

METHOD FOR RECOVERING RUTHENIUM FROM WASTE CATALYST OF ALUMINUM OXIDE LOADED WITH RUTHENIUM

FIELD OF THE INVENTION

[0001] The invention relates to the technical field of recovering noble metal from waste catalyst, in particular to a method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium.

BACKGROUND OF THE INVENTION

[0002] Ruthenium is a very expensive rare metal, has excellent catalytic performance, has widespread application in the catalyst industry, and is mostly used in synthesizing ammonia, preparing cyclohexene through selective hydrogenation of benzene, and manufacturing fuel cells. The annual output of ruthenium in the world is only dozens of tons; while the annual output of ruthenium in China is only several kilograms, which is less than 1% of the total demand. Therefore, most of the ruthenium used for manufacturing catalyst in China depends on importation, resulting in a very high cost of the ruthenium catalyst. In addition, the purity of the ruthenium in the natural minerals in China is only 0.028 g/t; while the purity of the ruthenium in the catalyst is generally not less than 500 g/t, which is much higher than the purity of the ruthenium in the natural minerals. Also, the composition in the waste catalyst is much simpler than those in the natural minerals. As such, recovering ruthenium from waste catalyst is capable of implementing the cyclic utilization of the ruthenium resources, is of great importance to

resources saving and environment protection, and is of great economic value.

[0003] One known method of recovering ruthenium from supported catalyst is to utilize the method of “alkali fusion - oxidizing distillation” to obtain β - $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ crystals. The Chinese Patent Application No. 200610052073.0 discloses a recovering method from ruthenium catalyst carried on activated carbon, including the steps of: calcining a ruthenium catalyst carried on activated carbon without alkali metal or alkaline-earth metallic promoter at 600-1000°C for 2-20 hours to obtain a grey black compound; mixing the grey black compound with KOH and KNO_3 , heating them at 300-950°C for 1-5 hours, and cooling them to obtain an alkali fusion product; dissolving the alkali fusion product in water of 50-90°C to obtain a K_2RuO_4 solution; introducing NaClO and concentrated H_2SO_4 into the K_2RuO_4 solution and distilling the K_2RuO_4 solution at 50-90°C for 2-4 hours to obtain RuO_4 gas; and using strong acid to absorb the RuO_4 gas and normal pressure distilling or reduced pressure distilling the concentrated acid to obtain ruthenium salt. The method is complicated to operate, has high energy consumption and low product recovery rate, and has long recycle period.

[0004] In addition, the Chinese Patent Application No. 200610106338.0 discloses a method of preparing ruthenium powder of high quality from solutions containing ruthenium. The method discloses a step of calcining $(\text{NH}_4)_3\text{RuCl}_6$ to prepare ruthenium powder, the step including first calcining $(\text{NH}_4)_3\text{RuCl}_6$ at 500-800°C to obtain rough ruthenium powder, then smashing the rough ruthenium powder, and finally calcining the rough ruthenium powder again at 800-1000°C to obtain ruthenium powder having chlorine in 100 PPM or less. This method uses ammonium chloride to directly precipitate Ru(III) in hydrochloric acid containing ruthenium and to produce $(\text{NH}_4)_3\text{RuCl}_6$, calcinates the $(\text{NH}_4)_3\text{RuCl}_6$, and uses hydrogen to reduce the $(\text{NH}_4)_3\text{RuCl}_6$ for obtaining

ruthenium. This method is capable of producing high quality ruthenium powder. However, because the $(\text{NH}_4)_3\text{RuCl}_6$ produced by precipitating Ru(III) has high water solubility, the precipitation of the ruthenium in the solution is not complete, and the recovery rate is very low.

SUMMARY OF THE INVENTION

[0005] In view of the above-described problems, it is one objective of the invention to provide a method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium, which is simple to operate, has a low cost, has a short recovery period, and has a high recovery rate.

[0006] To achieve the above objective, in accordance with one embodiment of the invention, there is provided a method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium, the method comprising:

[0007] 1) drying waste catalyst of aluminum oxide loaded with ruthenium at 100-150°C in a nitrogen atmosphere for 1-2 hours, calcining the waste catalyst of aluminum oxide loaded with ruthenium at 300-500°C for 2-4 hours, cooling the waste catalyst of aluminum oxide loaded with ruthenium to room temperature, and grinding the waste catalyst of aluminum oxide loaded with ruthenium into black powder comprising ruthenium oxide;

[0008] 2) placing the black powder inside a fluidized bed reactor, purging the fluidized bed reactor with nitrogen for 20-40 minutes and then purging the fluidized bed reactor with hydrogen, and reducing the black powder to obtain a powder comprising ruthenium at a temperature of 200-400°C at a pressure of 1-2 MPa for 2-3 hours;

[0009] 3) purging the fluidized bed reactor with nitrogen for 20-40 minutes, and then introducing a mixed gas of oxygen and ozone to oxidize the powder comprising ruthenium for obtaining RuO_4 gas at a temperature of 500-750°C at a pressure of 1-2 MPa for 1-8 hours;

