Description

The invention relates to a process for the preparation of a silver-containing catalyst, suitable for the preparation of ethylene oxide, to the prepared catalyst and to the use of the catalyst for the preparation of ethylene oxide and the ethylene oxide thus obtained. Moreover the invention relates to novel catalysts.

It is generally known for a silver-containing catalyst to be employed in the preparation of ethylene oxide. See for example British patent specification 1,413,251 and also the literature cited therein. In order to obtain improved silver catalysts, efforts have been directed for many years towards modifying the silver catalysts with the aid of promoters. For example, the above-mentioned British patent specification 1,413,251 describes a process in which a silver compound is applied to a carrier, after which the applied silver compound is reduced to silver and in which additionally a promoter in the form of potassium oxide, rubidium oxide or cesium oxide or a mixture thereof is present on the carrier.

Applicant has found a silver catalyst with improved activity and selectivity and a very high stability.

The invention relates to a process for the preparation of a silver-containing catalyst suitable for the oxidation of ethylene to ethylene oxide which comprises

a) mixing alumina with a tin compound and with an alkali metal compound,
b) calcining the mixture to obtain an alkali-enriched and tin-containing alumina carrier,
c) applying a silver compound to the alumina carrier and converting said silver compound to metallic silver.

The aluminium oxides can be several modifications of aluminium oxide, such as gamma-aluminium oxide, which when calcined at a temperature between 1200 °C and 1700 °C generally produce alpha-aluminium oxide. Another possibility is to choose a hydrated aluminium oxide, such as boehmite, which via gamma-aluminium oxide produces alpha-aluminium oxide.

The alkali metal compounds, used for mixing with the aluminium oxide carrier and the tin compound, comprise alkali metal hydroxides and alkali metal salts, such as fluorides, nitrates, chlorides or sulphates. Preferably potassium, rubidium or cesium compounds are used, most preferably cesium compounds, e.g. cesium chloride, cesium fluoride or cesium sulphate.

The quantity of alkali metal compound that is mixed with the alumina is chosen in such an amount, that the atom ratio of the alkali metal/aluminium is between 0.0001 and 0.1, preferably between 0.001 and 0.01.

Examples of tin compounds are tin salts, such as stannic chloride, stannic bromide, stannic fluoride, stannic iodide, stannic nitrate, stannic sulphate, stannic tartrate, stannic chromate. Salts of divalent tin may be suitable as well, e.g. stanno sulphate. Stannic sulphate and stanno sulphate are the most preferred.

The quantity of tin compound that is mixed with the alumina is chosen in such an amount, that the atom ratio of the tin/aluminium is between 0.001 and 0.1, preferably between 0.005 and 0.05.

It has been found that the Sn/Al atom ratio and the Cs/Al atom ratio at the surface of the carrier is greater than the weighed-out Sn/Al and Cs/Al atom ratios respectively. It has further been found that the tin particles at the surface of the carrier have a great influence on the distribution of the metallic silver over the surface, after impregnation of the carrier with the silver compounds and subsequent reduction.

Scanning electron microscopy revealed that the silver particles on the carrier surface were invisible and could not be detected apartly, which is in contrast to silver particles of a commercial catalyst, which particles could be seen and had a diameter of about 0.2-0.5 μm. One could also speak of a silver mirror on the surface of the carrier in the catalyst according to the invention.

For the preparation of the alkali metal-enriched and tin modified alpha-alumina carrier, preferably alumina is mixed with water, the tin compound and the alkali metal compound, and the resulting mixture is extruded to shaped carrier particles, which latter are calcined. The calcination can take place in one or more steps, depending on the choice of starting material. In general, sufficient water is added to make the mixture extrudable. The extrudable paste obtained is then extruded in an extruder to form shaped pieces. These shaped pieces are heated, during which water still present is evaporated. The solid pieces are then calcined. In order to prepare the alpha aluminium oxide modification, calcination up to a temperature of between 1200°C and 1700°C is necessary. Suitable starting materials are powders of gamma-aluminium oxide, alpha-aluminium oxide monohydrate, alpha-aluminium oxide trihydrate and beta-aluminium oxide monohydrate, which are sintered during the calcination, with fusion of the powder particles taking place. The heating and calcination also changes the crystal structure: the cubic structure of gamma aluminium oxide changes into the hexagonal structure of alpha aluminium oxide.

The effective catalyst surface area can vary from between 0.1 and 5 m^2/g, preferably between 0.2 and 2 m^2/g. It has also been found that for the alpha-aluminium oxide, the alkali metal (cesium) is present at the surface at a concentration higher than is to be expected on the basis of the weighed-out quantity of alkali metal.

In order to prepare the catalyst, the alkali enriched and tin modified alumina carrier is impregnated with a solution of a silver compound, sufficient to apply, as wished, 1 to 25 weight per cent of silver, calculat-

ed on the weight of the total catalyst, on the carrier. The impregnated carrier is separated from the solution, if necessary and the precipitated silver compound is reduced to metallic silver. It may be that the whole solution is impregnated on the carrier.

