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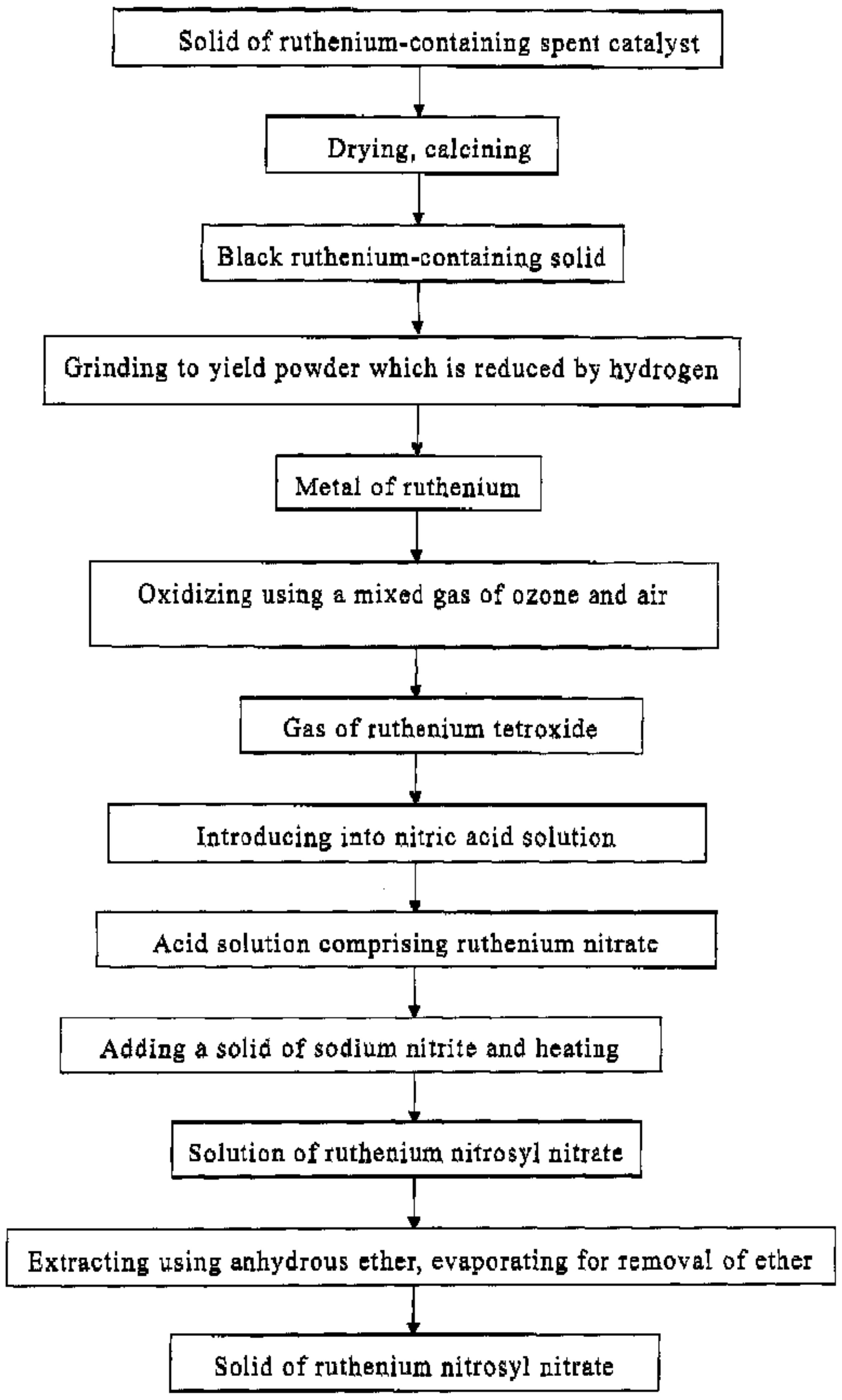
(54) **Titre : PROCEDE DE PREPARATION DE NITRATE DE RUTHENIUM-NITROSYLE SOLIDE AU MOYEN D'UN CATALYSEUR DE DECHETS CONTENANT DU RUTHENIUM**

(54) **Title: METHOD FOR PREPARING SOLID NITROSYL RUTHENIUM NITRATE BY USING WASTE CATALYST CONTAINING RUTHENIUM**



(57) **Abrégé/Abstract:**

Disclosed is a method for preparing solid nitrosyl ruthenium nitrate by using a waste catalyst containing ruthenium. Steps of the method are: drying and calcining a waste catalyst containing ruthenium to acquire a black solid containing ruthenium, grinding the

(57) **Abrégé(suite)/Abstract(continued):**

black solid containing ruthenium into powder, feeding hydrogen for reduction to form metal ruthenium, oxidizing metal ruthenium by using mixed gas of ozone and air to produce a ruthenium tetraoxide gas, collecting the gas, feeding the gas in a nitric acid solution, adding solid sodium nitrite to prepare a solution containing nitrosyl ruthenium nitrate, and finally using diethyl ether for extraction, and evaporating diethyl ether to acquire a nitrosyl ruthenium nitrate solid. The method can effectively reclaim noble metal ruthenium in various load-type waste catalysts containing ruthenium, so as to achieve effective recycling of ruthenium resources, and has simple operation steps and does not involve the introduction of ruthenium intermediates, which ensures a high product yield. The acquired solid nitrosyl ruthenium nitrate is free of halogen, has high purity, and is capable of being directly applied to the preparation of catalysts.