[0010] 4) introducing the RuO_4 gas into a 3-8 mol/L hydrochloric solution, and completely dissolving the RuO_4 gas to obtain an H_3RuCl_6 solution;

[0011] 5) introducing excess oxidant into the H_3RuCl_6 solution, stirring the H_3RuCl_6 solution for 0.5-1.5 hours to completely oxidize the H_3RuCl_6 solution to generate H_2RuCl_6 , introducing excess NH_4Cl into the H_2RuCl_6 solution, heating the H_2RuCl_6 solution to 60-90°C, stirring the H_2RuCl_6 solution for 1-3 hours, filtering the H_2RuCl_6 solution to obtain a filter cake, and washing the filter cake to obtain an $(\text{NH}_4)_2\text{RuCl}_6$ solid, in which the oxidant is soluble chlorate; and

[0012] 6) reducing the $(\text{NH}_4)_2\text{RuCl}_6$ solid at a temperature of 450-800°C using a mixed gas of hydrogen and nitrogen to obtain ruthenium, in which a volume fraction of the hydrogen in the mixed gas is 1-15%.

[0013] In a class of this embodiment, in step 3) the space rate of the mixed gas of oxygen and ozone is 1000-4000 h^{-1} .

[0014] In a class of this embodiment, in step 3), the volume fraction of the ozone in the mixed gas of oxygen and ozone is 1-20%.

[0015] In a class of this embodiment, in step 4) the concentration of the hydrochloric solution is 6 mol/L.

[0016] In a class of this embodiment, in step 5) the weight of the NH_4Cl is 1.2-2.5 times of the theoretical weight of the NH_4Cl that is required to completely react with the

H₂RuCl₆ solution.

[0017] In a class of this embodiment, in step 5) the oxidant is one or more of the following: ammonium chlorate, potassium chlorate, sodium chlorate, and magnesium chlorate.

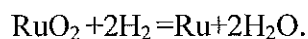
[0018] In a class of this embodiment, in step 5) the filter cake is washed by an ethanol solution.

[0019] In a class of this embodiment, in step 5) the H₂RuCl₆ solution is stirred at 100-400 r/min for 1-3 hours. Furthermore, it is preferred that the H₂RuCl₆ solution is stirred at 200 r/min for 1.5-2.5 hours.

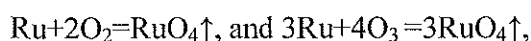
[0020] The function and principle of the technological parameters in each step of the method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium are as follows:

[0021] Step 1) utilizes a nitrogen atmosphere to dry and calcinate at high temperatures, which can effectively remove water and the residual organic substance in the waste catalyst. The obtained product mainly contains ruthenium oxide.

[0022] Step 2) reduces the ruthenium oxide in the waste catalyst into free state ruthenium, the reaction process being:



[0023] The reaction processes of step 3) are:



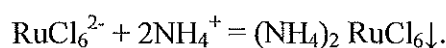
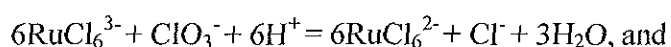
and air or pure oxygen can be used in the mixed gas.

[0024] In step 4), the RuO₄ gas is introduced into sufficient 3-8 mol/L hydrochloric

solution, and the RuO₄ gas is completely absorbed and is reduced into an H₃RuCl₆ solution, the reaction process being:



[0025] Step 5) uses oxidant to oxidize the H₃RuCl₆ solution into H₂RuCl₆, and then introduces excess ammonium chloride to obtain an (NH₄)₂RuCl₆ precipitate, the reaction processes being:



[0026] In step 5), in order to completely precipitate the ruthenium, excess ammonium chloride should be introduced. Preferably, the weight of the NH₄Cl should be 1.2-2.5 times of the theoretical weight of the NH₄Cl that is required to completely react with the H₂RuCl₆ solution and to increase the recovery rate. However, when excess ammonium chloride is introduced, unreacted ammonium chloride would be crystalized. In order to completely precipitate the H₂RuCl₆ and to reduce the water content of the precipitate, the quantity of the introduced ammonium chloride should be controlled, and it is necessary to stir the H₂RuCl₆ solution at 100-400 r/min for 1-3 hours when introducing the ammonium chloride.

[0027] In step 6) the (NH₄)₂RuCl₆ solid is reduced by hydrogen at high temperatures to obtain metal ruthenium. By further treating the metal ruthenium, ruthenium powder for preparing target material can be produced.

[0028] Compared to the conventional “alkali fusion - oxidizing distillation” method, in the method of this invention, after obtaining H₃RuCl₆ solution which contains ruthenium in the recovering step, oxidant is introduced to completely oxidize the H₃RuCl₆ solution

into H_2RuCl_6 , and then excess ammonium chloride is introduced to obtain an $(\text{NH}_4)_2\text{RuCl}_6$ precipitate, which increases the precipitation rate of the ruthenium in the solution. In addition, the $(\text{NH}_4)_2\text{RuCl}_6$ precipitate can be directly used to obtain metal ruthenium by calcining reduction by hydrogen at high temperatures. The recovering process of this method is simple to operate, has low reaction energy consumption, implements an efficient recycle of the ruthenium in waste catalyst of aluminum oxide loaded with ruthenium, increases the economic benefits, and is advantageous for the recycle utilization of the ruthenium.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0029] For further illustrating the invention of a method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium, detailed embodiments are described below. It should be noted that the following examples are intended to describe and not to limit the invention.

