

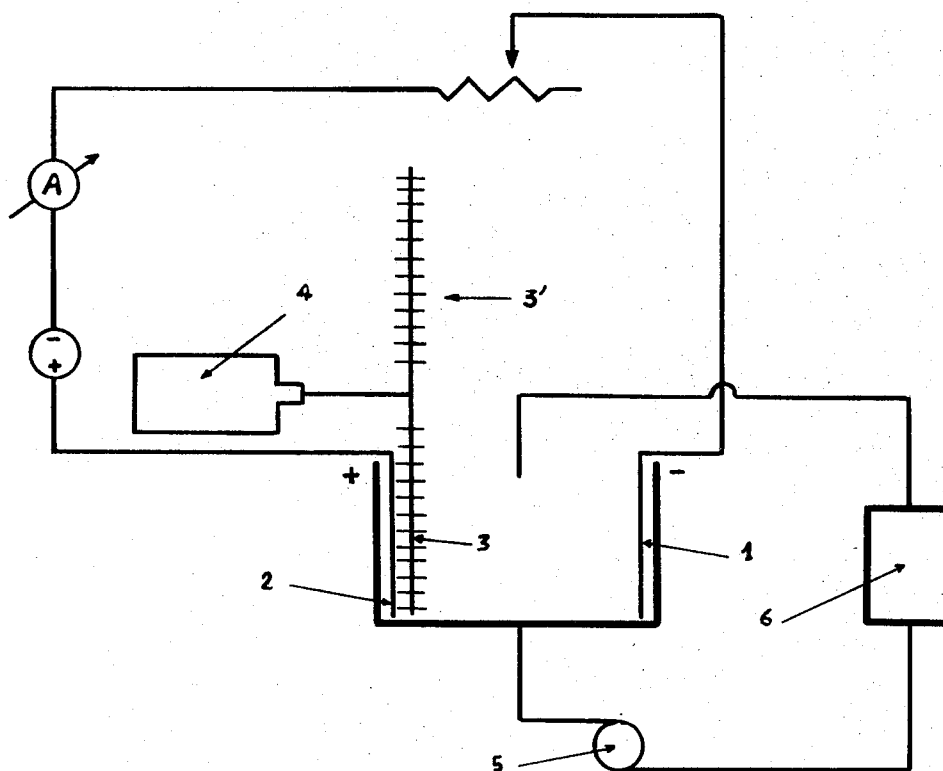
Oct. 22, 1974

M. PIRO ET AL

3,843,491

PROCESS FOR THE PREPARATION OF SILVER BASE CATALYST

Filed Dec. 27, 1972



1

3,843,491

PROCESS FOR THE PREPARATION OF  
SILVER BASE CATALYSTMario Piro, Milan, and Luigi Rivola and Bruno Notari,  
San Donato Milanese, Italy, assignors to Snam Progetti  
S.p.A., Milanese, Italy

Filed Dec. 27, 1972, Ser. No. 319,060

Claims priority, application Italy, Dec. 28, 1971,

33,010/71

Int. Cl. C22d 5/00, 1/12

U.S. Cl. 204—10

14 Claims

## ABSTRACT OF THE DISCLOSURE

A process is described whereby a catalyst grade of finely divided silver, having a particle size in the range from 300 A. to 1500 A., is produced through the electrolytic deposition of silver on a cathode and the mechanical removal of the silver from the cathode as it is formed, either by subjecting the cathode to ultrasonic vibrations or to a scrubbing action by means of brushes or jets of liquid under pressure or violent stirring.

The present invention refers to an improved process for the preparation of silver base catalysts which are useful in the synthesis of ethylene oxide.

More particularly the present invention refers to a process for the electrochemical preparation of silver base catalysts.

It is known that there are many processes for preparing silver base catalysts for the preparation of ethylene oxide; and it is also known that the silver structure and the working conditions which allow it to be obtained have a remarkable importance in obtaining high activities and selectivities. The chemical methods, previously proposed, substantially consist of the decomposition of silver salts or compounds in order to obtain silver in a finely subdivided state.

Such methods have the principal drawback of poor reproducibility and the inevitable silver losses which occur during the treatments: this fact imposes expensive recovery processes.

On the other hand silver production might be possible with high yields and in a reproducible way when using systems of electrochemic deposition of such metal; but it is also known that the electrolysis of silver solutions gives rise to a metal having a compact shape or, in any case, high particle sizes that render them unusable in the industrial process for the production of ethylene oxide by ethylene oxidation.