ABSTRACT

Disclosed is a method for preparing solid nitrosyl ruthenium nitrate by using a waste catalyst containing ruthenium. Steps of the method are: drying and calcining a waste catalyst containing ruthenium to acquire a black solid containing ruthenium, grinding the black solid containing ruthenium into powder, feeding hydrogen for reduction to form metal ruthenium, oxidizing metal ruthenium by using mixed gas of ozone and air to produce a ruthenium tetraoxide gas, collecting the gas, feeding the gas in a nitric acid solution, adding solid sodium nitrite to prepare a solution containing nitrosyl ruthenium nitrate, and finally using diethyl ether for extraction, and evaporating diethyl ether to acquire a nitrosyl ruthenium nitrate solid. The method can effectively reclaim noble metal ruthenium in various load-type waste catalysts containing ruthenium, so as to achieve effective recycling of ruthenium resources, and has simple operation steps and does not involve the introduction of ruthenium intermediates, which ensures a high product yield. The acquired solid nitrosyl ruthenium nitrate is free of halogen, has high purity, and is capable of being directly applied to the preparation of catalysts.

METHOD FOR PREPARING SOLID NITROSYL RUTHENIUM NITRATE BY USING WASTE CATALYST CONTAINING RUTHENIUM

FIELD OF THE INVENTION

[0001] The invention relates to the recycling of a platinum group metal, and more particularly to a method for preparing a solid of ruthenium nitrosyl nitrate using a ruthenium-containing spent catalyst.

BACKGROUND OF THE INVENTION

[0002] With excellent catalytic performance, ruthenium is widely used in preparation of ammonia, selective hydrogenation of benzene to yield cyclohexene, hydrogenation of carbon dioxide to yield methanol, and so on. However, ruthenium is expensive and has a limited resource, and the global annual production is only a few dozen tons, thereby greatly limiting the application of ruthenium. Recycling ruthenium from a ruthenium-containing spent catalyst for preparation of ruthenium-based catalysts can significantly reduce the production cost of the catalyst and environmental pollution caused by waste disposal, thereby having a bright prospect.

[0003] Solid ruthenium nitrosyl nitrate ($Ru(NO)(NO_3)_3$) contains no toxic element against catalysts such as halogen, sulfur, phosphorus, and is easily soluble in water, ether, and acetone, so it is an ideal precursor for preparation of a ruthenium-containing catalyst. Thus, preparing high purity of a solid of ruthenium nitrosyl nitrate from a ruthenium-containing spent catalyst has high industrial application value.

[0004] Conventionally, there are two typical methods for preparing ruthenium nitrosyl nitrate. One is to directly dissolve RuO_4 in a cooled nitric acid solution, and the other is to dissolve and reflux nitrosyl ruthenium hydroxide using nitric acid. Chinese Patent Publication No. CN101638727A discloses a method for recycling ruthenium from an activated carbon supported ruthenium catalyst, which involves the preparation of ruthenium nitrosyl nitrate. In the method, ruthenium hydroxide or $RuO_2 \cdot 2H_2O$ is mixed and stirred with micro-boiled nitric acid in a reflux device to yield a nitric acid solution of $Ru(NO)(NO_3)_3$, which has high acidity, and is difficult for storage and transportation.

[0005] Chinese Patent Publication No. CN102167405A discloses a preparation method of ruthenium nitrosyl nitrate. Ruthenium trichloride and sodium nitrite react to yield an intermediate of ruthenium nitrosyl chloride, which is allowed to react with silver nitrate to yield a ruthenium nitrosyl nitrate solution. The solution is extracted with ether and the ether extraction solution is evaporated to yield a solid of ruthenium nitrosyl nitrate. However, the method has the following disadvantages: 1. The chloride is involved, which is toxic to the catalyst; 2. The method involves the intermediate of ruthenium nitrosyl chloride, thereby reducing the product yield; 3. As raw materials, ruthenium trichloride presents in the form of a crystalline hydrate, which is expensive.