Preferably, a promoter is added, for example one or more of the alkali metals: potassium, rubidium or cesium. The promoters can be applied on the carrier before, during or after the impregnation with the silver compound. The promoter can also be applied on the carrier after the silver compound has been reduced to silver.

Also an additional source of fluoride-anions may be contacted with the carrier.

The alkali enriched and tin modified carrier, which has been calcined, is impregnated with a solution of a silver compound, sufficient to cause precipitation on the carrier of from 1 to 25 per cent by weight of silver, calculated on the total catalyst, and before, during or after that impregnation also with one or more dissolved potassium-, rubidium- or cesium compounds as promoter and with a source of fluoride-anions, and after precipitation the silver compound on the impregnated carrier is reduced to metallic silver.

The source of fluoride-anions may be for example ammonium fluoride, ammonium hydrogen fluoride, cesium fluoride, lithium fluoride, sodium fluoride and silver fluoride. The quantities of fluoride-anions are such that after impregnation and reduction the silver catalyst contains between 10 and 1000, preferably between 100 and 700 parts by weight of fluor, per million parts by weight of total catalyst.

In general, the carrier is mixed with an aqueous solution of a silver salt or a silver complex, so that the carrier is impregnated with this solution, after which the carrier may be separated from the solution if necessary and subsequently dried. The impregnated carrier is then heated to a temperature of between 100 °C and 400 °C for a period necessary for the silver salt (or complex) to decompose and form a finely distributed layer of metallic silver which adheres to the inner and outer surfaces. Temperatures above 400 °C should be avoided, since then sintering of the silver particles takes place.

Various methods are known for adding the silver. The carrier can be impregnated with an aqueous solution of silver nitrate, then dried, after which the silver nitrate is reduced with hydrogen or hydrazine. The carrier can also be impregnated with an ammoniacal solution of silver oxalate or silver carbonate, the deposition of silver metal being effected by thermally decomposing the salt. Special solutions of silver salt with certain solubilizing and reducing agents, such as combinations of vicinal alkanolamines, alkyldiamines and ammonia also serve the purpose.

The quantity of added promoter is generally between 20 and 1000 parts by weight of an alkali metal, such as potassium, rubidium or cesium (as metal) per million parts by weight of total catalyst. 50 to 300 parts by weight of alkali metal is particularly suitable. Suitable compounds to serve as starting material for promoters are, for example, nitrates, oxalates, carboxylic acid salts or hydroxides. The most preferred promoter is cesium.

Some excellent methods are known for adding the alkali metals in which these metals can be applied at the same time as the silver. Suitable alkali metal salts are generally salts which are soluble in the silver-depositing liquid phase. Besides the above-mentioned salts, it is also worth mentioning nitrates, chlorides, iodides, bromides, bicarbonates, acetates, tartrates, lactates and isopropoxides. The use of alkali metal salts which react with the silver present in the solution and thus cause silver salts to be prematurely precipitated from an impregnating solution should, however, be avoided. For example, potassium chloride should not be used for impregnating techniques in which an aqueous silver nitrate solution is used, but potassium nitrate can be used instead. Potassium chloride can be suitably used in a process in which an aqueous solution of silver amine complexes, from which no silver chloride will precipitate, is used.

In addition, the amount of alkali metal deposited on the carrier can be adjusted within certain limits by washing out a part of the alkali metal with, preferably, anhydrous methanol or ethanol. This method is employed subsequently if the concentration of the applied alkali metal is found to be too high. The temperatures, contact times and the drying with gases can be adjusted. Care should be taken to ensure that no traces of alcohol remain in the carrier.

A preferably employed process consists of the carrier being impregnated with an aqueous solution containing both alkali metal salt and silver salt, the impregnating solution being composed of a silver salt of a carboxylic acid, an organic amine, a salt of potassium, rubidium or cesium and an aqueous solvent. For example, a potassium-containing silver oxalate solution can be prepared in two ways. Silver oxide can be reacted with a mixture of ethylene diamine and oxalic acid, giving a solution containing a silver oxalate ethylene diamine complex, to which a certain amount of potassium and possibly other amines such as ethanolamine is added. Silver oxalate can also be precipitated from a solution of potassium oxalate and silver nitrate, the silver oxalate thus obtained then being repeatedly washed in order to remove the attached potassium salts until the desired potassium content is obtained. The potassium-containing silver oxalate is then solubilized with ammonia and/or amine. Solutions containing rubidium and cesium can also be prepared in this way. The thus impregnated carriers are then heated to a temperature of between 100 °C and 400 °C, preferably between 125 °C and 325 °C.

