of unreacted
35 synthesis gas.

The liquid stream 15 arising after the degassing 8 is passed into a phase separation vessel 16. Here the aqueous catalyst phase 2 is separated off and fed back to the circulation. The heat of reaction can be dissipated via
40 heat exchangers 17, 19, 20 lying outside the reactor. The product is taken off via line 18 and if appropriate further purified.

Examples 1-7 describe the hydroformylation of propene by the
45 process of the invention.

Examples 1-5:

A reactor 6 having a length of 3 m and a diameter of 17.3 mm was used which comprises static mixer elements from Sulzer
50 having a hydraulic diameter of 2 mm.

For this example the line 10 for recycling the gas was closed. The solvent used for the catalyst was water. The pH was 7. The flow through the reactor was at a temperature of

120°C at a catalyst loading of 400 kg/h. The reaction pressure was 50 bar. The catalyst used was rhodium at a concentration of 800 ppm based on the solvent phase. The ligand used was tri(m-sulfophenyl)phosphine (TSTPP) in the form of its sodium salt, and the P/Rh ratio was 60. For Experiment 2, the reaction conditions of Experiment 1 were set except that the reaction temperature was 130°C. For Experiment 3 the reaction conditions of Experiment 1 were set except that the reaction pressure was 70 bar. For Experiment 4 the reaction conditions of Example 1 were set except that the pH of the catalyst solution was set to 4. For Experiment 5 the reaction conditions of Example 1 were set except that the catalyst loading of the reactor was 300 kg/h. The starting material streams fed to the reactor and the product streams are given in the table in mol/h.

Example	1	2	3	4	5
Space-time yield [t/(m ³ *h)]	0.98	1.39	1.23	1.00	0.71
B	13.16	13.14	13.16	13.16	8.06
Starting material					
CO	22.79	16.99	28.24	23.92	12.73
H ₂	21.28	15.87	26.38	22.87	11.89
N ₂	0.12	0.09	0.15	0.10	0.07
Propene	51.49	35.57	31.13	36.01	33.45
Propane	0.17	0.12	0.10	0.11	0.11
Product					
CO	2.15	2.09	2.08	0.66	2.11
H ₂	0.89	0.93	0.98	0.37	0.97
Propene	3.35	6.73	3.04	3.45	4.00
Isobutanal	0.24	0.51	0.53	0.39	0.20
n-Butanal	5.46	11.03	9.82	6.19	4.66
Isobutanol	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
n-Butanol	0.07	0.07	0.07	0.06	0.07
2-Ethylhexanal	0.09	0.03	0.08	< 0.01	0.02
2-Ethylhexenal	0.26	0.19	0.18	< 0.01	0.09
Exhaust gas					
CO	9.50	3.06	13.23	13.72	6.81
H ₂	3.45	1.46	9.97	10.82	3.59
N ₂	0.29	0.10	0.09	0.10	0.16
Propene	37.37	13.56	17.72	19.47	36.93
Propane	0.17	0.10	0.17	0.10	0.09
Isobutanal	0.24	0.16	0.15	0.18	0.14
n-Butanal	4.59	3.13	2.72	2.62	2.56

Examples 6 and 7:

These examples illustrate the use of the gas recycle line 10. By this means the loss of valuable materials via the exhaust gas line can be minimized. Already with these examples, conversion rates > 90% can readily be achieved. On account of the cooler 13, the ejection of propene in the exhaust gas can be virtually completely prevented, so that

propene exits only with the liquid product. The product 18 which is taken off from the phase separation vessel and still contains propene is worked up according to the prior art by stripping it out with the synthesis gas or
5 separating it off by distillation. By this means propene conversions of > 99% are possible without penalties in the space-time yield.

In Examples 6 and 7 flow passed through the reactor at a
10 catalyst loading of 400 kg/h at a temperature of 120°C. The reaction pressure was 50 bar. The rhodium concentration was 800 ppm based on the solvent phase. The ligand used was TSTPP in the form of its sodium salt, and the P/Rh ratio was 60. The starting material streams fed into the reactor
15 and the product streams are given in the table in mol/h.