SUMMARY OF THE INVENTION

[0006] In view of the above-described problems, it is one objective of the invention to a method for preparing a solid of ruthenium nitrosyl nitrate using a ruthenium-containing spent catalyst. The method is simple and highly efficient, can produce high purity of a solid of ruthenium nitrosyl nitrate from a supported ruthenium-containing spent catalyst. The solid of ruthenium nitrosyl nitrate can be used for preparation of a ruthenium-containing catalyst.

[0007] To achieve the above objective, in accordance with one embodiment of the invention, there is provided a method for preparing a solid of ruthenium nitrosyl nitrate using a ruthenium-containing spent catalyst, the method comprises the following steps:

[0008] 1) drying a ruthenium-containing spent catalyst, and calcining the spent catalyst at a temperature of between 300 and 500°C for between 2 and 4 hours, and cooling to room temperature to yield a black ruthenium-containing solid;

[0009] 2) grinding the black ruthenium-containing solid obtained in step 1) to yield a powder, introducing the powder to a fluidized bed reactor, aerating the fluidized bed reactor with nitrogen or an inert gas for between 0.5 and 2 hours, charging hydrogen, heating the fluidized bed reactor to a temperature of between 100 and 600°C for a reduction reaction, whereby obtaining a metal of ruthenium;

[0010] 3) contacting a mixed gas of ozone and air with the metal of ruthenium obtained in step 2), allowing the mixed gas and the metal of ruthenium to react at a temperature of between 600 and 650°C, whereby obtaining a gas of ruthenium tetroxide;

[0011] 4) introducing the gas of ruthenium tetroxide obtained in step 3) into a three-stage absorption plant comprising a nitrite acid solution, to yield an acid solution comprising ruthenium nitrate;

[0012] 5) adding a solid of sodium nitrite to the acid solution comprising ruthenium nitrate obtained in step 4), stirring, and heating a resulting solution in the state of micro-boiling reflux, to yield a solution of ruthenium nitrosyl nitrate; and

[0013] 6) extracting the solution of ruthenium nitrosyl nitrate obtained in step 5) with anhydrous ether, collecting and evaporating an extraction solution for removal of ether, to yield a solid of ruthenium nitrosyl nitrate.

[0014] In step 1), the ruthenium-containing spent catalyst is dried in the presence of nitrogen or an inert gas at a temperature of 100 and 150°C for between 1 and 2 hours. The ruthenium-containing spent catalyst is calcined in a muffle furnace.

[0015] In step 2), a flow rate of the hydrogen is preferably between 1200 and 4000 h^{-1}, and a reduction time is between 1 and 12 hours, preferably, between 6 and 12 hours. The redox chemical equation is: $RuO_2 + 2H_2 = Ru + 2H_2O$.

[0016] In step 3), a flow rate of the mixed gas of ozone and air is between 1200 and 4000 h^{-1}, a volume percent of the ozone in the mixed gas is between 1 and 20%, preferably, 15%; and an oxidation time is between 1 and 12 hours, preferably, between 8 and 12 hours. The chemical equation is: $Ru + 2O_2 = RuO_4\uparrow$, $3Ru + 4O_3 = 3RuO_4\uparrow$.

[0017] In step 4), the nitrite acid solution has a temperature of between 50 and 95°C, a mass concentration of between 45 and 68%, an actual addition thereof is between 1.2 and 2.0 times a theoretical consumption amount calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst, and the three-stage absorption plant is three brown containers connected in series. The chemical equation is: $2RuO_4 + 16HNO_3 = 2Ru(NO_3)_3 + 8H_2O + 5O_2\uparrow + 10NO_2\uparrow$.

[0018] In step 5), an actual addition of the solid of sodium nitrite is between 1.5 and 2.0 times a theoretical consumption amount thereof calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst. The solid of sodium nitrite is slowly added to the acid solution comprising ruthenium nitrate with stirring. A heating time is between 1 and 8 hours, preferably, between 4 and 8 hours. The reaction vessel is a three-necked round bottom flask. The chemical equation is: $Ru(NO_3)_3+2NaNO_2 + 2HNO_3 = Ru(NO)(NO_3)_3 + 2NaNO_3+ NO_2\uparrow + H_2O$.

[0019] In step 6), the extraction with anhydrous ether is carried out for several times for improving the yield of the solid of ruthenium nitrosyl nitrate.

[0020] In a class of this embodiment, the ruthenium-containing spent catalyst is a supported catalyst, and a supporter thereof is alumina, silica, zirconia, titania, zeolite, or a combination thereof. The shape of the supporter is spherical, cylindrical, clover-type, four-leaf, ring type, or honeycomb type.

