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Patent application

Heraeus Precious Metals GmbH & Co. KG

Method for the production of noble metal oxalate complexes

The present invention relates to the production of noble metal oxalate complexes. Hereinafter, noble metal oxalate complexes shall also be referred to as noble metal oxalates for reasons of simplicity. Specifically, the invention relates to the production of noble metal oxalate complexes from noble metal precursors and oxalic acid and/or oxalic acid salts.

The production of noble metal oxalate complexes from noble metal precursors and oxalic acid and/or oxalic acid salts has been known for a long time. The production of platinum oxalate complexes usually proceeds through the reaction of platinum oxide hydrate (platinum(IV)-hydroxoacid, dihydrogenhexahydroxoplatinate(IV), hydroxoplatinic acid) and oxalic acid at a temperature of 60°C (K. Krogmann, P. Dodel, Chem. Ber. 1966, 99, 3408-3418).

EP 0 254 935 A1 describes a method for the production of silver oxalate having a large particle diameter. According to said method, silver salt and oxalic acid or oxalic acid salts are reacted at a pH value of no more than 5. The reaction is carried out at a temperature from 0 to 80°C, preferably at a temperature from 40 to 60°C.

The production of noble metal oxalate complexes from noble metal precursors and oxalic acid and/or oxalic acid salts is an exothermic reaction, in which heat and CO₂ are produced. The temperature can increase above the decomposition point of the noble metal oxalate complexes in the course of the reaction, which simultaneously releases more CO₂. In this context, refer to, e.g., Sano, Isamu, Bulletin, 15 (1940), 196 pp, "On the Catalytic Decomposition of Oxalic Acid by Colloidal Platinum", and Szabó, Z.G. and Biro-Sugar, E., Zeitschrift für Elektrochemie, vol. 50, no. 8, 1956, p. 869-874, "Kinetik der thermischen Zersetzung von Silberoxalat".

For safety reasons, when the reaction is carried out on a large scale, it is therefore necessary to take into consideration that the product must not be decomposed by heat that is produced during the reaction.

It is therefore the object of the present invention to provide a method for the production of noble metal oxalate complexes that can be carried out on a large scale.

Accordingly, a method is to be developed that enables the course of the reaction to be controlled. It needs to be made sure that the amounts of gas and heat produced during the synthesis can be guided away reliably from the reactor.

Said object is met by a method having the features of claim 1. Refinements of the invention are defined through the sub-claims.

The invention provides a method for the production of noble metal oxalate complexes, in which noble metal precursors are reacted with oxalic acid and/or oxalic acid salts, and in which noble metal oxalate is introduced into the reaction mixture as an auto-catalyst.

According to the invention, noble metal precursors and oxalic acid and/or oxalic acid salts are used as educts. Many starting substances are conceivable, whereby the noble metal precursor and oxalic acid and/or oxalic acid salt educts are obviously different from the noble metal oxalate end-product.

The term of noble metal comprises, in particular, the classical noble metals, Pt, Pd, Ir, Rh, Os, Ru, Ag, and Au, but also the semi-noble metal Re. Preferred noble metals include silver, palladium, and platinum, whereby platinum is particularly preferred.

Examples of noble metal precursors include noble metal salts and noble metal oxide hydrate. Examples of noble metal salts include noble metal nitrate and noble metal acetate or mixtures thereof. It is also conceivable to use mixtures of noble metal oxide hydrate and noble metal salt or salts. However, noble metal oxide hydrate, in particular platinum oxide hydrate, also referred to as platinum(IV) hydroxoacid (refer to Gmelin, Verlag Chemie GmbH, Berlin 1940, p. 47-48) has proven to be preferred. Which salt to use also depends on the type of noble metal. Accordingly, e.g. silver oxalate can be produced from silver nitrate. It is preferable to use

platinum-(IV) hydroxoacid or any of the salts thereof, such as, e.g., $\text{K}_2\text{Pt}(\text{OH})_6$, $\text{Na}_2\text{Pt}(\text{OH})_6$ etc., as starting substance for platinum oxalate. As a matter of rule, the free acid is preferred.

