

STABILIZING RHODIUM CATALYSTS FOR THE HYDROFORMYLATION OF OLEFINS

The present invention relates to an improved process for manufacturing aldehydes through hydroformylation of olefins by reducing catalyst deactivation in the regeneration of rhodium catalysts.

On a commercial scale, hydroformylation of olefins is performed with cobalt or with rhodium catalysts. Here, the use of rhodium catalysts is mostly advantageous, as greater selectivity and product yields can be achieved thereby. However, compared to cobalt, rhodium is more expensive; in the hydroformylation of olefins to the corresponding aldehydes with rhodium catalysts the catalyst is a cost factor that is not insignificant. To increase the economic efficiency, the specific catalyst consumption must be reduced. This is understood to be the quantity of catalyst that must be provided to the process during long-term operation in order to guarantee a constant activity level.

The rhodium-catalyzed conversion of olefins to the corresponding aldehydes occurs mostly in the homogenous liquid phase. With the hydroformylation of propene a process has been established in the meantime wherein the catalyst is present dissolved in a second liquid phase; however, the applicability of this process to longer-chain olefins is limited.

With hydroformylation in the homogenous phase, that is, catalyst, olefins, products, solvents etc. are present in one phase, the problem arises of separating the catalyst from the products after the reaction is complete. This can be done by distilling off the unconverted educt and the products. The catalyst, mostly dissolved in high-boiling constituents in the bottom, is then returned to the reactor. Distillation can be performed either continuously or discontinuously.

In the case of separation by means of distillation, a degree of decomposition or deactivation of the catalyst is often determined. In particular, in the hydroformylation of longer-chain olefins, distillation of the products can only be carried out at increased temperatures and/or reduced pressures due to the boiling points of the products.

Several methods are known for reducing rhodium deactivation during regeneration of the reactor discharge in hydroformylation processes.

EP 0272608 B1 describes a process wherein a rhodium catalyst with triphenylphosphine oxide ligands is utilized for hydroformylation. In the regeneration of the reaction discharge triphenylphosphine (nine-fold quantity relative to rhodium) is added prior to its distillation. The distillation residue contains rhodium complexes with triphenylphosphine as ligands as well as triphenylphosphine and triphenylphosphine oxide. In this mixture the free and complexed triphenylphosphine is oxidized to triphenylphosphine oxide. This catalyst solution is returned to the reactor. Oxygen or a peroxide is utilized for oxidizing the triphenylphosphine. Further variants of this method are known and described in JP 63 222 139, JP 63 208 540, DE 3 338 340 and JP 63 218 640.

These processes have the following disadvantages: Triphenylphosphine is consumed constantly. The equivalent quantity of triphenylphosphine oxide is produced by oxidation. In order to limit its concentration in the reactor, a discharge flow system is required by which again rhodium is discharged. An oxidizing apparatus is also necessary. The oxidation process involves costs for the oxidizer unless it is carried out with air.

Other processes using other phosphorus ligands for stabilizing the rhodium are described in the relevant literature, such as US 4 400 547.

Patents US 5 731 472, US 5 767 321 and EP 0 149 894 describe processes for the hydroformylation of n-butenes. Rhodium catalysts containing phosphite ligands and stabilized by addition of amines are used therein. The drawback to this is that amines can act as catalysts for aldol condensation and thus the formation of high boilers is favored.

Hydroformylation of a C_8 olefin mixture, manufactured by dimerizing butenes, under the catalysis of rhodium complexes and their stabilization with substituted phenols is described in JP-04-164042. The rhodium compound, ligand and stabilizer are used here in a molar ratio of 1/10/50. The disadvantages of this process are the costs for the stabilizer and the expense of separating it.

The aim was therefore to develop a process for the hydroformylation of olefins wherein deactivation of the rhodium catalyst is extensively suppressed.