[0021] Advantages of the present disclosure are summarized as follows. 1. The method has low recycling costs, and the resulting solid product is convenient for storage and transportation. 2. The solid of ruthenium nitrosyl nitrate contains no halogen, and thus the toxicity is prevented. 3. The method has a simple process and involves no intermediate of ruthenium, which is conducive to improving the product yield. In short, the method has low costs, simple process, high product yield, and the resulting product has high purity, and is suitable for large-scale production.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] FIG. 1 is a flow chart of a method for preparing a solid of ruthenium nitrosyl nitrate using a ruthenium-containing spent catalyst according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0023] For further illustrating the invention, experiments detailing a method for preparing a solid of ruthenium nitrosyl nitrate using a ruthenium-containing spent catalyst are described below. It should be noted that the following examples are intended to describe and not to limit the invention.

Example 1

[0024] 60 g of a ruthenium-containing spent catalyst (Ru/Al_2O_3, spherical, comprising 5 wt. % of Ru) was put into a crucible, and transported to a muffle furnace. The furnace was aerated with nitrogen. The catalyst was dried at 120°C for 2 hours, calcined at 450°C for 3 hours for removal of organic residues in the spent catalyst, and cooled to room temperature. 58.6 g of a black solid was obtained. The black solid was ground into powders and transported to a fluidized bed reactor. The fluidized bed reactor was aerated first with nitrogen for 30 min, and then with hydrogen having a flow rate of 1200 h^{-1}, heated to 300°C for reduction for 12 hours. The temperature was further increased to 600°C. A mixed gas of ozone and air comprising 15 vol. % of ozone was charged into the reactor, with a flow rate of 1200 h^{-1} for 12 hours, to yield a gas of RuO_4. The gas of RuO_4 was successively introduced to three absorption bottles each comprising 40 g of 68 wt. % a nitrite acid solution having a temperature of about 75°C, to yield an acid solution comprising ruthenium nitrate ($Ru(NO_3)_3$).

[0025] The acid solution comprising ruthenium nitrate was added to a three-necked round bottom flask, followed by 6 g (which is 1.5 times a theoretical consumption amount calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst) of $NaNO_2$ powder, stirred, and heated for reflux for 8 hours to yield a dark red black solution. The dark red black solution was extracted thrice using 130 mL of anhydrous ether, and an extraction solution was collected and evaporated for removal of ether, to yield 8.84 g of a brown yellow solid, which, based on KBr Pellets-infrared analysis, had a characteristic peak at 1924 cm^{-1}, identical to the characteristic structural parameters of $Ru(NO)(NO_3)_3$. The yield of $Ru(NO)(NO_3)_3$ was 96.2%, and metallic impurities were less than 30 ppm.

Example 2

[0026] 50 g of a ruthenium-containing spent catalyst (Ru/SiO_2, cylindrical, comprising 3 wt. % of Ru) was put into a crucible, and transported to a muffle furnace. The furnace was aerated with nitrogen. The catalyst was dried at 120°C for 2 hours, calcined at 450°C for 3 hours, and cooled to room temperature. 48.9 g of a black solid was obtained. The black solid was ground into powders and transported to a fluidized bed reactor. The fluidized bed reactor was aerated first with nitrogen for 30 min, and then with hydrogen having a flow rate of 2500 h^{-1}, heated to 350°C for reduction for 10 hours. The temperature was further increased to 620°C. A mixed gas of ozone and air comprising 15 vol. % of ozone was charged into the reactor, with a flow rate of 2500 h^{-1} for 10 hours, to yield a gas of RuO_4. The gas of RuO_4 was successively introduced to three absorption bottles each comprising 24 g of 60 wt. % a nitrite acid solution having a temperature of about 75°C, to yield an acid solution comprising ruthenium nitrate ($Ru(NO_3)_3$).

[0027] The acid solution comprising ruthenium nitrate was added to a three-necked round bottom flask, followed by 3.6 g (which is 1.8 times a theoretical consumption amount calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst) of $NaNO_2$ powder, stirred, and heated for reflux for 4 hours to yield a dark red black solution. The dark red black solution was extracted thrice using 80 mL of anhydrous ether, and an extraction solution was collected and evaporated for removal of ether, to yield 4.41 g of a brown yellow solid, which, based on KBr Pellets-infrared analysis, had a characteristic peak at 1924 cm^{-1}, identical to the characteristic structural parameters of $Ru(NO)(NO_3)_3$. The yield of $Ru(NO)(NO_3)_3$ was 95.8%, and metallic impurities were less than 30 ppm.

Example 3

[0028] 120 g of a ruthenium-containing spent catalyst (Ru/ZrO_2, clover-type, comprising 4 wt. ‰ of Ru) was put into a crucible, and transported to a muffle furnace. The furnace was aerated with nitrogen. The catalyst was dried at 120°C for 2 hours, calcined at 450°C for 3 hours, and cooled to room temperature. 118.2 g of a black solid was obtained. The black solid was ground into powders and transported to a fluidized bed reactor. The fluidized bed reactor was aerated first with nitrogen for 30 min, and then with hydrogen having a flow rate of 4000 h^{-1}, heated to 350°C for reduction for 6 hours. The temperature was further increased to 650°C. A mixed gas of ozone and air comprising 15 vol. % of ozone was charged into the reactor, with a flow rate of 4000 h^{-1} for 8 hours, to yield a gas of RuO_4. The gas of RuO_4 was successively introduced to three absorption bottles each comprising 13 g of 45 wt. % a nitrite acid solution having a temperature of about 75°C, to yield an acid solution comprising ruthenium nitrate ($Ru(NO_3)_3$).