Example	6	7
Space-time yield [t/(m ³ *h)]	1.06	1.04
B	12.12	12.12
20 Propene conversion	93.70%	92.33%
Synthesis gas conversion	92.09%	90.27%
Feed		
Starting material		
CO	10.41	10.23
25 H ₂	9.56	9.63
N ₂	0.07	0.07
Propene	12.42	12.43
Propane	0.07	0.07
Product		
30 CO	1.27	1.65
H ₂	0.24	0.39
Propene	0.58	0.73
Isobutanal	0.86	0.77
n-Butanal	8.04	8.24
35 Isobutanol	< 0.001	< 0.001
n-Butanol	0.13	0.11
2-Ethylhexanal	0.15	0.12
2-Ethylhexenal	0.29	0.18
Exhaust gas		
40 CO	0.18	0.09
H ₂	0.09	0.05
N ₂	0.01	0.01
Propene	0.10	0.09
45 Propane	0.003	0.002

Hydroformylation of 1-hexene

Example 8:

This example describes the use of the process according to
50 the invention for the continuous hydroformylation of 1-hexene. The course of the conversion over a longer

reactor was determined by reusing the resultant crude product again and again. Values are thus obtained as from a reactor several meters long in which gas is added again after each 1 m. The solvent used for the rhodium catalyst was water. The flow through the reactor having a volume of 235 ml (1 m length) was at a catalyst loading of 400 kg/h at a temperature of 130°C. The reaction pressure was 30 bar. The rhodium concentration was 800 ppm based on the solvent phase. The ligand used was TSTPP in the form of its sodium salt, and the P/Rh ratio was 60. The synthesis gas loading was on average 132.8 l (S.T.P.)/h. The feed stream of the liquid starting material was set to 1.3 l/h. After 8 passages (= 8 m of reactor length), a conversion rate of just 90% is reached, but the RZA is still 0.44 t/(m³*h) calculated over the entire reactor length.

This value is far above technically known data. The overall selectivity after 8 passages is virtually 93%.

Number of passages	1	2	3	4	5	6	7	8
Overall conversion rate [%]	19.1	36.9	49.8	59.8	68.5	76.5	82.9	86.8
High boilers	0	0.37	0.28	2.1	2.65	4.29	4.59	4.62
Overall selectivity [%]	85.1	89.1	91.7	92.1	92.4	92.8	93.1	92.9
Overall space-time yield [t/(m ³ *h)]	0.748	0.743	0.689	0.619	0.568	0.521	0.486	0.444
	14.26	14.26	14.26	14.26	14.26	14.26	14.26	14.26

Example 9: Hydroformylation of 1-decene

A reactor having a length of 6 m and a diameter of 17.3 mm was used which comprised static mixer elements from Sulzer having a hydraulic diameter of 2 mm.

For this example, the line 10 for recycling the gas was closed. The solvent used for the catalyst was water. The pH was 4.5. The flow was passed through the reactor at a catalyst loading of 400 kg/h at a temperature of 125°C. The reaction pressure was 70 bar. The rhodium concentration was 800 ppm based on the solvent phase. The ligand used was TSTPP in the form of its sodium salt, and the P/Rh ratio was 5. The starting material streams fed to the reactor and the product streams are given in the table in mol/h.

5	Example	0
	Space-time yield [t/(m ³ *h)]	0.05
	B	13.96
	Starting material	
	CO	11.38
10	H ₂	10.52
	N ₂	0.05
	1-Decene	7.12
	Product	
	1-Decene	6.67
15	Undecanal	0.34
	2-Methyldecanal	0.11
	Exhaust gas	
	CO	10.36
	H ₂	9.89
	N ₂	0.05



Patent Claims:

1. A process for carrying out multiphase reactions catalytically in a tubular reactor which comprises the catalyst being present in the continuous phase and at least one starting material in a disperse phase and the loading factor B of the tubular reactor being equal to or greater than 0.8.
2. The process as claimed in claim 1, wherein olefins are hydroformylated via the multiphase reaction.
3. The process as claimed in claim 2, wherein the olefins contain 2 to 25 carbon atoms.
4. The process as claimed in claims 1 to 3, wherein the catalyst used is a metal of subgroup 8.
5. The process as claimed in one of claims 1 to 4, wherein the catalyst used is rhodium.
6. The process as claimed in one of claims 1 to 5, wherein the catalyst used is a water-soluble rhodium compound.
7. The process as claimed in one of claims 1 to 6, wherein the continuous phase used is water or a mixture of water and an organic solvent.
8. The process as claimed in one of claims 1 to 7, wherein the loading factor B is greater than or equal to 0.9.
9. The process as claimed in one of claims 1 to 7, wherein the loading factor B is greater than or equal to 1.0.
10. The process as claimed in one of claims 1 to 9, wherein the mass ratio of the continuous phase to the disperse phase or phases is greater than 2.
11. The process as claimed in one of claims 1 to 10, wherein the continuous phase drives a jet nozzle upstream of the tubular reactor.
12. The process as claimed in one of claims 1 to 11, wherein at least one starting material is dispersed by the energy introduced into the tubular reactor by the continuous phase.
13. The use of aldehydes prepared as claimed in claims 1 to 12 for the preparation of alcohols.



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14. The use of aldehydes prepared as claimed in claims 1 to 12 in aldol condensations.
- 5 15. The use of aldehydes prepared as claimed in claims 1 to 12 for the preparation of carboxylic acids.