The object of the present invention is therefore a process for manufacturing aldehydes having 3 to 21 carbon atoms by the hydroformylation of the corresponding olefins with rhodium catalysts, whereby the discharge of the hydroformylation reactor

a) is separated into a gaseous phase and a liquid phase,

- b) the liquid phase is separated into a top fraction containing unconverted olefins and aldehydes, and a bottom fraction containing the rhodium catalyst, and
- c) the bottom fraction is cooled below the temperature of the discharge of the hydroformylation reactor and a gas containing carbon monoxide is fed in.

The activity loss of the catalyst during the regeneration of the hydroformylation discharge can be considerably reduced by means of the process according to the present invention. It was surprisingly discovered that a rhodium catalyst solution stabilized with carbon monoxide is stable in storage for several weeks.

It is therefore a further object of the invention to store catalyst solutions containing rhodium, in particular those which are obtained in carbonylation processes, while maintaining their activity. According to the present invention, the activity is maintained by the catalyst solutions being stored at a temperature below 90°C, preferably below 60°C, under a carbon monoxide partial pressure of 0.1 to 300 bar, preferably from 5 to 64 bar.

The processes according to the present invention have the following advantages when compared to known processes: the catalyst is barely deactivated during regeneration. No additional materials, which burden the process by their material costs, are required. The catalyst is stabilized with a substance present in the reactor anyway. It is possible to store the catalyst solution without loss of activity. This is of particular advantage in the case of longer stoppages, such as for major repairs or inspections, or for batch production.

Hydroformylation is carried out in a homogenous phase in a reactor according to known processes (B. Cornils, W. A. Herrmann, 'Applied Homogeneous Catalysis with Organometallic Compounds', vol. 1 & 2, VCH, Weinheim, New York, 1996). All olefins having 2 to 20 carbon atoms can be considered as educts, in particular butenes, pentenes, hexenes and octenes, and in particular dibutene obtained from butene oligomerization. The product flow, consisting of aldehydes, alcohols, unconverted olefins, high boilers, catalyst system, by-products and decomposition products, is first separated in a separating stage, process step a) into a gaseous and a liquid phase. The gaseous phase contains the majority of the unconverted synthesis gas and, depending on the temperature and pressure, varying proportions of unconverted olefins, aldehydes, hydrocarbons and other constituents. The liquid phase, by comparison, predominantly comprises the hydroformylation products and unconverted olefins. The temperature in this separating stage is 30-180°C, preferably 50-150°C. Separation takes place under a carbon monoxide partial pressure of 0.5 to 100 bar, preferably at 1 to 35 bar. Thereby, stabilizing of the rhodium is guaranteed also in this part of

the plant. Technically, this separating can take place both at the top of the hydroformylation reactor or in a separate apparatus, such as in a flasher. If the reactor is operated at a higher pressure than the separation stage, pressure is released between these stages. The carbon monoxide partial pressure can be maintained either by the gas mixture introduced to the hydroformylation reactor or by the addition of a gas containing carbon monoxide.

Because the catalyst can react further with unconverted olefins, the risk of catalyst decomposition is increased due to a possible impoverishment of synthesis gas in the liquid phase; consequently, a short dwell time of the liquid phase is sought in this separation stage. Dwell times of less than 30 and preferably less than 15 minutes are beneficial.

After being separated into gas and liquid the liquid phase is separated off by distilling into a top and bottom fraction (fractionating step, process step b)). The catalyst is accordingly found in the bottom fraction, dissolved in high boilers, which are either added to the process or formed therein. The lower boiling top fraction primarily contains the oxo products and the unconverted olefins.

The average dwell time of the liquid phase in the fractionating step is less than 15 minutes, preferably less than 5 minutes and especially preferably less than 2 minutes. For separating, the fractionating step b) can have a flasher, a falling film evaporator, a thin film evaporator or comparable apparatus, which enable a mild separation. Combinations of these units may also be employed, such as for example a falling film evaporator whose bottom product is transferred to a thin film evaporator.

The pressure in the fractionating step is between 0.01 mbar and 1 bar, preferably between 10 mbar and 1 bar. The temperature is 40°C to 180°C, preferably 80°C to 150°C. The bottom fraction originating from the fractionating step is promptly cooled down to temperatures of 10°C to 120°C, preferably to temperatures of 40°C to 90°C and under a carbon monoxide partial pressure of 0.1 bar to 300 bar, in particular 5 to 64 bar. Pure carbon monoxide, synthesis gas or other mixtures of carbon monoxide with inert gases such as nitrogen, carbon dioxide, hydrogen and/or methane can be used as a carbon monoxide-containing gas.