It should be noted that, irrespective of the nature of the silver in the solution before the precipitation onto the carrier, reference is always made to reduction to metallic silver, whereas it could also be referred to as decomposition on heating. It is preferred to think in terms of reduction, since positively charged Ag ions are converted into metallic Ag. The reduction times can be simply adapted to the start-

ing materials employed.

As mentioned above, a promoter is preferably added to the silver. Cesium is the most preferred promoter in view of the fact that its selectivity for ethylene oxide has been found to be the highest in comparison with the use of potassium or rubidium as promoter.

The invention further relates to a silver-containing catalyst, comprising

a) from 1 to 25 per cent by weight of silver, calculated on the total catalyst weight, on the surface of the carrier and

b) an alkali enriched and tin modified alpha alumina carrier.

Preferably the catalyst contains between 20 and 1000 ppm of potassium, rubidium or cesium on the surface of the carrier. Also the catalyst may contain between 10 and 1000, preferably between 100 and 700 parts by weight per million parts by weight of total catalyst, of fluoride ion.

The silver catalysts prepared by the process according to the present invention appear to be particularly stable catalysts for the direct catalytic oxidation of ethylene to ethylene oxide with the aid of molecular oxygen. The conditions for carrying out the oxidation reaction in the presence of the silver catalysts according to the invention are fairly similar to those already described in the literature. This applies to, for example, suitable temperatures, pressures, residence times, diluents such as nitrogen, carbon dioxide, steam, argon, methane or other saturated hydrocarbons, the presence or absence of moderating agents to control the catalytic action, for example 1,2-dichloroethane, vinyl chloride or chlorinated polyphenyl compounds, the desirability of employing either recirculating treatments or successive conversions in different reactors to enhance the yield of ethylene oxide, as well as any other special conditions which may be chosen for processes for the preparation of ethylene oxide. Usually, the pressures employed vary from about atmospheric pressure to about 35 bar. Higher pressures are, however, by no means excluded. The molecular oxygen employed as reactant can be obtained from conventional sources. The oxygen feed can consist of substantially pure oxygen, of a concentrated oxygen stream consisting of a large amount of oxygen with smaller amounts of one or more diluents, such as nitrogen, argon, etc., or of another oxygen-containing stream, such as air.

In a preferably employed application of the silver catalysts according to the present invention, ethylene oxide is prepared by contacting an oxygen-containing gas that has been separated from air and that contains not less than 95% oxygen with ethylene in the presence of the catalysts in question at a temperature within the range of 210 °C to 285 °C and preferably between 225 °C and 270 °C.

In the reaction of ethylene with oxygen to ethylene oxide, the ethylene is present in at least a double molecular quantity, but the quantity of ethylene employed is often much higher. The conversion is therefore calculated according to the quantity of converted oxygen in the reaction and we therefore speak of oxygen conversion. This oxygen conversion is dependent on the temperature of the reaction and is a measure of the activity of the catalyst. The values T_{30}, T_{40} and T_{50} refer to the temperatures at 30 mol%, 40 mol% and 50 mol% conversion respectively of the oxygen in the reactor. The temperatures are generally higher for a higher conversion and are highly dependent on the catalyst employed and the reaction conditions. In addition to these T-values, one also comes across selectivity values, which indicate the molar percentage of ethylene oxide in the reaction mixture obtained. The selectivity is indicated as S_{30}, S_{40} or S_{50}, which refers to the selectivity at 30%, 40% or 50% oxygen conversion respectively.

The concept "stability of a catalyst" cannot be expressed directly. Stability measurements require trials of long duration. For measuring the stability, the applicant has a number of tests which are carried out under extreme conditions with space velocities of 30,000 litre. (litre catalyst)$^{-1}$.h^{-1}, where litres of throughput gas are understood to be litres STP (standard temperature and pressure). This space velocity is many times higher than the space velocity in commercial processes, which may range from 2800 to 8000 h^{-1}. The test is carried out for at least 1 month. The above-mentioned T- and S-values are measured during the entire period of the test. After the test has been broken off, the total quantity of ethylene oxide per ml catalyst is determined. The difference in selectivity and activity is calculated for a catalyst which would have produced 1000 gram ethylene oxide per ml catalyst. A new catalyst is considered to be more stable than a known catalyst if the differences in the T- and S-values of the new catalyst are less than those of the standard catalyst which is present during each test. The stability tests are carried out at 35% oxygen conversion.