Oxalic acid salts can include, for example, sodium oxalate, ammonium oxalate or potassium oxalate or mixtures thereof. However, it is also feasible to use a mixture of oxalic acid and one or more oxalic acid salt(s). As before, the preferred educts depend on the type of noble metal. Accordingly, e.g. ammonium oxalate can be used to advantage for the production of silver oxalate. However, as a matter of rule, the use of free oxalic acid is particularly preferred. Accordingly, it is preferable also to use oxalic acid for the production of platinum oxalate.

According to the invention, an educt combination of noble metal oxide hydrate and oxalic acid is particularly preferred since only carbon dioxide and water are produced in addition to noble metal oxalate complexes.

It is particularly preferred to add oxalic acid or oxalic acid salt at a suitable stoichiometric ratio. Referring to the production of platinum oxalate complexes, this means that 1.8 to 2.8 molar equivalents of oxalic acid or oxalic acid salt relative to platinum in the form of the platinum precursor are added. This reaction produces a mixture of different dioxalatoplatinic acids or platinum oxalate complexes. For a detailed description of mixtures of this type, refer to K.Krogmann, P.Dodel, Chem. Ber. 1966, 99, 3402-3407, and 3408-3418.

The form, in which to add oxalic acid and/or oxalic acid salt, depends on the noble metal oxalate complex to be produced. Preferably, it is added in the form of an aqueous solution or as a solid. Oxalic acid is preferred and is preferably added as a solid in the form of oxalic acid dihydrate.

The reaction is carried out at a temperature below the decomposition temperature of the noble metal oxalate complexes. For definition of the safety margin for the reaction temperature in the present case, a hazard evaluation needs to be considered that takes into account important parameters of process technology, parameters of equipment technology, considerations and data of safety technology, such as, e.g. the decomposition temperature or decomposition range of the noble metal oxalate complexes. The reaction temperature can then be made to come close to the decomposition temperature as a function of the existing data.

The reaction is therefore preferably carried out at a temperature below the decomposition temperature of the noble metal oxalate complexes. In this context, the difference between

reaction temperature and decomposition temperature should be at least 1°C, preferably the difference is at least 5°C. The decomposition temperature is defined to be the temperature at which decomposition starts, whereby the start of decomposition is determined using long-term differential thermal analysis in glass ampoules at a heating rate of 0.05 K/min according to temperature differential thermal analysis in accordance with DIN 51007. Proven to be preferred for the reaction of noble metal precursors and oxalic acid and/or oxalic acid salts is a temperature range between 0°C and 56°C, particularly preferably between 30°C and 52°C, and even more particularly preferably between 35°C and 45°C.

Referring, in particular, to platinum oxalate complexes decomposing already at a temperature of 57°C (see figure), it is preferable to carry out the reaction at a temperature of up to 56°C, particularly preferably at up to 52°C, and even more particularly preferably at up to 45°C. The reaction is carried out above 0°C, preferably above 30°C, and particularly preferably at a temperature of 35°C to 42°C.

According to the scope of the invention, the decomposition temperature of the noble metal oxalate complexes is to be determined by means of long-term differential thermal analysis (DTA) in accordance with DIN 51007 (Jun 1994). The determination can be done on solutions of noble metal oxalate complexes that correspond to the product solution, in a closed glass ampoule at a heating rate of 0.05 K/min between 0°C and a temperature above the measured peak trough (see figure). According to the invention, the decomposition temperature shall be understood to be the temperature when the first deviation (see figure, 57°C) of the measuring curve from the starting baseline curve is noted (5.2 DIN 51007).

In the present case, 2934.5 mg of a 10 % by weight platinum oxalate solution in water were used. The measurement proceeded in glass ampoules at a heating rate of 0.05 K/min. The figure shows the heat flow W/g as a function of the temperature between 2°C and 83°C.