One possible configuration of this process stage is to cool the high boiler from the fractionation step in a cooler or alternatively by mixing it with a cooler liquid, preferably with feed olefin, and then to pump it by means of a pump into a vessel containing carbon monoxide, such as for example an agitated tank, a pressure vessel or high-pressure piping.

The catalyst solutions are stored preferably at temperatures that are lower than the outlet temperatures of the catalyst solution from process step b). Preferred storage temperatures of the bottom fraction are therefore 10 to 120°C, in particular 40 to 90°C. Optionally, a solvent can be added to the catalyst solution to be stored; appropriately a substance present in the process, such as for example educt (olefin), product (aldehyde) or hydrogenated product (alcohol).

This catalyst solution, that is, the bottom fraction of process step b), can be returned wholly or partly to the hydroformylation reactor. The vapors accumulating in fractionation step b), that is, unconverted olefin and the hydroformylation products, are processed according to known methods.

The following examples will describe the invention without limiting its protective scope, as defined in the claims.

Example 1

Hydroformylation was performed in a technical pilot plant (Figure 1) as follows:

Olefin (10), synthesis gas (11) and catalyst solution (21) are introduced to a bubble column (1) with a volume of 60 liters. The pressure of the hydroformylation discharge (13) is reduced to 5 bar in a flash chamber (2). The escaping gas (14) is cooled in a cooler, not illustrated, and the accumulating condensate is combined with liquid (15). The liquid phase (15) accumulating in the flash container (2) is separated into a top fraction (17) and a bottom fraction (16) in the thin film evaporator (3). Crude product (17) is condensed in the cooler (8) and collected in container 9. Bottom product (16) containing the catalyst dissolved in high boilers is cooled in cooler (4) (see Table 3) and conveyed to interim tank (6) by means of pump (5). A pressure of 10 bar is adjusted in tank (6) with synthesis gas (18). The temperature of the catalyst solution (16) in tank (6) was determined as per Table 3. The catalyst solution (16) was brought to the desired activity in reactor (1) by removing a partial quantity (19) and adding a catalyst precursor (rhodium compound and ligand) (20), and was then returned to the hydroformylation reactor (1) as a solution (21) via pump (7).

Table 1 illustrates typical mass throughput of the educts and catalyst concentrations

Olefin	di-n-butene	5 kg/h
Synthesis gas	CO/H ₂ (1/1)	2 kg/h
Rhodium compound	rhodium octanoate	(30-90 ppm Rh in reactor 1)
Ligand	tris(2,4-di-tert-butylphenyl)phosphite	(20 mol ligand/mol Rh)

Table 2 illustrates the test parameters that were maintained during the overall trial.

Pressure in reactor 1	50 bar
Temperature in reactor 1	130°C
Pressure in thin film evaporator 3	60 mbar
Temperature in thin film evaporator 3 (Outlet temperature at the bottom)	140°C

The activity of the catalyst was monitored by the conversion achieved in the reactor. As soon as the conversion of olefin dropped below 95% a part of the catalyst solution was removed from tank (6) and replaced by fresh catalyst precursor (rhodium salt and ligand), so that the conversion rate returned to over 95%. A small catalyst loss contained in the high boiler discharge was also replaced.