[0029] The acid solution comprising ruthenium nitrate was added to a three-necked round bottom flask, followed by 1.29 g (which is 2.0 times a theoretical consumption amount calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst) of $NaNO_2$ powder, stirred, and heated for reflux for 6 hours to yield a dark red black solution. The dark red black solution was extracted thrice using 60 mL of anhydrous ether, and an extraction solution was collected and evaporated for removal of ether, to yield 1.44 g of a brown yellow solid, which, based on KBr Pellets-infrared analysis, had a characteristic peak at 1924 cm^{-1}, identical to the characteristic structural parameters of $Ru(NO)(NO_3)_3$. The yield of $Ru(NO)(NO_3)_3$ was 97.3%, and metallic impurities were less than 30 ppm.

Example 4

[0030] 60 g of a ruthenium-containing spent catalyst (Ru/TiO_2, four-leaf type, comprising 5 wt. % of Ru) was put into a crucible, and transported to a muffle furnace. The furnace was aerated with nitrogen. The catalyst was dried at 120°C for 2 hours, calcined at 450°C for 3 hours for removal of organic residues in the spent catalyst, and cooled to room temperature. 58.1 g of a black solid was obtained. The black solid was ground into powders and transported to a fluidized bed reactor. The fluidized bed reactor was aerated first with nitrogen for 30 min, and then with hydrogen having a flow rate of 2000 h^{-1}, heated to 350°C for reduction for 8 hours. The temperature was further increased to 620°C. A mixed gas of ozone and air comprising 10 vol. % of ozone was charged into the reactor, with a flow rate of 1500 h^{-1} for 5 hours, to yield a gas of RuO_4. The gas of RuO_4 was successively introduced to three absorption bottles each comprising 27 g of 68 wt. % a nitrite acid solution having a temperature of about 75°C, to yield an acid solution comprising ruthenium nitrate ($Ru(NO_3)_3$).

[0031] The acid solution comprising ruthenium nitrate was added to a three-necked round bottom flask, followed by 3.56 g (which is 0.9 times a theoretical consumption amount calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst) of $NaNO_2$ powder, stirred, and heated for reflux for 6 hours to yield a dark red black solution. The dark red black solution was extracted thrice using 100 mL of anhydrous ether, and an extraction solution was collected and evaporated for removal of ether, to yield 8.21 g of a brown yellow solid, which, based on KBr Pellets-infrared analysis, had a characteristic peak at 1924 cm^{-1}, identical to the characteristic structural parameters of $Ru(NO)(NO_3)_3$. The yield of $Ru(NO)(NO_3)_3$ was 90.3%, and metallic impurities were less than 30 ppm.

Example 5

[0032] 60 g of a ruthenium-containing spent catalyst (Ru/Al_2O_3-ZSM-5, ring type, comprising 1 wt. % of Ru) was put into a crucible, and transported to a muffle furnace. The furnace was aerated with nitrogen. The catalyst was dried at 120°C for 2 hours, calcined at 450°C for 3 hours for removal of organic residues in the spent catalyst, and cooled to room temperature. 59.0 g of a black solid was obtained. The black solid was ground into powders and transported to a fluidized bed reactor. The fluidized bed reactor was aerated first with nitrogen for 30 min, and then with hydrogen having a flow rate of 2000 h^{-1}, heated to 350°C for reduction for 8 hours. The temperature was further increased to 620°C. A mixed gas of ozone and air comprising 15 vol. % of ozone was charged into the reactor, with a flow rate of 3000 h^{-1} for 8 hours, to yield a gas of RuO_4. The gas of RuO_4 was successively introduced to three absorption bottles each comprising 16 g of 45 wt. % a nitrite acid solution having a temperature of about 75°C, to yield an acid solution comprising ruthenium nitrate ($Ru(NO_3)_3$).

[0033] The acid solution comprising ruthenium nitrate was added to a three-necked round bottom flask, followed by 1.2 g (which is 1.5 times a theoretical consumption amount calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst) of $NaNO_2$ powder, stirred, and heated for reflux for 6 hours to yield a dark red black solution. The dark red black solution was extracted thrice using 50 mL of anhydrous ether, and an extraction solution was collected and evaporated for removal of ether, to yield 1.78 g of a brown yellow solid, which, based on KBr Pellets-infrared analysis, had a characteristic peak at 1924 cm^{-1}, identical to the characteristic structural parameters of $Ru(NO)(NO_3)_3$. The yield of $Ru(NO)(NO_3)_3$ was 96.6%, and metallic impurities were less than 30 ppm.

