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PROCESS FOR PRODUCING GAMMA-BUTYROLACTONE

The invention relates to a process for the preparation of gamma-butyrolactone by the catalytic hydrogenation of maleic anhydride in the vapour phase.

Gamma-butyrolactone is an important chemical which is of significance as a starting material for numerous syntheses. For example, it plays a part in the preparation of butyric acid and derivatives thereof, butanediol, tetrahydrofuran, N-methylpyrrolidone, polyvinylpyrrolidone, methionine and the like. Gamma-butyrolactone is also an important solvent, inter alia for acrylates and styrene-based polymers. It can furthermore be used as a solvent, inter alia in the manufacture of synthetic fibres.

A number of preparative methods start from maleic anhydride or derivatives such as maleic acid, succinic anhydride or maleic acid ester, which are subjected to hydrogenation. The hydrogenation is usually carried out in the vapour phase and in the presence of catalysts. Numerous catalysts for these reactions are described in the patent literature. Thus, for example, US-PS 3 065 243 discloses a process in which copper chromite is used as the catalyst. As can be seen from the description and the Examples in said patent specification, appreciable amounts of succinic anhydride are also formed in this reaction and this has to be recycled.

There has been no lack of attempts to develop catalysts for improving the yield and selectivity. Another aim of the studies was to improve the life of the catalysts, the lives of many catalysts being too short for continuous operation, i.e. the catalyst is deactivated too rapidly in continuous operation, usually due to carbonization.

Thus Canadian patent specification no. 840 452 describes developed catalysts based on copper/zinc. These can be processed together with asbestos to give appropriate



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catalyst particles. Neither the catalyst claimed in said Canadian patent specification, nor the copper chromite/asbestos catalyst prepared in comparable manner, is able to satisfy all the requirements of a good catalyst for the preparation of gamma-butyrolactone.

DE-OS 24 04 493 describes a process which involves hydrogenation in the presence of steam. This is said to reduce the carbonization of the catalyst. One of the disadvantages of this process is that water is not an inert compound, i.e. it takes part in the equilibrium as a reactant.

Other catalysts based on copper chromite are described for example in US-PS 4 006 165, it being necessary for this catalyst to contain nickel as well. These catalysts can be applied to aluminium oxide or silica, such as kieselguhr, or can also be prepared by mixing with said substances.

Although numerous catalysts have already been described for the reaction of hydrogen and maleic anhydride to give gamma-butyrolactone, there is still a need for catalysts with which this reaction can be carried out in a better and more advantageous manner.

The object of the invention is therefore to provide a process for the preparation of gamma-butyrolactone by the hydrogenation of maleic anhydride in the vapour phase and in the presence of a catalyst, which process gives high yields, has an outstanding selectivity, can be carried out either under elevated pressure or under normal or sub-atmospheric pressure, is economic and flexible, offers advantages particularly as regards the working-up of the reaction product and the recycling of certain components, and can also be carried out in such a way that the recycling of succinic anhydride, formed as an intermediate, is not necessary.

This object is achieved by a process for the preparation of gamma-butyrolactone by the catalytic hydrogenation of maleic anhydride in the vapour phase and in the presence of catalysts based on copper chromite in reduced form, characterized in that the reaction is carried out using a substantially homogeneous catalyst derived essentially from the 3 components copper oxide, chromium oxide and silicon dioxide. It is preferable to use a catalyst based on 68 - 85 wt.% of CuO, 15 - 30 wt.% of Cr₂O₃, and 0.5 - 5% of SiO₂, these proportions relating to the catalyst before it has been prepared by reduction. In one particularly advantageous embodiment, the ratio of CuO to Cr₂O₃ to SiO₂ is about 78 : 20 : 2.

In one particularly advantageous embodiment of the process according to the invention, the hydrogenation is carried out in the presence of an inert gas as diluent, nitrogen being preferred. Apart from nitrogen, it is also possible to use the known noble gases such as argon, krypton, helium or mixtures thereof with one another or with nitrogen. It is self-evident that the catalyst based on the 3 components is reduced in a manner known per se before being used in the reaction in conventional manner. The reduction is preferably carried out in the reactor itself.

The reduction can be carried out for example by the following procedure. The catalyst, in the form of a catalyst bed, is heated to 150°C in the reactor in a stream of nitrogen. Hydrogen is fed in slowly at this temperature until the inlet concentration is up to 8 vol.%. The temperature in the catalyst bed should not increase by more than 25°C during this process.

After the heat of reaction has subsided, the hydrogen concentration is increased to 80 - 100% by cutting down the nitrogen stream, and the temperature is raised to 280°C. The temperature is maintained for 12 hours with H₂ flowing

through; this process is generally referred to as the after-reaction.