In the present description, temperature-equilibrate shall be understood to mean that the reaction mixture is set to a certain temperature. The temperature equilibration can be effected, e.g., by means of water.

It is advantageous to first produce an aqueous solution or suspension of noble metal oxide hydrate or noble metal salt. Referring to the production of platinum oxalate complexes, it is preferred to first produce an aqueous suspension of platinum oxide hydrate ($\text{H}_2[\text{Pt}(\text{OH})_6]$) or

platinum-(IV) hydroxoacid). It is preferable to produce a 5 to 25 % by weight suspension, particularly preferably a 7-15 % by weight suspension relative to platinum in water.

Surprisingly, it has been evident that the introduction of small amounts of noble metal oxalate complexes into the reaction mixture has an auto-catalytic effect. The addition of noble metal oxalate complexes significantly shortens an induction period of the reaction (very slow starting phase of the reaction). This enables the course of the reaction to be controlled. Therefore, the added noble metal oxalate complexes are also referred to as auto-catalysts hereinafter.

According to the invention, a small amount of auto-catalyst is added. Preferably, the amount of auto-catalyst to be added is 1×10^{-4} to 5×10^{-2} molar equivalents of noble metal relative to the noble metal in the noble metal precursor. Particularly preferably, the amount of auto-catalyst to be added is 5×10^{-4} to 1×10^{-2} molar equivalents of noble metal relative to the noble metal in the noble metal precursor, and particularly preferably the amount of auto-catalyst to be added is 5×10^{-4} to 7×10^{-3} molar equivalents of noble metal relative to the noble metal in the noble metal precursor. It is preferable to add the auto-catalyst in aqueous solution. Customary concentrations are 5-20 % by weight, e.g. 8-15 % by weight.

Expediently, the noble metal oxalate complexes corresponding to the product to be produced are used as auto-catalyst (in line with the meaning of the term, "auto-catalyst"). This means that platinum oxalate is used as auto-catalyst for the production of platinum oxalate and silver oxalate, etc. is used as auto-catalyst for the production of silver oxalate, etc.

The order, in which noble metal precursor, auto-catalyst, and oxalic acid and/or oxalic acid salt are added, is less important. The auto-catalyst can be added to the reaction solution or suspension concurrently with the total amount of oxalic acid and/or oxalic acid salt, concurrently with part of the oxalic acid and/or oxalic acid salt or before the addition of oxalic acid and/or oxalic acid salt. Either a solution or a suspension of noble metal precursor can be provided first or added later in this context.

If the noble metal precursor is provided first and the auto-catalyst and oxalic acid are added concurrently, the addition should be made at a temperature below the desired reaction temperature. The addition preferably is made at a temperature of up to 37°C, particularly preferably at up to 32°C. The reaction mixture thus formed is then heated up to the desired reaction temperature. The heating rate is then a function of when the reaction starts.

However, it has proven to be advantageous to first provide the noble metal precursor in solution or suspension, then add the auto-catalyst and to add at least the major part of the oxalic acid or oxalic acid salt only after the reaction temperature is reached.

The oxalic acid or the oxalic acid salt can be added in one or more aliquots. The aliquots can be equal in size, or multiple aliquots differing in size can be added just as well. In case said aliquots differ in size, it is advantageous to first add a larger aliquot and then one or more smaller aliquots or progressively smaller aliquots. Accordingly, it has proven to be advantageous to first add an aliquot of 0.4 to 1.4 molar equivalents relative to platinum in the form of the platinum precursor and to subsequently add, e.g., multiple equal amounts of the remaining oxalic acid or the remaining oxalic acid salt. This can be done, for example, in a single further addition of e.g. 0.4 to 1.4 molar equivalents, in 2 further additions of, e.g., 0.2 to 0.9 molar equivalents, in 3 further additions of, e.g., 0.1 to 0.7 molar equivalents, in 4 further additions of, e.g., 0.1 to 0.6 molar equivalents, etc. However, it is conceivable just as well to add the oxalic acid or the oxalic acid salt evenly and continuously.