Example 6

[0034] 160 g of a ruthenium-containing spent catalyst (Ru/Al_2O_3-SiO_2, honeycomb type, comprising 2 wt. ‰ of Ru) was put into a crucible, and transported to a muffle furnace. The furnace was aerated with nitrogen. The catalyst was dried at 120°C for 2 hours, calcined at 450°C for 3 hours for removal of organic residues in the spent catalyst, and cooled to room temperature. 156.4 g of a black solid was obtained. The black solid was ground into powders and transported to a fluidized bed reactor. The fluidized bed reactor was aerated first with nitrogen for 30 min, and then with hydrogen having a flow rate of 2000 h^{-1}, heated to 350°C for reduction for 8 hours. The temperature was further increased to 620°C. A mixed gas of ozone and air comprising 15 vol. % of ozone was charged into the reactor, with a flow rate of 2500 h^{-1} for 8 hours, to yield a gas of RuO_4. The gas of RuO_4 was successively introduced to three absorption bottles each comprising 8.6 g of 45 wt. % a nitrite acid solution having a temperature of about 75°C, to yield an acid solution comprising ruthenium nitrate ($Ru(NO_3)_3$).

[0035] The acid solution comprising ruthenium nitrate was added to a three-necked round bottom flask, followed by 0.64 g (which is 1.5 times a theoretical consumption amount calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst) of $NaNO_2$ powder, stirred, and heated for reflux for 8 hours to yield a dark red black solution. The dark red black solution was extracted thrice using 30 mL of anhydrous ether, and an extraction solution was collected and evaporated for removal of ether, to yield 0.95 g of a brown yellow solid, which, based on KBr Pellets-infrared analysis, had a characteristic peak at 1924 cm^{-1}, identical to the characteristic structural parameters of $Ru(NO)(NO_3)_3$. The yield of $Ru(NO)(NO_3)_3$ was 97.2%, and metallic impurities were less than 30 ppm.

[0036] Result analysis:

[0037] As shown in the measurement results in Examples 1-6, the product yields of the method for preparing the solid of ruthenium nitrosyl nitrate using a ruthenium-containing spent catalyst all exceed 90%, and under preferable reaction conditions, the product yield reaches 95% and more. The method effectively utilizes waste resources of ruthenium, and has low costs, simple process, and high product yield. The resulting product has high purity, and is suitable for large-scale production.

CLAIMS

1. A method for preparing a solid of ruthenium nitrosyl nitrate using a ruthenium-containing spent catalyst, the method comprising the following steps:

    1) drying a ruthenium-containing spent catalyst, and calcining the spent catalyst at a temperature of between 300 and 500°C for between 2 and 4 hours, and cooling to room temperature, whereby yielding a black ruthenium-containing solid;

    2) grinding the black ruthenium-containing solid obtained in step 1) to yield a powder, introducing the powder to a fluidized bed reactor, aerating the fluidized bed reactor with nitrogen or an inert gas for between 0.5 and 2 hours, charging hydrogen, heating the fluidized bed reactor to a temperature of between 100 and 600°C for a reduction reaction, whereby yielding a metal of ruthenium;

    3) contacting a mixed gas of ozone and air with the metal of ruthenium obtained in step 2), allowing the mixed gas and the metal of ruthenium to react at a temperature of between 600 and 650°C, whereby yielding a gas of ruthenium tetroxide;

    4) introducing the gas of ruthenium tetroxide obtained in step 3) into a three-stage absorption plant comprising a nitric acid solution having a temperature of between 50 and 95°C and a mass concentration of between 45 and 68%, whereby yielding an acid solution comprising ruthenium nitrate;

    5) adding a solid of sodium nitrite to the acid solution comprising ruthenium nitrate obtained in step 4), stirring, and heating a resulting solution in the state of micro-boiling reflux, whereby yielding a solution of ruthenium nitrosyl nitrate; and

    6) extracting the solution of ruthenium nitrosyl nitrate obtained in step 5)

with anhydrous ether, collecting and evaporating an extraction solution for removal of ether, whereby yielding a solid of ruthenium nitrosyl nitrate.

2. The method of claim 1, **characterized in that** in step 1), the ruthenium-containing spent catalyst is dried in the presence of nitrogen or an inert gas at a temperature of 100 and 150°C for between 1 and 2 hours.

3. The method of claim 1, **characterized in that** in step 2), a flow rate of the hydrogen is between 1200 and 4000 h^{-1}, and a reduction time is between 1 and 12 hours.

4. The method of claim 3, **characterized in that** in step 2), the reduction time is between 6 and 12 hours.

5. The method of claim 1, **characterized in that** in step 3), a flow rate of the mixed gas of ozone and air is between 1200 and 4000 h^{-1}, a volume percent of the ozone in the mixed gas is between 1 and 20%, and an oxidation time is between 1 and 12 hours.

