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(54) Benævnelse: **Fremgangsmåde til fremstilling af fast nitrosylrutheniumnitrat ved anvendelse af en affaldskatalysator, der indeholder ruthenium**

(56) Fremdragne publikationer:
CN-A- 101 331 240
CN-A- 101 663 242
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CN-A- 102 167 405
US-A1- 2001 024 700

DESCRIPTION

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 Ru04 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. CN 102 108 444 A discloses a method for recovering ruthenium from a ruthenium metal catalyst by a method comprising process steps of heating, roasting, grinding and reducing to obtain a tri ruthenium chloride aqueous solution. CN 101 331 240 A discloses a process for recovering ruthenium from a used ruthenium-comprising catalyst by a process comprising the steps of reducing ruthenium oxide to metallic ruthenium, treating with hydrochloric acid to dissolve the metallic ruthenium as ruthenium(III) chloride in solution, and optionally working further up the ruthenium(III) chloride solution.

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:

1. 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;
2. 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;
3. 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;
4. 4) introducing the gas of ruthenium tetroxide obtained in step 3) into a three-stage absorption plant comprising a nitric acid solution, to yield an acid solution comprising ruthenium nitrate;
5. 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
6. 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.

[0008] 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.

[0009] 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: $RuO_2 + 2H_2 = Ru + 2H_2O$.

[0010] 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: $Ru + 2O_2 = RuO_4\uparrow$, $3Ru + 4O_3 = 3RuO_4\uparrow$.

[0011] In step 4), the nitric 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: $2RuO_4 + 16HNO_3 = 2Ru(NO_3)_3 + 8H_2O + 5O_2\uparrow + 10NO_2\uparrow$.

[0012] 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. 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: $Ru(NO_3)_3+2NaNO_2 + 2HNO_3 = Ru(NO)(NO_3)_3 + 2NaNO_3+ NO_2\uparrow + H_2O$.

[0013] 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.

[0014] 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.

[0015] 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

[0016] 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

[0017] 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

[0018] 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 nitric acid solution having a temperature of about 75°C, to yield an acid solution comprising ruthenium nitrate ($Ru(NO_3)_3$).

[0019] 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

[0020] 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 nitric acid solution having a temperature of about 75°C, to yield an acid solution comprising ruthenium nitrate ($Ru(NO_3)_3$).

[0021] 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

[0022] 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 nitric acid solution having a temperature of about 75°C, to yield an acid solution comprising ruthenium nitrate ($Ru(NO_3)_3$).

[0023] 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

[0024] 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 nitric 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 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

[0026] 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 nitric 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 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

[0028] 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 nitric 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 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 130 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.

Result analysis:

[0030] 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.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- CN101638727A [0004]
- CN102167405A [0005]
- CN102108444A [0005]
- CN101331240A [0005]

PATENTKRAV

1. Fremgangsmåde til fremstilling af et faststof af rutheniumnitrosylnitrat under anvendelse af en rutheniumindeholdende udtjent katalysator, hvor fremgangsmåden omfatter følgende trin:

1) at tørre en rutheniumindeholdende udtjent katalysator, og at calcinere den udtjente katalysator ved en temperatur på mellem 300 og 500°C mellem 2 og 4 timer, og at afkøle til omgivelsestemperatur, hvorved der udvindes et sort rutheniumindeholdende faststof;
2) at formale det sorte rutheniumindeholdende faststof opnået i trin 1) for at udvinde et pulver, at indføre pulveret i en fluid-bed-reaktor, at lufte fluid-bed-reaktoren med nitrogen eller en inertgas mellem 0,5 og 2 timer, at påfylde hydrogen, at opvarme fluid-bed-reaktoren til en temperatur på mellem 100 og 600°C til en reduktionsreaktion, hvorved der udvindes et metal af ruthenium;
3) at bringe en blandet gas af ozon og luft i kontakt med metallet af ruthenium opnået i trin 2), at lade den blandede gas og metallet af ruthenium reagere ved en temperatur på mellem 600 og 650°C, hvorved der udvindes en gas af rutheniumtetroxid;
4) at indføre gassen af rutheniumtetroxid opnået i trin 3) i et tretrinsabsorptionsanlæg, der omfatter en salpetersyreopløsning, hvorved der udvindes en syreopløsning indeholdende rutheniumnitrat;
5) at tilsætte et faststof af natriumnitrat til syreopløsningen, omfattende rutheniumnitrat og opnået i trin 4), at omrøre og opvarme en resulterende opløsning i tilstanden af mikrokogende tilbagestrømning, hvorved der udvindes en opløsning af rutheniumnitrosylnitrat; og
6) at ekstrahere opløsningen af rutheniumnitrosylnitrat opnået i trin 5) med vandfri æter, at opsamle og fordampe en ekstraktionsopløsning til fjernelse af æter, hvorved der udvindes et faststof af rutheniumnitrosylnitrat.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** i trin 1) tørres den rutheniumindeholdende udtjente katalysator i nærvær af nitrogen eller en inertgas ved en temperatur på 100 og 150°C mellem 1 og 2 timer.

3. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** i trin 2) er en gennemstrømningsrate af hydrogen mellem 1200 og 4000 h^{-1}, og en reduktionstid er mellem 1 og 12 timer.

4. Fremgangsmåde ifølge krav 3, **kendetegnet ved, at** i trin 2) er reduktionstiden mellem 6 og 12 timer.

5. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** i trin 3) er en gennemstrømningsrate af den blandede gas af ozon og luft mellem 1200 og 4000 h^{-1}, en volumenprocent af ozonen i den blandede gas er mellem 1 og 20%, og en oxidationsperiode er mellem 1 og 12 timer.