The reduction can of course be carried out in other ways, for example as indicated in column 2, lines 54 to 66, of US-PS 3 065 243.

The homogeneous catalyst based on the 3 components can be prepared in the following manner. Copper and chromium, in the form of dissolved salts, are mixed together with an appropriate soluble silicon compound, preferably in an aqueous system. Examples of silicon compounds which can be used are water glass or silica sol. In a suitable manner, for example by the addition of alkali, the copper, chromium and silicon are precipitated together, for example in the form of the corresponding oxides or hydroxides, to form a homogeneous precipitate of uniform structure. After filtration and washing, the precipitate is optionally dried and then calcined. The calcined masses are appropriately comminuted and optionally divided up into appropriate particle sizes, for example by passage through several sieves.

Within the framework of the invention, homogeneous catalyst is understood as meaning that the 3 components from which the catalyst is derived are homogeneously bound together, as is the case, for example, when the components are precipitated together from a solution or when the 3 components are melted together and left to solidify. This does not therefore include coarse-grained mixtures of the individual components in which the individual components still exist as discrete particles. The catalysts according to the invention also do not include conventional copper chromite catalysts on silica supports. The catalyst according to the invention can of course be applied to supports.

The catalyst can then be introduced immediately into the reactor and used for the reaction after appropriate reduction.

The hydrogenation of maleic anhydride, i.e. the reaction of maleic anhydride with hydrogen, is carried out in the vapour phase, i.e. at elevated temperatures, for example in the range from about 100 to 400°C, preferably in the range from about 250 to 280°C.

The vaporous maleic anhydride can be introduced into the reaction chamber on its own by being heated, converted to the vapour phase and appropriately metered in. It is also possible, however, to carry the requisite amounts of maleic anhydride vapours into the reactor by means of the hydrogen stream which is to be metered in. This can of course also be effected by the inert gas, such as nitrogen, if it is used.

The molar ratio of maleic anhydride to hydrogen in the stream of starting materials can vary within wide limits and can be for example between 1 : 20 and 1 : 250, the preferred range being 1 : 50 to 1 : 150.

The reaction can be carried out either under normal pressure or under negative pressure or elevated pressure, for example at between 0.1 and 10 bar.

Within the framework of the invention, inert gas is understood as meaning a gas which does not take part in the reaction as a reactant or reaction product and which also does not itself change due to a reaction.

By using an inert gas as diluent, it is possible to have a favourable influence on the reaction. The proportion of inert gas, which is preferably nitrogen but can also be one of the other noble gases such as helium, argon, krypton and

xenon, it also being possible to use mixtures of noble gases or mixtures of nitrogen and noble gases, can also vary within wide limits. It is self-evident that, as a function of the other chosen reaction conditions, the dilution reaches its limit when the proportion of diluent is so large that too little hydrogen is present and the yield based on maleic anhydride decreases sharply. This limit can be determined by a few simple experiments which are within the technical capability of the average person skilled in the art.

It is possible to influence the reaction by varying a very wide diversity of process parameters. Thus the dwell time can be altered; this can be done by setting different metering rates, but can also be effected by lengthening the reaction path, for example by using a longer reaction tube appropriately filled with catalyst.

The reaction can be controlled in such a way that the succinic anhydride formed as an intermediate is no longer present at the end of the reactor and therefore no longer has to be recycled. On the other hand, where necessary, the reaction can also be controlled in such a way that succinic anhydride is still present in larger or smaller amounts in the emerging reaction products and is then either separated off and processed further on its own, or else recycled.

It was completely surprising that the use of the catalyst in the manner according to the invention affords both a high selectivity and a high yield. The advantages of the catalyst used according to the invention are evident not only when the reaction is carried out with or without a diluent, but also when the molar ratios of the reactants are changed and when the temperatures are varied. This catalyst can thus be used with great advantages in the preparation of gamma-butyrolactone by the reduction of maleic anhydride

with hydrogen under a very wide variety of process conditions.

To prove the completely surprising and superior mode of reaction of the catalyst according to the invention, nine different catalysts based on copper chromite are prepared, catalyst no. 4 corresponding to the invention and the remaining catalysts being conventional known copper chromite catalysts. The catalysts are obtained by precipitation from appropriate solutions. Table 1 shows the composition of the catalysts used before reduction.