Example 1

4.21 g stannosulphate and 0.89 g cesiumfluoride dissolved in 150 ml water was mixed with 132.3 g Kaiser aluminium oxide ($Al_2O_3.H_2O$) by adding the stannosulphate-cesiumfluoride aqueous solution to the aluminium oxide during 1 min, and the mixture was kneaded for 10 min in a masticator and extruded. The resulting shaped pieces were dried for 12 hours at 120 °C and subsequently calcined at progressively higher temperatures. Calcination was started with the temperature rising at a rate of 200 °C/h to 500 °C. Calcination was continued for 1 hour at 500 °C, after which the temperature was raised in 2 hours to 1500 °C and continued for 1 hour at 1500 °C. The pore volume of the shaped aluminium oxide pieces was 0.41 ml/g^{-1} and the average pore diameter was 1.66 µm. The weighed-out cesium/aluminium atom ratio was

0.003, the weighed-out tin/aluminium atom ratio was 0.01. X-ray photo-electron spectroscopy of the carrier surface revealed that there the cesium/aluminium atom ratio was 0.042 and the tin/aluminium atom ratio 0.034.

The resulting shaped pieces were impregnated with an aqueous solution of silver oxalate, to which cesium hydroxide was added. The impregnation was carried out for 10 min under vacuum, after which the shaped pieces were separated from the solution and placed in a hot air stream at a temperature of 250-270 °C for 10 min in order to convert the silver salt to metallic silver. The aqueous solution of silver oxalate was a 28 %wt Ag-containing aqueous solution in which the silver oxalate was complexed with ethylene diamine and to which solution cesium hydroxide had been added. After the hot air treatment the thus impregnated shaped pieces contained 15.5 %wt Ag (calculated on total catalyst weight) and 310 ppm of (impregnated) cesium on the total catalyst weight.

The silver catalyst obtained by the above-described method was then tested. A cylindrical steel reactor with a length of 15 cm and a diameter of 3 mm was filled entirely with catalyst particles of about, 0.3 mm in size. The reactor was placed in a bath in which silicon/aluminium particles were present in a fluidized state. A gas mixture with the following composition was passed through the reactor: 30 mol% ethylene, 8.5 mol% oxygen, 7 mol% carbon dioxide and 54.5 mol% nitrogen and 7 parts per million parts of gas of vinyl chloride as moderator. The space velocity was 30,000 $1.1^{-1}.h^{-1}$. The pressure was 15 bar and the temperature was dependent on the set oxygen conversion. The measuring equipment was connected to the reactor and to a computer. The conversion and the temperature could be accurately controlled. The concentrations of the reaction components were determined with the aid of gas chromatography. The stability test was carried out at an oxygen conversion of 35%.

The reaction temperature at 35% oxygen conversion was determined during the entire duration of the test. The selectivity in respect of ethylene oxide was also determined. After 30 days the total quantity of ethylene oxide produced per ml catalyst was determined. From the measured reaction temperatures the temperature rise in °C was calculated for the moment at which 1000 g ethylene oxide per ml catalyst would have been produced (ΔT_{35}^{1000}). From the measured selectivities, the selectivity decrease in %mol was calculated for the moment at which 1000 g ethylene oxide per ml catalyst would have been produced (ΔS_{35}^{1000}). The same measurements and calculations were carried out for a standard catalyst in the test.

The table gives the relative value of the ΔS_{35}^{1000} and ΔT_{35}^{1000} expressed in a percentage of the ΔS_{35}^{1000} and ΔT_{35}^{1000}-values of the standard silver catalyst:

Table

Example	Catalyst		ΔS_{35}^{1000} (rel.)	ΔT_{35}^{1000} (rel.)
	%wt Ag	ppm cesium	%	%
1	15.5	310	20	20
Comparison	Standard commercial catalyst		100	100

It is observed that the silver particles on the standard commercial catalyst after 30 days of operation under the severe conditions, had already sintered with each other, while the silver on the catalyst made by the process according to our invention showed no signs of sintering after the same time of operation under the severe conditions. Consequently the catalyst according to the invention has a much greater stability than the standard catalyst.

Actually the catalyst according to the invention showed a selectivity loss of 0.7% (to ethylene oxide) and an activity loss in terms of increase in reaction temperature of 2 °C.

The catalyst according to the invention had an S_{40}-value and a T_{40}-value of 79.6% and 230 °C respectively (measured on the catalyst under normal working conditions with GHSV of 3300 h^{-1}).

Example 2

A shaped aluminium oxide carrier was prepared in the same way as in example 1, except that 1.79 g cesium fluoride was used. The Sn/Al atom ratio was 0.01 and the Cs/Al atom ratio was 0.006. Drying and calcination temperatures were the same as in example 1.

The carrier was impregnated with an aqueous solution of silver oxalate complexed with ethylene diamine, to which solution cesium hydroxide and ammonium fluoride had been added. The impregnation was carried out for 10 min under vacuum, whereafter the shaped pieces were separated from the aqueous solution and then placed in a heat air stream at a temperature of 250-270 °C during 10 min, in order to convert the silver compound into metallic silver.

The aqueous solution of silver oxalate contained 28 per cent by weight of Ag (on the total weight of the solution) and to which solution was added cesium hydroxide and ammonium fluoride. The catalyst contained 20.6 %wt Ag (calculated on the total catalyst), 450 ppm of (impregnated) cesium and 200 ppm of F (calculated on one million parts by weight of total catalyst).