With different temperatures in the cooler (4) (outlet temperature of catalyst solution), the following quantities of rhodium (calculated as a metal) had to be added subsequently in order to maintain the conversion level. (Table 3):

Cooler 4 temperature	Tank 6 temperature	Rhodium (g), per metric ton of converted olefin
No cooling	70 - 90°C	2.1
60°C	40 - 55°C	0.9

Example 2

Decrease of catalytic activity depending on synthesis gas pressure

In a 3-liter autoclave (Büchi) 350 g toluene, 3.03 g tris(2,4-di-tert-butylphenyl)phosphite and 0.096 g rhodium octanoate were pretreated under 50 bar synthesis gas pressure (1/1/CO/H₂) for one hour at 120°C. A sample was then taken and the activity of the catalyst was determined in a second autoclave through a hydroformylation reaction with cyclooctene (at 120°C, 50 bar synthesis gas pressure). Next, the catalyst was subjected to thermal stress in the first autoclave over a period of several hours, during which time samples were taken and tested for catalytic activity in a similar manner to which the initial activity was tested. The experiment was repeated at different temperatures and synthesis gas pressures.

Diagram 1 illustrates the influence of the synthesis gas pressure on the activity of the catalyst (standardized activity, fresh catalyst has 100% or 1 activity). At a synthesis gas pressure of 50 bar more than 80% of the initial activity is still present after more than 100 hours, while at 20 bar synthesis gas pressure the activity drops below 40% of the initial activity after just 65 hours.

Stabilizing of the catalyst by synthesis gas
– Influence of the synthesis gas pressure at 120°C

Catalytic activity (standardized)

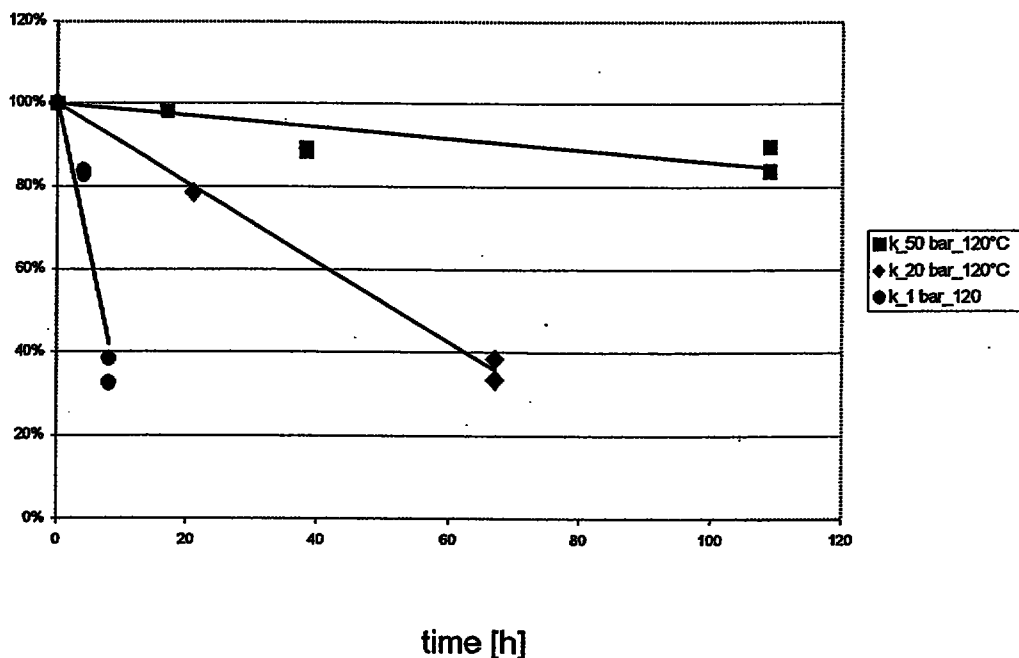


Diagram 1

Diagram 2 illustrates the influence of the temperature on the catalyst stability at a constant synthesis gas pressure of 50 bar. A temperature increase of 120°C to 140°C leads to a sharp acceleration in the decomposition of the catalyst.