It has now been found that it is possible to produce, electrochemically, silver catalysts whose particles have sizes lower than 1500 A. and preferably between 300 A. and 1500 A. which, when used in the synthesis of ethylene oxide by ethylene oxidation, give high activities and selectivities.

Moreover it has been found that it is possible to produce silver, which is useful for the synthesis of ethylene oxide, whose crystalline aggregates show sizes ranging between 300 A. and 1500 A. by an electrolysis of silver compounds, wherein silver is removed from the cathode as it is formed.

The detaching of stored silver from the cathode may be effected by mechanical methods or by ultra-sonic vibrations.

Helpful uses can be made of the following mechanical techniques: employment of brushes sliding on the cathode and vice versa, employment of a vibrating or oscillating cathode, jets of liquid under pressure onto the cathode, violent stirring of the electrolytic solution.

2

The silver compounds usefully employable as electrolytic solution in the process of our invention can be selected from salts such as silver nitrates, silver sulphate, silver acetate, silver halides, silver oxalate, or complexed basic compounds such as ammoniacal silver hydroxides.

Furthermore it is preferable that the silver salts be complexed with ammonia or with fluoboric ions.

It is also advantageous to use a buffer keeping the solution pH at a value ranging from 10 to 14.

Electrolysis is generally carried out in the presence of protector colloids such as cellulose derivatives, for instance carboxymethylcellulose.

The electrolytic operation is generally performed at low temperatures, between 10° and 50° C. The current density may vary over a large range: however use is preferably made of values ranging between 2 mampers/cm.<sup>2</sup> and 50 mampers/cm.<sup>2</sup>. The following working examples illustrate the invention but are not limitative thereof.

## EXAMPLE 1

100 g. of AgNO<sub>3</sub>, 750 g. of borax (N<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 10 H<sub>2</sub>O), 400 g. of NaOH were dissolved in distilled water and diluted up to a 100:1 volume. Thereto were added 600 cc. of aqueous ammonia solution (28 Bé.) and 10 g. of carboxymethylcellulose (before solubilized on another side). 3.5 liters of the aforesaid solution were poured into the electrolytic cell shown in FIG. 1 with an anode consisting of compact graphite 1 and a cathode consisting of a silver plate 2.

The cell was provided with the system of mechanical removal of the deposited silver constituted by two plastic brushes 3,3 whose speed of rotation may range over large limits by means of a geared motor 4.

The brushes were arranged so as to lap the cathode surface.

A peristaltic pump, outside the cell, took in the electrolytic solution, made it pass through a heat exchanger and sent it again into the cell.

During electrolysis the silver titre was kept constant by means of periodic additions of silver nitrate complexed with ammonia in excess.

The electrolysis was carried out at constant current by means of an amperostat. A reference electrode (saturated calomel) contacted to cathode to measure the electrode potential.

The electrodeposition was carried out under the following conditions:

Temperature	20° C.
Cathode surface	80 cm. <sup>2</sup> .
Anode surface	80 cm. <sup>2</sup> .
Current density	6 ma./cm. <sup>2</sup> .
Distance between the electrodes	3 cm.
Cathode potential	—1000 mv. on S.C.E.
Brushing speed	60 rotations per minute.
Tension applied to cell	3 v.

The electric energy consumption was about 0.7 kwh. per kg. of produced silver, the yield was close to 80%.

The produced silver, having average sizes of 800 A., was washed with water made free from ions, dried in an oven at 80° C. and then deposited, by suitable technics, on a ceramic carrier in order to carry out a test of catalyst activity.

The catalyst, constituted by carrier and silver in an amount of 15%, was introduced into a 2.4 cm. pipe, equipped with an external jacket allowing the thermostating liquid to circulate. The catalytic bed height was about 1 m.

A gaseous mixture was fed into the reactor at atmospheric pressure having the following composition: 5% ethylene, 6.5% CO<sub>2</sub>, 5% O<sub>2</sub>, 83.5% N<sub>2</sub>. The feed flow was 210 Nl/h. and the contact time was about 4.6 sec.

At 200° C. we obtained conversion and selectivity values of 30 and 80% respectively.

#### EXAMPLE 2

An electrolysis was performed on the solution of Example 1 by working according to the following experimental conditions:

Temperature	18° C.
Apparent current density	70 ma./cm. <sup>2</sup> .
Cathode potential	-1000 mv. on S.C.E.
Cathode	Silver net having 1 x 1 mm. <sup>2</sup> meshes.
Brushing speed	200 rotations/minute.
Tension	12 v.

The energy consumption was about 3 kwh. per kg. of produced silver.