The silver catalyst was employed in the preparation of ethylene oxide from ethylene and oxygen. A cylindric steel reactor with a length of 40 cm and a diameter of 5 mm was completely filled with crushed catalyst particles of about 1 mm. The reactor was placed in a bath of silica and alumina particles in fluid bed state. A gas mixture of the following composition was introduced into the reactor: 30 mol% ethylene, 8.5 mol% oxygen, 7 mol% carbon dioxide and 54.5 mol% nitrogen and 5.5 ppm vinyl chloride as moderator. The GHSV was 3300 h^{-1}. The pressure was maintained at 15 bar and the temperature dependent on the oxygen conversion.

Measuring-instruments were connected to the reactor and to a computer, such that conversion and reaction temperature could be precisely regulated. With the aid of gaschromatography and mass spectroscopy the amounts of reaction products were determined. The oxygen conversion was 40%.

The selectivity (S_{40}) of the above-mentioned silver catalyst was 82.0%, while the T_{40}-value was 235 °C.

Example 3

A shaped aluminium oxide carrier with the same Sn/Al and Cs/Al atom ratio as in example 2 was prepared (Sn/Al = 0.01; Cs/Al = 0.006).

The calcination temperatures were the same as in example 2, except that the product was calcinated during 6 h at 1600 °C, instead of at 1500 °C during 1 h.

The carrier was impregnated with an aqueous solution of silver oxalate complexed with ethylene diamine, to which solution cesium hydroxide and ammonium fluoride had been added. The impregnated carrier was worked up in the same way as in example 2. The catalyst contained 21.7 %wt Ag (calculated on the total catalyst), 420 ppm of (impregnated) cesium and 200 ppm of F (calculated on one million parts by weight of total catalyst).

The obtained silver catalyst was employed in the preparation of ethylene oxide from ethylene and oxygen. The experiment was carried out in the same way as described in example 2.

The selectivity (S_{40}) was 82.5% and the T_{40}-value was 230 °C.

Claims

1. A process for the preparation of a silver-containing catalyst suitable for the oxidation of ethylene to ethylene oxide which comprises
   a) mixing alumina with a tin compound and with an alkali metal compound,
   b) calcining the mixture to obtain an alkali-enriched and tin-containing alumina carrier,
   c) applying a silver compound to the alumina carrier and converting said silver compound to metallic silver.
2. A process as claimed in claim 1, wherein the alumina is anhydrous or hydrated alumina.
3. A process as claimed in claim 1 or 2, wherein the alkali metal compound is a salt or a hydroxide of the alkali metal.
4. A process as claimed in one or more of the claims 1-3, wherein the alkali metal salt is a fluoride, nitrate, chloride or a sulphate.
5. A process as claimed in one or more of the claims 1-4, wherein the alkali metal is cesium.
6. A process as claimed in one or more of the claims 1-5, wherein the tin compound is a tin salt.
7. A process as claimed in claim 6, wherein the tin salt is stanno sulphate or stannic sulphate.
8. A process as claimed in one or more of the claims 1-7, wherein the calcination under b) is carried out at a temperature of between 1200 °C and 1700 °C.
9. A process as claimed in one or more of the claims 1-8, wherein alumina is mixed with water, the tin compound and the alkali metal compound, the resulting mixture is extruded to shaped carrier particles, which latter are calcined.
10. A process as claimed in one or more of the claims 1-9, wherein the calcined alumina carrier is impregnated with a solution of a silver salt or -complex sufficient to apply 1 to 25 per cent by weight of silver, calculated on the weight of total catalyst, on the carrier surface, and the precipitated silver salt or -complex is reduced to metallic silver.
11. A process as claimed in claim 10, wherein additionally a promoter is applied, either simultaneously or not.
12. A process as claimed in claim 11, wherein besides the silver salt or -complex a sufficient quantity of one or more compounds of the alkali metals potassium, rubidium or cesium is applied to the carrier to deposit between 20 and 1000 parts by weight of the alkali metal (measured as the metal) per million parts by weight of total catalyst.
13. A process as claimed in one or more of the claims 1-12, wherein an alkali metal enriched and tin modified alumina carrier, which has been calcined, is impregnated with a solution of a silver compound, suffi-

The aqueous solution of silver oxalate contained 28 per cent by weight of Ag (on the total weight of the solution) and to which solution was added cesium hydroxide and ammonium fluoride. The catalyst contained 20.6 %wt Ag (calculated on the total catalyst), 450 ppm of (impregnated) cesium and 200 ppm of F (calculated on one million parts by weight of total catalyst).