Stabilizing of the catalyst by synthesis gas
- Influence of the temperature at 50 bar synthesis gas pressure

Catalytic activity (standardized) [1/min]

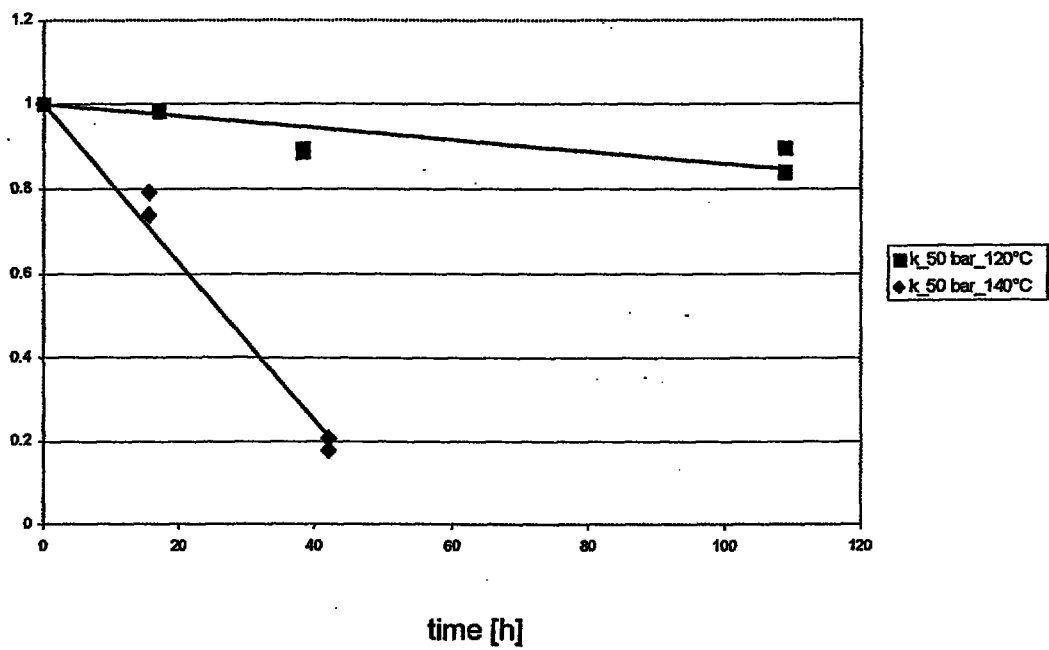


Diagram 2

CLAIMS:

1. A process for manufacturing aldehydes having 3 to 21 carbon atoms by hydroformylation of the corresponding olefins with rhodium catalysts, characterized in that the discharge of the hydroformylation reactor
 - a) is separated into a gaseous phase and a liquid phase,
 - b) the liquid phase is separated into a top fraction containing unconverted olefins and aldehydes and a bottom fraction containing the rhodium catalyst, and
 - c) the bottom fraction is cooled below the temperature of the discharge of the hydroformylation reactor and that a gas containing carbon monoxide is fed into the bottom fraction.
2. Process as claimed in Claim 1, characterized in that a carbon monoxide partial pressure of 0.5 to 100 bar is adjusted in process step a).
3. Process as claimed in either Claim 1 or 2, characterized in that process step b) has a falling film evaporator, a thin film evaporator, a flasher or a combination of these units.
4. Process as claimed in any one of Claims 1 to 3, characterized in that the average dwell time of the liquid phase in process step b) is less than 15 minutes.
5. Process as claimed in any one of Claims 1 to 4, characterized in that the average dwell time of the bottom fraction of process step b) is less than 2 minutes.
6. Process as claimed in any one of Claims 1 to 5, characterized in that the temperature in process step b) is 40 to 180°C.
7. Process as claimed in any one of Claims 1 to 6, characterized in that the pressure in process step b) is 0.01 to 1 bar.
8. Process as claimed in any one of Claims 1 to 7, characterized in that a carbon monoxide partial pressure of 0.1 to 300 bar is applied to the bottom fraction of process step c).



9. Process as claimed in any one of Claims 1 to 8, characterized in that synthesis gas, pure carbon monoxide, or mixtures of carbon monoxide with nitrogen, methane, hydrogen and/or carbon dioxide are used as a gas containing carbon monoxide.
10. Process as claimed in any one of Claims 1 to 9, characterized in that the bottom fraction of process step c) is cooled to temperatures of 10 to 120°C.
11. Process as claimed in any one of Claims 1 to 10, characterized in that the bottom fraction of process step c) is returned wholly or partly to the hydroformylation reactor.