6. The method of claim 5, **characterized in that** in step 3), the volume percent of the ozone in the mixed gas is 15%, and the oxidation time is between 8 and 12 hours.

7. The method of claim 1, **characterized in that** in step 4), an actual addition of the nitric acid is between 1.2 and 2.0 times a theoretical consumption amount calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst, and the nitric acid solution is loaded in three brown containers connected in series.

8. The method of claim 1, **characterized in that** in step 5), an actual addition of the solid of sodium nitrite is between 1.2 and 2.0 times a theoretical

consumption amount thereof calculated on the basis of a ruthenium content in the ruthenium-containing spent catalyst, and a heating time is between 1 and 8 hours.

9. The method of claim 8, **characterized in that** in step 5), the heating time is between 4 and 8 hours.

10. The method of any one of claims 1-9, **characterized in that** the ruthenium-containing spent catalyst is a supported catalyst, and a supporter thereof is alumina, silica, zirconia, titania, zeolite, or a combination thereof.

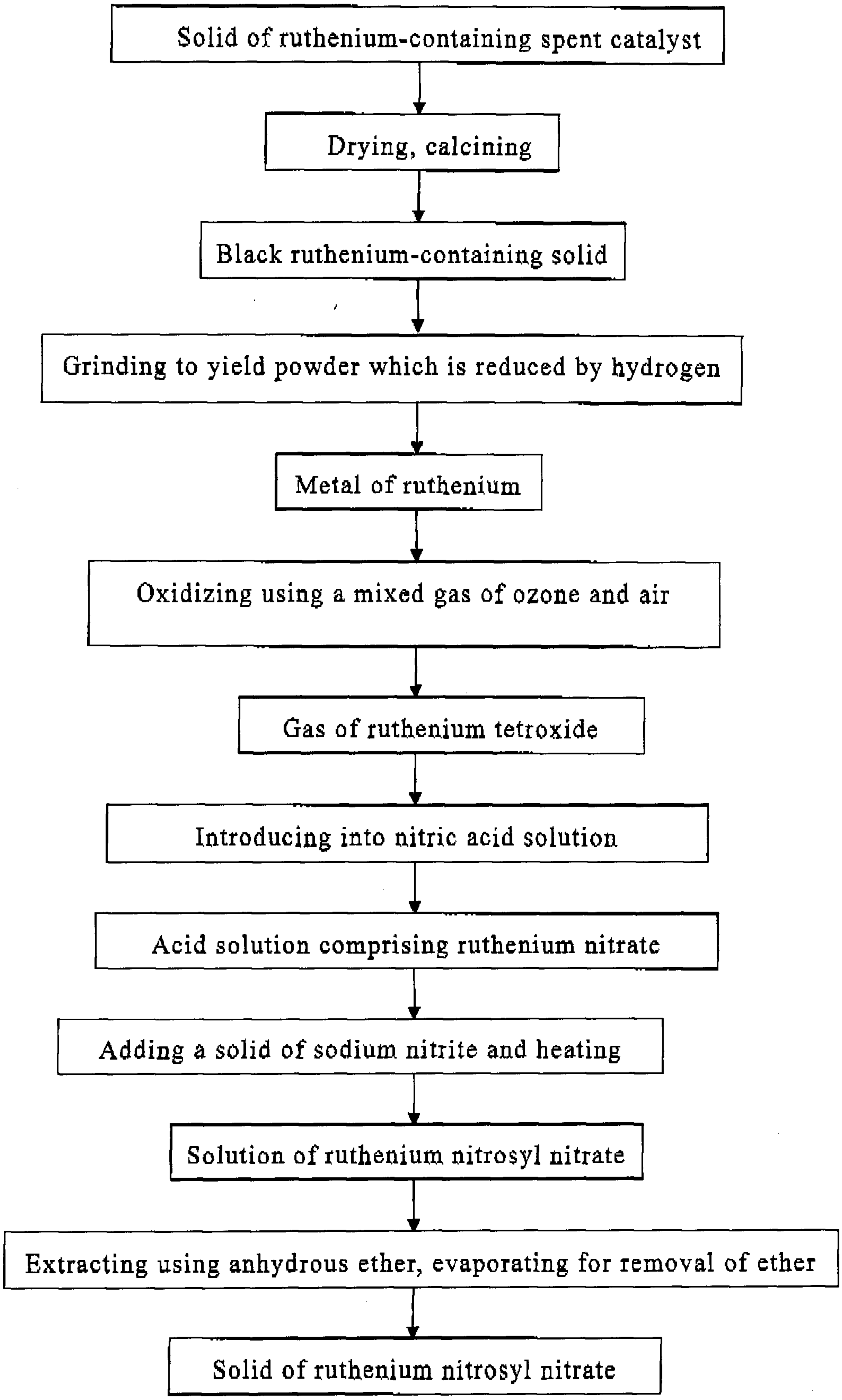

Solid of ruthenium-containing spent catalyst
Drying, calcining
Black ruthenium-containing solid
Grinding to yield powder which is reduced by hydrogen
Metal of ruthenium
Oxidizing using a mixed gas of ozone and air
Gas of ruthenium tetroxide
Introducing into nitric acid solution
Acid solution comprising ruthenium nitrate
Adding a solid of sodium nitrite and heating
Solution of ruthenium nitrosyl nitrate
Extracting using anhydrous ether, evaporating for removal of ether
Solid of ruthenium nitrosyl nitrate

FIG. 1

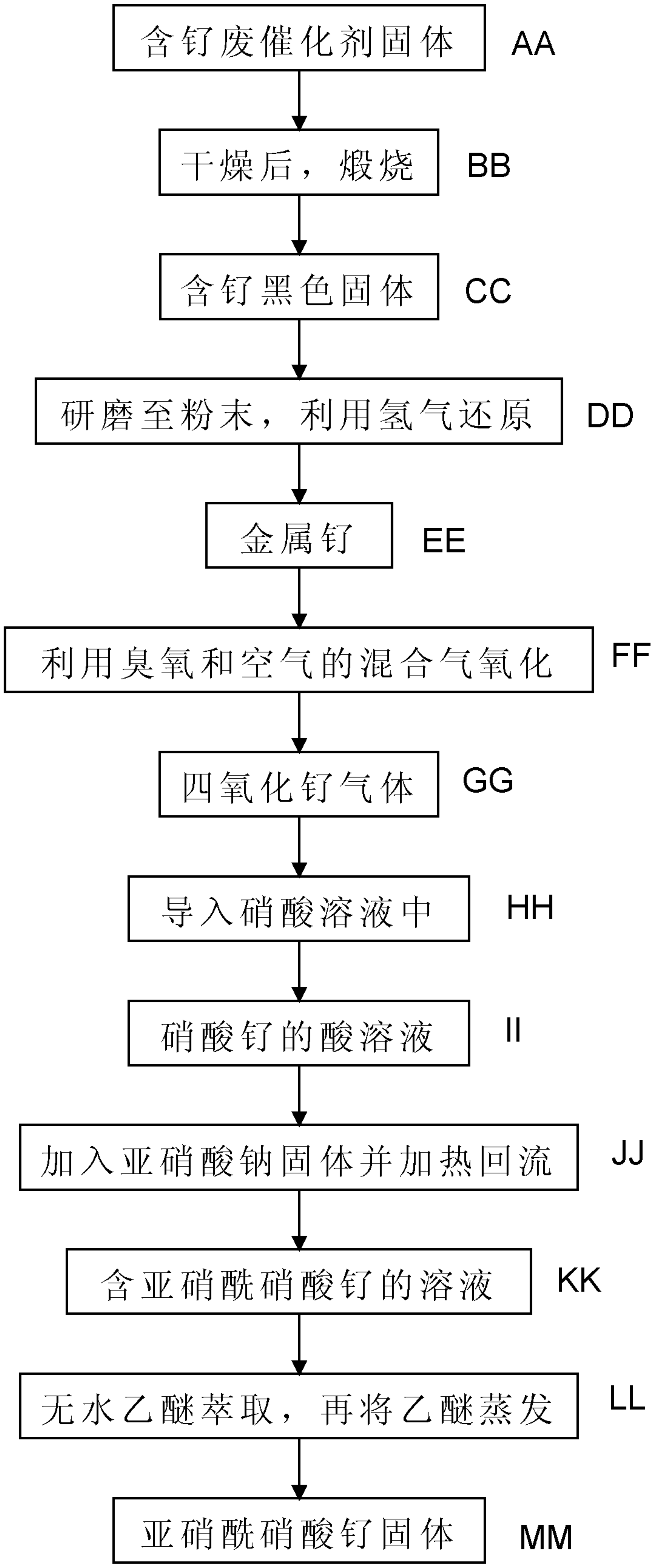


图 1 / Fig.1

AA Waste catalyst solid containing ruthenium
BB Drying and calcination
CC Black solid containing ruthenium
DD Grind to powder, and use hydrogen for reduction
EE Metal ruthenium
FF Oxidition using mixed gas of ozone and air
GG Ruthenium tetraoxide gas
HH Introduction into a nitric acid solution
II Acid solution of ruthenium nitrate
JJ Add a sodium nitrite solid, perform heating and backflow
KK Solution containing nitrosyl ruthenium nitrate
LL Use anhydrous diethyl ether for extraction, and evaporate diethyl ether
MM Nitrosyl ruthenium nitrate solid