It is advantageous to stir the solution or suspension during the reaction. In the preferred embodiment, the oxalic acid or the oxalic acid salt is added as a function of the stirring conditions, concentration of the solution or suspension, and reactor dimensions. As a matter of principle, the rate at which oxalic acid or oxalic acid salt can be added can be set quite well based on the production of CO_2 and on the temperature profile.

Noble metal oxalate complexes produced as specified above can be used to advantage as precursors for noble metal catalysts.

Examples

The following examples serve purposes of illustration and are not to be construed as to limit the invention.

Measuring methods, analyses

NMR and UV spectroscopy were used in the qualitative analyses.

The UV spectrum was measured at room temperature using a Specord® 200 UV spectrometer made by Analytic Jena AG and 1 cm cuvettes (QS Suprasil® quartz glass cuvettes made by

Heraeus Quarzglas GmbH) over a measuring range from 190 nm -1,100 nm at a resolution of 2 nm.

The nuclear resonance spectroscopic measurements were carried out using a Bruker Avance 400 MHz NMR spectrometer (reference example 1) and a Bruker Avance 600 MHz NMR spectrometer (example, reference examples 2 and 3).

The platinum content was determined by gravimetry.

The educts used were platinum(IV) hydroxoacid ($\text{H}_2[\text{Pt}(\text{OH})_6]$) from in-house production (w(Pt): 55.51 %), oxalic acid dihydrate for analysis EMSURE® ACS, ISO, Reag. Ph Eur made by Merck KGaA, art. no. 100495, and platinum oxalate from in-house production (w(Pt): 11.72 %).

Example 1 (Production of platinum oxalate at 40°C, in the presence of auto-catalyst, oxalic acid added in 5 aliquots)

A total of 10 g Pt (50 mmol), in the form of 18.01 g $\text{H}_2[\text{Pt}(\text{OH})_6]$ were placed in 54.29 ml demineralised water ("VEW") in a 250 ml three-necked round flask.

Then, 0.04 g Pt oxalate (0.24 mmol Pt) were added as auto-catalyst at room temperature (23°C) while stirring (250 U/min) with a magnetic stirrer. A pale-greenish suspension was thus produced.

Time: 0 min:

The suspension was heated in a water bath from room temperature to 40°C over the course of 20 minutes.

Time 20 min:

As soon as the temperature of the suspension had reached 40°C, one of five equal aliquots of 2.568 g (20 mmol) oxalic acid dihydrate each was added. Gas was observed to be produced instantaneously, which lasted for a period of 60 minutes. A total of 270 ml CO_2 were captured.

Time 80 min:

Once gas production ceased, another aliquot of 2.568 g (20 mmol) oxalic acid dihydrate was added. A total of 40 ml CO_2 were captured.

Time 140 min:

Once gas production ceased, another aliquot of 2.568 g (20 mmol) oxalic acid dihydrate was added. The colour of the solution changed from green to turquoise-blue after 10 min. A total of 300 ml CO₂ were captured over the course of 60 min.

Time 200 min:

Once gas production ceased, another aliquot of 2.568 g (20 mmol) oxalic acid dihydrate was added. A total of 270 ml CO₂ were captured over the course of 60 min.

Time 260 min:

Once gas production ceased, another aliquot of 2.568 g (20 mmol) oxalic acid dihydrate was added. A total of 300 ml CO₂ were captured over the course of 110 min. No further gas production was observed during 10 more minutes of stirring at 40°C.

Time 380 min:

The heating system was switched off. The solution was stirred further until room temperature was reached.

The mixture was filtered through a 0.2 µm membrane filter (Sartorius filtration unit). Filtration was carried out within 30 minutes.

A total of 74.49 g of product having a Pt content of 13.40 % by weight were obtained with the yield being 99.82 % relative to platinum.