6. Fremgangsmåde ifølge krav 5, **kendetegnet ved, at** i trin 3) er volumenprocenten af ozonen i den blandede gas 15%, og oxidationsperioden er mellem 8 og 12 timer.

7. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** i trin 4) har salpetersyreopløsningen en temperatur på mellem 50 og 95°C, en massekoncentration på mellem 45 og 68%, en faktisk tilsætning deraf er mellem 1,2 og 2,0 gange en teoretisk forbrugsmængde beregnet på basis af et rutheniumindhold i den rutheniumindeholdende udtjente katalysator, og salpetersyreopløsningen fyldes i tre brune serieforbundne beholdere.

8. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** i trin 5) er en faktisk tilsætning af faststoffet af natriumnitrit mellem 1,2 og 2,0 gange en teoretisk forbrugsmængde deraf beregnet på basis af et rutheniumindhold i den

rutheniumindeholdende udtjente katalysator, og en opvarmningsperiode er mellem 1 og 8 timer.

9. Fremgangsmåde ifølge krav 8, **kendetegnet ved, at** i trin 5) er opvarmningsperioden mellem 4 og 8 timer.

10. Fremgangsmåde ifølge et hvilket som helst af kravene 1-9, **kendetegnet ved, at** den rutheniumindholdende udtjente katalysator er en støttet katalysator, og en støtte deraf er aluminiumoxid, siliciumdioxid, zirkoniumoxid, titaniumdioxid, zeolit eller en kombination deraf.

DRAWINGS

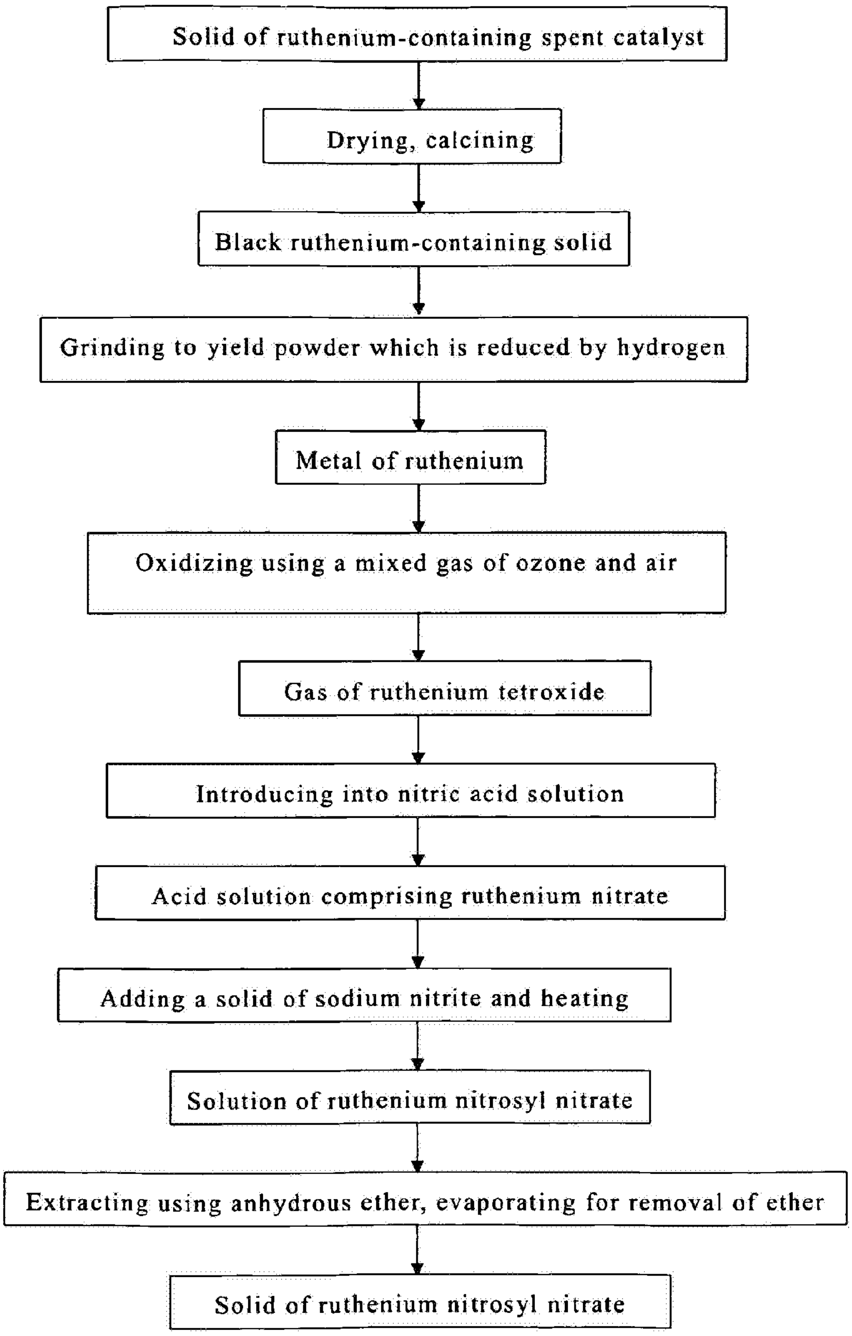

FIG. 1