Table 1

Composition (before reduction)	Cat. no.
2 CuO * Cr ₂ O ₃	1
Cu chromite (9.7% BaO)	2
80% CuO, 20% Cr ₂ O ₃	3
78% CuO, 20% Cr ₂ O ₃ , 2% SiO ₂	4
42% CuO, 38% Cr ₂ O ₃	5
33% CuO, 38% Cr ₂ O ₃ , 9% BaO	6
76% CuO, 24% Cr ₂ O ₃	7
72% CuO, 18% Cr ₂ O ₃ *	8
66% CuO, 25% Cr ₂ O ₃ **	9

* commercial product E-113 T from Mallinckrodt

** commercial product T-4421 from Süd-Chemie

The reduction was carried out by the following procedure, which is conventional per se:

The catalyst bed, already present in the reactor provided, is heated to 150°C in a stream of nitrogen. Hydrogen is slowly fed in at this temperature until the inlet concentration is up to 8 vol.%. The rise in temperature of the bed should not be greater than 25°C (reduction step).

When the heat of reaction has subsided, the hydrogen concentration is increased to 80 to 100% and the temperature is raised to up to 280°C. The temperature is maintained for 12 h with H₂ flowing through (after-reduction).

Procedures:

Embodiment A:

The catalyst pellets are comminuted and the 0.8 to 1.2 mm fraction is selected. These are placed in a quartz glass tube of internal diameter 1 cm and length 30 cm, which can be heated with silicone oil. The experiment is performed after the reduction step has been carried out. Hydrogen is metered in via a mass flow regulator and the maleic anhydride partial pressure is established via a so-called saturator. This is done by passing hydrogen and, if appropriate, nitrogen through the saturator containing liquid maleic anhydride, a known maleic anhydride partial pressure being established by virtue of the precisely fixed temperature. The mixture is fed through heated pipes into the reactor. The fixing of the reaction temperature is described in Embodiment C.

Embodiment B:

This embodiment is completely analogous to Embodiment A, the only differences being that the reactor (i.e. the quartz glass tube) has an internal diameter of 3 cm and the pellets are used in their original size, i.e. uncomminuted (diameter ca. 3 to 3.2 mm). The fixing of the reaction temperature is described in Embodiment C.

Embodiment C:

Uncomminuted pellets are used (see B). The reactor was made of stainless steel; the dimensions are an internal diameter of 3 cm and a length of 1.2 m. Heating is effected by means

of a jacket containing silicone oil, the temperature of the silicone oil being equated to the reaction temperature in the embodiment examples. Hydrogen and nitrogen are metered in via mass flow regulators; a short distance upstream of the reactor, mixing takes place with recycle gas, which is fed back into the reactor after the liquid products have been separated off. However, a certain proportion of the recycle gas is simultaneously withdrawn and removed from the system in order to prevent an accumulation of gaseous by-products. Liquid maleic anhydride is fed directly into the reactor through heated pipes; the first 20 cm of the reactor, which are filled with quartz glass wool, act as the vaporization zone. This is followed by the catalyst.

Experimental Examples with Embodiment A:

A.1.

The catalysts were reduced as described above. A bulk volume of 20 ml of each one was filled into the reactor and brought to a reaction temperature of 275°C with a flow rate of 0.38 mol N₂/h and 2 mol H₂/h. The gas mixture was then passed through the saturator, thereby establishing a maleic anhydride stream of 0.02 mol/h. The product mixture was analyzed after a reaction time of 2 h. The results are recorded in Table 2 below.

Table 2

Cat. no.	Yield (in %)	Yield (in %)	Conversion (in %)
	gamma-butyro-lactone	succinic anhydride	maleic anhydride
1	22.1	77.6	100
2	49.8	49.6	100
3	64.9	34.2	100
4	98.1	-	100
5	25.0	62	100
6	4.7	14.0	19.5
7	90.9	6.9	100

This shows the special quality of catalyst no. 4, it being of particular significance that even the intermediate succinic anhydride is completely converted; otherwise technical problems with the crystallization of the succinic anhydride, resulting in the blocking of pipelines etc., can often be expected.

A.2.

The two experiments described below were carried out exclusively with catalyst no. 4 under conditions which are intended to illustrate the advantage of using inert gas.

10 ml of the catalyst were filled into the reactor. The MA stream was 0.01 mol/h. The total stream was 1.20 mol/h. The Table below shows the different conditions and results. The MA conversion was 100% in both cases.

Table 3

N ₂ (mol/h)	H ₂ (mol/h)	Yield (%): GBL	SA	T (°C)
0.00	1.19	97.0	-	275
0.19	1.00	97.5	-	275
0.49	0.70	98.7	-	275
0.69	0.50	87.0	11.7	275

This means that although SA was no longer formed at 275°C in the first three cases, the selectivity and hence yield of GBL increases with the proportion of inert gas.

If the proportion of inert gas is too high (see 4th Example), however, the intermediate SA is no longer completely hydrogenated to GBL, i.e. only a certain proportion of inert gas is optimal.