The silver produced, deposited on a ceramic material, was put in a reactor under the conditions of Example 1. At 220° C. we obtained, in the conversion reaction of ethylene to ethylene oxide, conversion and selectivity values of 20 and 80% respectively. The obtained silver had crystal sizes of 700 Å.

#### EXAMPLE 3

An electrolysis was carried out on the solution of Example 1 by using ultra-sonic vibrations for detaching silver. The experimental conditions were the following ones:

Position of the sound head	Close to cathode.
Temperature	15° C.
Cathode	Ag plate.
Cathode surface	50 cm. <sup>2</sup> .
Anode	Compact graphite.
Anode surface	100 cm. <sup>2</sup> .
Current density	50 ma./cm. <sup>2</sup> .
Tension	10 v.
Cathode potential	-1300 mv.

The sound head of ultra-sonic vibrations was electrically connected to the cathode so as to avoid possible corrosion processes.

The silver obtained under the aforesaid experimental conditions had sizes of about 800 Å. and gave rise to conversion and selectivity values, in the ethylene-ethylene oxide reaction, of 25% and 78%.

#### EXAMPLE 4

This example relates to one of the possible industrial processes for preparing silver base catalyst by an electrodeposition from silver nitrate solutions with continuous current and continuous detaching of the electrodeposited material in an electrolytic cell of bipolar type.

Use was made of an electrolyte having the following composition:

AgNO <sub>3</sub>	0.5÷10 g/C
Borax	5÷20 g/C
Carboxymethylcellulose	0.04÷0.5 g/C
NH <sub>3</sub>	5÷100 g/C
NaOH	3÷100 g/C

Use was made of a cell of the bipolar type. The electrodes consisted of silver plates (or stainless steel plates) and compact graphite. The bipole was realized by tightly coupling a graphite plate with a silver one (or stainless steel one).

The detaching of the electrodeposited material from cathode was performed by means of brushes as aforesaid.

The electrolytic solution was drawn from the bottom of the electrolytic cell, cooled, corrected as to silver titre and pH, put in a centrifuge which separates metallic silver

from electrolyte and then again pumped into the electrolytic cell.

What we claim is:

1. A process for the preparation of silver useful as a catalyst by silver electrochemical deposition comprising: complexing a silver compound with a member selected from the group consisting of ammoniac and fluoboric ions, electrolytically depositing the silver compound on a cathode, and concurrently removing the deposited silver from said cathode whereby the removed silver has a size of less than 1500 Å.

2. The process for the preparation of silver useful as catalyst by means of electrochemical deposition according to claim 1 characterized in that the silver removed from cathode is carried out by brushing cathode.

3. The process for the preparation of silver useful as catalyst by means of electrochemical deposition according to claim 1 characterized in that the removal of the silver from the cathode is carried out by employing ultra-sonics.

4. The process for the preparation of silver useful as catalyst by means of electrochemical deposition according to claim 1 characterized in that the removal of silver from the cathode is carried out by spouts of liquid under pressure.

5. The process for the preparation of silver useful as catalyst by means of electrochemical deposition according to claim 1 characterized in that the silver is removed from the cathode by subjecting the electrolytic solution to a strong stirring.

6. The process for the preparation of silver useful as catalyst by means of electrochemical deposition according to claim 1 characterized in that the silver compound subjected to electrolysis in solution is a salt selected from the group consisting of nitrates, sulphates, acetates, halides, oxalates and basic compounds as silver ammoniacal hydroxides.

7. The process according to claim 6 characterized in that the silver salts are complexed with ammoniac ions.

8. The process according to claim 6 characterized in that a buffer is included in the solution which maintains the solution pH at a value of about between 10 and 14.

9. The process according to claim 6 characterized in that the electrolysis is carried out in presence of protector colloids selected from the cellular derivatives.

10. The process according to claim 1 characterized in that the electrolysis is carried out at temperatures ranging between 10° and 50° C.

11. The process according to claim 10 characterized in that the current density ranges from 2 m. amperes/cm.<sup>2</sup> to 100 m. amperes/cm.<sup>2</sup>.

12. The process according to claim 1 wherein said silver catalyst has a size of about between 300 Å. and 1500 Å.

13. The process according to claim 12 wherein said silver catalyst is used in the production of ethylene oxide from ethylene and oxygen or air.

14. The process according to claim 6 characterized in that the silver salts are complexed with fluoboric ions.

#### References Cited

##### UNITED STATES PATENTS

532,209	1/1895	Moebius	204—109
1,954,316	4/1934	Hickman et al.	204—109
2,810,682	10/1957	Brown	204—10
3,616,277	10/1971	Adamson et al.	204—10

T. TUFARIELLO, Primary Examiner

U.S. Cl. X.R.

204—109