¹³C-NMR (151 MHz, 299.6 K, DMSO-d₆ capillary): δ = 168.70; 167.16 ppm

UV-VIS: 627 nm (A=0.399); 417 nm (0.415)

Reference example 1 (Production of platinum oxalate at 50°C)

A total of 10 g Pt (50 mmol), in the form of 18.01 g H₂[Pt(OH)₆] were placed in 54.29 ml demineralised water ("VEW") in a 250 ml three-necked round flask. Then, 12.93 g (100 mmol) oxalic acid dihydrate were added while stirring (250 U/min) with a magnetic stirrer. A milky, yellowish-white suspension was thus produced.

Time: 0 min:

The suspension was heated in a water bath at a rate of approx. 1°C/10 min starting at 19°C.

Time 180 min:

The solution started to turn greenish at a temperature of 35°C.

Time 210 min:

The solution turned turquoise-blue at a temperature of 38°C.

Time 220 min:

The solution turned deep-blue at a temperature of 39°C.

Time 230 min:

The temperature of the solution reached 40°C. Gas production was for a period of 50 min, in which the temperature of the solution reached 45°C.

Time 350 min:

The temperature reached 50°C. There was no gas production any longer.

Time 510 min:

The heating system was switched off, the solution was stirred further until room temperature was reached.

The mixture was filtered through a 0.2 µm membrane filter (Sartorius filtration unit). Filtration was carried out within 90 minutes.

A total of 47.82 g of product having a Pt content of 20.75 % by weight were obtained with the yield being 99.23 % relative to platinum.

¹³C-NMR (100.6 MHz, 303 K, DMSO-d₆ capillary): δ = 168.43; 166.72 ppm

UV-VIS 664 nm (A=0.731); 417 nm (0.763)

Reference example 2 (Production of platinum oxalate at 40°C, no auto-catalyst)

Reference experiment 1 was repeated except that the solution was heated for a period of 210 minutes from 23°C to a temperature of 40°C. The colour of the solution turned greenish after

150 minutes at a temperature of 35°C. After 190 minutes, when the temperature was 37°C, the solution began to turn blueish, and after 230 minutes gas production was observed for a period of 65 minutes.

A total of 80.972 g of product having a Pt content of 12.25 % by weight were obtained with the yield being 99.19 % relative to platinum.

^{13}C -NMR (151 MHz, 298 K, DMSO- d_6 capillary): δ = 168.16; 166.67 ppm

UV-VIS 641.05 nm ($A=0.342$); 417 nm (0.374)

Reference example 3 (Production of platinum oxalate at 40°C, no auto-catalyst, oxalic acid added in 5 aliquots)

A total of 10 g Pt (50 mmol), in the form of 18.01 g $\text{H}_2[\text{Pt}(\text{OH})_6]$ were placed in 54.29 ml demineralised water ("VEW") in a 250 ml three-necked round flask.

Time 0 min:

The suspension was heated in a water bath from 20°C to 40°C over the course of 40 minutes.

Time 40 min:

As soon as the temperature of the suspension had reached 40°C, one of five equal aliquots of 2.568 g (20 mmol) oxalic acid dihydrate each was added. Neither a colour change nor the production of gas were observed. After another 60 minutes, another aliquot of 2.568 g (20 mmol) oxalic acid dihydrate was added. As before, neither a colour change nor the production of gas were observed.

Time 160 min:

Another 2.568 g (20 mmol) aliquot of oxalic acid dihydrate was added. Ten minutes later, the solution turned greenish. Another 30 minutes later (at 200 minutes), the colour of the solution changed from green to turquoise-blue.

Time 220 min:

Another 2.568 g (20 mmol) aliquot of oxalic acid dihydrate was added. Ten minutes later, gas production was observed.

Time 280 min:

Another 2.568 g (20 mmol) aliquot of oxalic acid dihydrate was added. Gas production continued until the 300 minutes time point. No gas production was observed any longer after this time.