The silver catalyst was employed in the preparation of ethylene oxide from ethylene and oxygen. A cylindric steel reactor with a length of 40 cm and a diameter of 5 mm was completely filled with crushed catalyst particles of about 1 mm. The reactor was placed in a bath of silica and alumina particles in fluid bed state. A gas mixture of the following composition was introduced into the reactor: 30 mol% ethylene, 8.5 mol% oxygen, 7 mol% carbon dioxide and 54.5 mol% nitrogen and 5.5 ppm vinyl chloride as moderator. The GHSV was 3300 h^{-1}. The pressure was maintained at 15 bar and the temperature dependent on the oxygen conversion.

Measuring-instruments were connected to the reactor and to a computer, such that conversion and reaction temperature could be precisely regulated. With the aid of gaschromatography and mass spectroscopy the amounts of reaction products were determined. The oxygen conversion was 40%.

The selectivity (S_{40}) of the above-mentioned silver catalyst was 82.0%, while the T_{40}-value was 235 °C.

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A shaped aluminium oxide carrier with the same Sn/Al and Cs/Al atom ratio as in example 2 was prepared (Sn/Al = 0.01; Cs/Al = 0.006).

The calcination temperatures were the same as in example 2, except that the product was calcinated during 6 h at 1600 °C, instead of at 1500 °C during 1 h.

The carrier was impregnated with an aqueous solution of silver oxalate complexed with ethylene diamine, to which solution cesium hydroxide and ammonium fluoride had been added. The impregnated carrier was worked up in the same way as in example 2. The catalyst contained 21.7 %wt Ag (calculated on the total catalyst), 420 ppm of (impregnated) cesium and 200 ppm of F (calculated on one million parts by weight of total catalyst).

The obtained silver catalyst was employed in the preparation of ethylene oxide from ethylene and oxygen. The experiment was carried out in the same way as described in example 2.

The selectivity (S_{40}) was 82.5% and the T_{40}-value was 230 °C.

Claims

1. A process for the preparation of a silver-containing catalyst suitable for the oxidation of ethylene to ethylene oxide which comprises
a) mixing alumina with a tin compound and with an alkali metal compound,
b) calcining the mixture to obtain an alkali-enriched and tin-containing alumina carrier,
c) applying a silver compound to the alumina carrier and converting said silver compound to metallic silver.

2. A process as claimed in claim 1, wherein the alumina is anhydrous or hydrated alumina.

3. A process as claimed in claim 1 or 2, wherein the alkali metal compound is a salt or a hydroxide of the alkali metal.

4. A process as claimed in one or more of the claims 1-3, wherein the alkali metal salt is a fluoride, nitrate, chloride or a sulphate.

5. A process as claimed in one or more of the claims 1-4, wherein the alkali metal is cesium.

6. A process as claimed in one or more of the claims 1-5, wherein the tin compound is a tin salt.

7. A process as claimed in claim 6, wherein the tin salt is stanno sulphate or stannic sulphate.

8. A process as claimed in one or more of the claims 1-7, wherein the calcination under b) is carried out at a temperature of between 1200 °C and 1700 °C.

9. A process as claimed in one or more of the claims 1-8, wherein alumina is mixed with water, the tin compound and the alkali metal compound, the resulting mixture is extruded to shaped carrier particles, which latter are calcined.

10. A process as claimed in one or more of the claims 1-9, wherein the calcined alumina carrier is impregnated with a solution of a silver salt or -complex sufficient to apply 1 to 25 per cent by weight of silver, calculated on the weight of total catalyst, on the carrier surface, and the precipitated silver salt or -complex is reduced to metallic silver.

11. A process as claimed in claim 10, wherein additionally a promoter is applied, either simultaneously or not.

12. A process as claimed in claim 11, wherein besides the silver salt or -complex a sufficient quantity of one or more compounds of the alkali metals potassium, rubidium or cesium is applied to the carrier to deposit between 20 and 1000 parts by weight of the alkali metal (measured as the metal) per million parts by weight of total catalyst.

13. A process as claimed in one or more of the claims 1-12, wherein an alkali metal enriched and tin modified alumina carrier, which has been calcined, is impregnated with a solution of a silver compound, suffi-

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cient to cause precipitation on the carrier of from 1 to 25 per cent by weight, on the total catalyst, of silver, and before, during or after that impregnation also with one or more dissolved potassium-, rubidium- or cesium compounds as promoter and with a source of fluoride-anions, and after precipitation the silver compound on the impregnated carrier is reduced to metallic silver.

14. A process as claimed in claim 13, wherein the source of fluoride-anions is ammonium fluoride or ammonium hydrogen fluoride.

15. A silver-containing catalyst suitable for the oxidation of ethylene to ethylene oxide comprising

a) from 1 to 25 per cent by weight of silver, calculated on the total catalyst weight, on the surface of the carrier

b) an alkali enriched and tin modified alpha-alumina carrier.

16. A silver-containing catalyst as claimed in claim 15, wherein a promoter is present on the surface of the carrier.

17. A silver-containing catalyst as claimed in claim 16, wherein between 20 and 1000 parts by weight of potassium, rubidium or cesium (measured as the metal) per million parts by weight of total catalyst is present on the surface of the carrier.