Experimental Examples with Embodiment B:

B.1.

Comparative Examples cat. no. 3 and no. 4

As the catalysts actually have very similar compositions - except for the proportion of SiO₂ - the following comparative experiments were performed. In no case was nitrogen added. The amount of catalyst was always 200 g and the first 10 cm of the bed were diluted with 100 g of quartz glass spheres of diameter 1 mm. The MA conversion was always 100%.

The Examples below indicate that the hydrogenating activity of no. 4 is much higher than that of no. 3, i.e. even a low proportion of SiO₂ significantly reduces the formation of SA, which is of appreciable industrial importance.

Table 4

Cat. H ₂ no. (mol/h)	MA (mol/h)	T (°C)	Yield GBL (%)	Yield SA (%)	Example no.	
3	15.8	0.158	270	85.7	11.0	1B
4	15.8	0.158	270	85.3	0.1	2B
3	7.87	0.105	255	91.2	5.5	3B
4	7.87	0.105	255	92.5	2.0	4B
3	7.87	0.105	260	89.5	6.8	5B
4	7.87	0.105	260	90.5	0.7	6B
3	15.75	0.21	270	82.8	14.3	7B
4	15.75	0.21	270	91.6	1.3	8B
3	7.87	0.105	275	85.6	0.6	9B

Although no. 3 can also achieve complete SA conversion if the reaction temperature is raised, this is at the expense of considerable selectivity losses (see Example 9B).

If Example 4B is compared with 9B, an appreciably higher selectivity and yield of GBL can be achieved with a similar SA yield.

Experimental Examples with Embodiment C:

C.1.

The following pairs of experiments illustrate the effects of the inert gas admixture on the GBL yield, which are extremely favourable especially when the experiments are carried out under pressure (catalyst no. 4 only):

Table 5

MA pressure (bar)	Total pressure (bar)	T (°C)	Amount of cat. (g)	Proportion of N ₂ (%)	Dwell time (sec)	GBL yield (%)
0.1188	6	270	360	0	2.69	41
0.1188	6	270	360	62	2.69	86
0.1131	6	270	625	46	3.14	92
0.1188	6	260	360	0	2.74	67
0.1188	6	260	360	30	2.74	83

C.2. Comparative Experiments under pressure

The technical superiority of catalyst no. 4 when carrying out the reaction under pressure will be demonstrated again in the following comparative experiments with industrially available catalysts (no. 8 and no. 9). The most important features here are the GBL yields as well as the corresponding selectivities and the residual amount of intermediate SA.

Table 6

MA Cat. pres- sure (bar)	Total pres- sure (bar)	T(°C)	Amount of cat. (g)	Proportion of N ₂ (%)	Dwell time (sec)	GBL yield (%)	SA yield (%)	No.
0.116	6	270	630	0	2.69	69	3.1	8
0.116	6	270	630	0	2.69	75	0.2	4
0.116	6	270	630	50	2.69	81	13.0	8
0.116	6	270	630	50	2.69	89	1.5	4

The experimental results show that the catalyst according to the invention differs unexpectedly from the other catalysts, whether the reaction is carried out with or without a diluent,

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at different temperatures, under pressure or at normal pressure.

It is self-evident that the reaction can additionally be controlled by selecting the reaction conditions such as the ratio of the starting materials, the dwell time, the temperature and the like. The conditions which are most favourable in each particular case can be determined by means of a few simple preliminary experiments which are within the technical capability of the average person skilled in the art.

Claims

1. A process for the preparation of gamma-butyrolactone by the catalytic hydrogenation of maleic anhydride in the vapour phase and in the presence of catalysts based on copper chromite in reduced form, characterized in that the reaction is carried out using a catalyst containing the three components copper oxide, chromium oxide and silicon dioxide.
2. A process according to Claim 1, characterized in that the 3 components are 68 - 85 wt.% of CuO, 15 - 30 wt.% of Cr₂O₃ and 0.5 - 5% of SiO₂, these proportions being relative to the catalyst before it has been prepared by reduction.
3. A process according to Claim 2, characterized in that the ratio of CuO to Cr₂O₃ to SiO₂ is 78 : 20 : 2.
4. A process according to one of Claims 1 to 3, characterized in that the hydrogenation of the maleic anhydride is carried out in the presence of an inert gas as diluent.
5. A process according to Claim 4, characterized in that nitrogen is used as the inert gas.
6. A process according to one of Claims 1 to 5, characterized in that the catalyst is prepared by reduction in the reactor.
7. A process according to one of Claims 1 to 6, characterized in that maleic anhydride and hydrogen are used for the reaction in a molar ratio of 1 : 50 to 1 : 150.