Time 330 min:

The heating system was switched off. The solution was stirred further until room temperature was reached.

The mixture was filtered through a 0.2 μm membrane filter (Sartorius filtration unit). Filtration was carried out within 30 minutes.

A total of 77.39 g of product having a Pt content of 12.85 % by weight were obtained with the yield being 99.45 % relative to platinum.

^{13}C -NMR (151 MHz, 299.6 K, DMSO- d_6 capillary): δ = 168.16; 166.66 ppm

UV-VIS 664 nm ($A=0.373$); 417 nm (0.403)

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Patent application

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Method for the production of noble metal oxalate complexes

Patent claims

1. Method for the production of noble metal oxalate complexes, in which a noble metal precursor is reacted with oxalic acid and/or oxalic acid salt, characterised in that noble metal oxalate complexes corresponding to the product are added as an auto-catalyst.
2. Method for the production of noble metal oxalate complexes according to claim 1, characterised in that the reaction is carried out at a temperature below the decomposition temperature of the noble metal oxalate complexes.
3. Method for the production of noble metal oxalate complexes according to claim 2, characterised in that the reaction is carried out at a maximal temperature of 1°C below the decomposition temperature of the noble metal oxalate complexes.
4. Method for the production of noble metal oxalate complexes according to claim 1, characterised in that the reaction is carried out at a temperature between 0 and 56°C.
5. Method according to any one of the preceding claims, characterised in that
in the first step, an aqueous solution or suspension of noble metal precursor and noble metal oxalate complexes is produced,
in the second step, the aqueous solution or suspension from the first step is temperature-equilibrated to reaction temperature,
and,
in the third step, oxalic acid and/or oxalic acid salt is added.

6. Method according to any one of the claims 1 to 5, characterised in that the amount of auto-catalyst to be added is 1×10^{-4} to 5×10^{-2} molar equivalents of noble metal relative to the noble metal in the noble metal precursor solution.
7. Method according to any one of the claims 1 to 6, characterised in that oxalic acid and/or oxalic acid salt are selected from the group consisting of oxalic acid, sodium oxalate, ammonium oxalate, and potassium oxalate, and mixtures thereof.
8. Method according to any one of the preceding claims, characterised in that, the noble metal precursor is selected from the group consisting of noble metal oxide hydrate, noble metal nitrate, and noble metal acetate, and mixtures thereof.
9. Method according to any one of the claims 1 to 8, characterised in that the noble metal is platinum.
10. Method according to claim 9, characterised in that the platinum precursor is platinum oxide hydrate (platinum-(IV) hydroxoacid) or any of the salts thereof.
11. Method according to claim 9 or 10, characterised in that the reaction is carried out at a temperature from 30°C to 45°C.
12. Method according to any one of the claims 9 to 11, characterised in that 1.8 to 2.8 molar equivalents of oxalic acid relative to platinum in the platinum precursor are added.
13. Method according to any one of the claims 9 to 12, characterised in that
 - 1) a suspension of platinum oxide hydrate (platinum-(IV) hydroxoacid) in water is produced;
 - 2) a solution of platinum oxalate complexes in water is produced;
 - 3) the suspension from 1) and the solution from 2) are combined and the resulting mixture is temperature-equilibrated to reaction temperature;
 - 4) a first aliquot of 0.4 to 1.4 molar equivalents of oxalic acid, relative to platinum in platinum oxide hydrate (platinum-(IV) hydroxoacid), is added; and
 - 5) a second aliquot of 0.1 to 1.4 molar equivalents of oxalic acid, relative to platinum in platinum oxide hydrate (platinum-(IV) hydroxoacid), is added, and
 - 6) as an option, step 5) is repeated one or more times until a total amount of 1.8 to 2.8

molar equivalents of oxalic acid, relative to platinum in platinum oxide hydrate (platinum-(IV) hydroxoacid), has been added.