18. A silver-containing catalyst as claimed in claims 15-17, wherein a fluoride anion is present in an amount between 10 and 1000 parts by weight per million parts by weight of total catalyst.

19. A silver-containing catalyst as claimed in claim 18, wherein the fluoride anion is present in an amount between 100 and 700 parts by weight per million parts by weight of total catalyst.

20. A process for the preparation of ethylene oxide by oxidation of ethylene in the presence of a silver-containing catalyst, which has been prepared by means of a process as claimed in claims 1-14 or a silver-containing catalyst as claimed in claims 15-19.

Patentansprüche

1. Verfahren zur Herstellung eines silberhaltigen Katalysators für die Oxidation von Ethylen zu Ethylenoxid durch folgende Verfahrensstufen:

a) Mischen von Aluminiumoxid mit einer Zinnverbindung und einer Alkaliverbindung,

b) Brennen des Gemischs zu einem an Alkali angereicherten und zinnhaltigen Tonerdeträger,

c) Aufbringung einer Silberverbindung auf den Tonerdeträger und Überführen der Silberverbindung in metallisches Silber.

2. Verfahren nach Anspruch 1, wobei die Tonerde wasserfrei oder hydratisiert sein kann.

3. Verfahren nach Anspruch 1 oder 2, wobei die Alkaliverbindung ein Alkalisalz oder -hydroxid ist.

4. Verfahren nach einem oder mehreren der Ansprüche 1 bis 3, worin das Alkalisalz ein Fluorid, Nitrat, Chlorid oder Sulfat ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, worin das Alkalimetall Caesium ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, worin die Zinnverbindung ein Zinnsalz ist.

7. Verfahren nach Anspruch 6, worin das Zinnsalz Stanni- oder Stannosulfat ist.

8. Verfahren nach einem der Ansprüche 1 bis 7, worin die Stufe b) bei einer Temperatur zwischen 1200 und 1700°C durchgeführt wird.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei Tonerde mit Wasser, der Zinnverbindung und der Alkaliverbindung gemischt, das Gemisch zu den Trägerteilchen stranggepreßt wird und die Trägerteilchen gebrannt werden.

10. Verfahren nach einem der Ansprüche 1 bis 9, worin der gebrannte Tonerdeträger mit einer Lösung eines Silbersalzes oder Silberkomplexes bis zur Aufnahme von 1 bis 25 Gew.-% Silber, berechnet auf das Gesamtgewicht des Katalysators, an der Trägeroberfläche imprägniert wird, worauf das ausgefällte Silbersalz oder der Silberkomplex zu metallischem Silber reduziert wird.

11. Verfahren nach Anspruch 10, wobei zusätzlich, gegebenenfalls gleichzeitig, ein Promotor angewandt wird.

12. Verfahren nach Anspruch 11, wobei außer dem Silbersalz oder dem Silberkomplex eine ausreichende Menge einer oder mehrerer Verbindung(en) von Kalium, Rubidium oder Caesium für eine Abscheidung von 20 bis 1000 Gew.-Teile Alkali (als Metall) je Million Gewichtsteile gesamter Katalysator aufgebracht wird.

13. Verfahren nach einem der Ansprüche 1 bis 12, wobei der mit Alkali angereicherte und mit Zinn modifizierte und gebrannte Tonerdeträger mit einer Lösung einer Silberverbindung getränkt wird, um auf dem Träger 1 bis 25 Gew.-%, bezogen auf das Gesamtgewicht des Katalysators, Silber abzuscheiden, und vor, während oder nach dieser Imprägnierung mit einer oder mehreren gelösten Kalium-, Rubidium- oder Caesiumverbindung(en) als Promotor und mit einer Quelle für Fluoridanionen imprägniert und nach der Ausfällung der Silberverbindung auf dem imprägnierten Träger das Silber zu Metall reduziert wird.

14. Verfahren nach Anspruch 13, wobei die Quelle für Fluoridanionen Ammoniumfluorid oder Ammoniumhydrogenfluorid ist.

15. Silberhaltiger Katalysator für die Oxidation von Ethylen zu Ethylenoxid, enthaltend

a) 1 bis 25 Gew.-% Silber, bezogen auf das Gesamtgewicht des Katalysators, auf der Oberfläche des Trägers,

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b) mit Alkali angereicherter und mit Zinn modifizierter α-Tonerdeträger.

16. Katalysator nach Anspruch 15, wobei an der Oberfläche des Trägers ein Promotor anwesend ist.

17. Katalysator nach Anspruch 16, wobei 20 bis 1000 ppm Kalium, Rubidium oder Caesium (als Metall), bezogen auf das Gesamtgewicht des Katalysators, an der Oberfläche des Trägers vorhanden sind.

18. Katalysator nach Anspruch 15 bis 17, enthaltend ein Fluoridanion in einer Menge von 10 bis 1000 ppm, bezogen auf das Gesamtgewicht des Katalysators.

19. Katalysator nach Anspruch 18, wobei das Fluoridanion in einer Menge von 100 bis 700 ppm, bezogen auf das Gesamtgewicht des Katalysators, vorliegt.

20. Verfahren zur Herstellung von Ethylenoxid durch Oxidation von Ethylen in Gegenwart eines silberhaltigen Katalysators der Ansprüche 15 bis 19, hergestellt nach dem Verfahren der Ansprüche 1 bis 14.

Revendications

1. Procédé de préparation d'un catalyseur contenant de l'argent convenant pour l'oxydation d'éthylène en oxyde d'éthylène, qui comprend les étapes qui consistent à

a) mélanger de l'alumine avec un composé d'étain et avec un composé de métal alcalin,

b) calciner le mélange pour obtenir un support d'alumine enrichi en métal alcalin et contenant de l'étain,

c) appliquer un composé d'argent sur le support d'alumine et transformer le composé d'argent en argent métallique.

2. Procédé selon la revendication 1, dans lequel l'alumine est une alumine anhydre ou hydratée.

3. Procédé selon la revendication 1 ou 2, dans lequel le composé de métal alcalin est un sel ou un hydroxyde du métal alcalin.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le sel de métal alcalin est un fluorure, un nitrate, un chlorure ou un sulfate.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le métal alcalin est le césium.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le composé d'étain est un sel d'étain.

7. Procédé selon la revendication 6, dans lequel le sel d'étain est le sulfate stanneux ou le sulfate stannique.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel la calcination en b) est réalisée à une température comprise entre 1200°C et 1700°C.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel l'alumine est mélangée avec de l'eau, le composé d'étain et le composé de métal alcalin, le mélange résultant est extrudé pour donner des particules de support formées, ces dernières étant calcinées.

10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel le support d'alumine calcinée est imprégné d'une solution d'un sel d'argent ou d'un complexe d'argent en quantité suffisante pour appliquer 1 à 25% en poids d'argent, calculé par rapport au poids du catalyseur total, sur la surface du support, et le sel d'argent ou le complexe d'argent précipité est réduit en argent métallique.

11. Procédé selon la revendication 10, dans lequel on applique en outre un promoteur, simultanément ou non.

12. Procédé selon la revendication 11, dans lequel, en plus du sel ou du complexe d'argent, on emploie une quantité suffisante d'un ou plusieurs composés des métaux alcalins potassium, rubidium ou césium sur le support pour déposer entre 20 et 1000 parties en poids du métal alcalin (exprimées en métal) pour un million de parties en poids du catalyseur total.

13. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel un support d'alumine enrichi en métal alcalin et modifié par l'étain, qui a été calciné, est imprégné d'une solution d'un composé d'argent, en quantité suffisante pour provoquer la précipitation, sur le support, de 1 à 25% en poids d'argent, par rapport au catalyseur total, et est également imprégné, avant pendant ou après cette imprégnation, d'un ou plusieurs composés de potassium, de rubidium ou de césium dissous, à titre de promoteur, et d'une source d'anions fluorure et, après la précipitation, le composé d'argent sur le support imprégné est réduit en argent métallique.

14. Procédé selon la revendication 13, dans lequel la source d'anions fluorure est du fluorure d'ammonium ou du fluorure acide d'ammonium.

15. Catalyseur contenant de l'argent convenant pour l'oxydation d'éthylène en oxyde d'éthylène, comprenant

a) de 1 à 25% en poids d'argent, calculé par rapport au poids total du catalyseur, sur la surface du support, et

b) un support d'α-alumine enrichi en métal alcalin et modifié par l'étain.

16. Catalyseur contenant de l'argent selon la revendication 15, dans lequel le promoteur est présent sur la surface du support.

17. Catalyseur contenant de l'argent selon la revendication 16, dans lequel entre 20 et 1000 parties en poids de potassium, de rubidium ou de césium (exprimées en métal), pour un million de parties en poids du catalyseur total, sont présentes sur la surface du support.

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18. Catalyseur contenant de l'argent selon l'une quelconque des revendications 15 à 17, dans lequel un anion fluorure est présent en une quantité comprise entre 10 et 1000 parties en poids par million de parties en poids de catalyseur total.

19. Catalyseur contenant de l'argent selon la revendication 18, dans lequel l'anion fluorure est présent en une quantité comprise entre 100 et 700 parties en poids par million de parties en poids du catalyseur total.

20. Procédé de préparation d'oxyde d'éthylène par oxydation d'éthylène en présence d'un catalyseur contenant de l'argent ayant été préparé au moyen d'un procédé selon l'une quelconque des revendications 1 à 14 ou d'un catalyseur contenant de l'argent selon l'une quelconque des revendications 15 à 19.

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