Example 1

[0030] A method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium, the method comprising:

[0031] 1) weighing 90 g of waste catalyst of aluminum oxide loaded with ruthenium (in which the weight percentage of the ruthenium is 5.0%) and putting the waste catalyst into a crucible, placing the crucible inside a muffle, purging the muffle with nitrogen, drying waste catalyst of aluminum oxide loaded with ruthenium loaded with ruthenium at

100-150°C in a nitrogen atmosphere for 1-2 hours, calcining the waste catalyst of aluminum oxide loaded with ruthenium at 300-500°C for 2-4 hours for removing the residual organic substance in the waste catalyst, cooling to room temperature to obtain 81.2 g black solid, and grinding the black solid into black solid powder;

[0032] 2) placing 60 g of the obtained black powder inside a fluidized bed reactor, purging the fluidized bed reactor with nitrogen for 30 minutes and then purging the fluidized bed reactor with hydrogen, and reducing the black powder to obtain a powder comprising metal ruthenium at a temperature of 300°C at a pressure of 1.0 MPa for 2 hours;

[0033] 3) purging the fluidized bed reactor with nitrogen for 20 minutes, and then introducing a mixed gas of oxygen and ozone to oxidize the powder comprising ruthenium for obtaining RuO₄ gas at a temperature of 600-650°C at a pressure of 1 MPa for 4 hours, in which the space rate of the mixed gas of oxygen and ozone is 1200 h⁻¹ and the volume fraction of the ozone in the mixed gas of oxygen and ozone is 20%;

[0034] 4) introducing the RuO₄ gas into 6 mol/L hydrochloric solution, and completely absorbing the RuO₄ gas to obtain an H₃RuCl₆ solution;

[0035] 5) slowly introducing 0.63 g (which is 1.2 times of the theoretical weight 0.525 g that is required for complete reaction) oxidant NaClO₃ powder into the H₃RuCl₆ solution, stirring the H₃RuCl₆ solution for 0.5 hour to completely oxidize the H₃RuCl₆ solution to generate H₂RuCl₆, introducing 3.81 g NH₄Cl (which is 1.2 times of the theoretical weight 3.18 g of the NH₄Cl that is required for complete reaction) into the H₂RuCl₆ solution, heating the H₂RuCl₆ solution to 90°C, stirring the H₂RuCl₆ solution for 1.5 hours at 200 r/min to obtain a (NH₄)₂RuCl₆ precipitate, filtering the H₂RuCl₆ solution to obtain a filter

cake, washing the filter cake by an ethanol solution to remove the impurities and the muriatic acid on the filter cake, and drying the filter cake to obtain an $(\text{NH}_4)_2\text{RuCl}_6$ solid; and

[0036] 6) reducing the $(\text{NH}_4)_2\text{RuCl}_6$ solid at a temperature of 650°C using a mixed gas of hydrogen and nitrogen to obtain metal ruthenium, the volume fraction of the hydrogen in the mixed gas being 5%, the weight of the metal ruthenium being measured to be 2.941 g.

[0037] In this embodiment, the recovering rate of the ruthenium is 98.03%.

Example 2

[0038] A method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium, the method comprising:

[0039] 1) weighing 90 g of waste catalyst of aluminum oxide loaded with ruthenium (in which the weight percentage of the ruthenium is 5.0%) and putting the waste catalyst into a crucible, placing the crucible inside a muffle, purging the muffle with nitrogen, drying waste catalyst of aluminum oxide loaded with ruthenium loaded with ruthenium at $100\text{--}150^\circ\text{C}$ in a nitrogen atmosphere for 1-2 hours, calcining the waste catalyst of aluminum oxide loaded with ruthenium at $300\text{--}500^\circ\text{C}$ for 2-4 hours for removing the residual organic substance in the waste catalyst, cooling to room temperature to obtain 81.2 g black solid, and grinding the black solid into black solid powder;

[0040] 2) placing 60 g of the obtained black powder inside a fluidized bed reactor, purging the fluidized bed reactor with nitrogen for 20 minutes and then purging the fluidized bed reactor with hydrogen, and reducing the black powder to obtain a powder comprising metal ruthenium at a temperature of 200°C at a pressure of 1.5 MPa for 3

hours;

[0041] 3) purging the fluidized bed reactor with nitrogen for 30 minutes, and then introducing a mixed gas of oxygen and ozone to oxidize the powder comprising ruthenium for obtaining RuO_4 gas at a temperature of 600°C at a pressure of 1.5 MPa for 4 hours, in which the space rate of the mixed gas of oxygen and ozone is 3000 h^{-1} and the volume fraction of the ozone in the mixed gas of oxygen and ozone is 10%;

[0042] 4) introducing the RuO_4 gas into 3 mol/L hydrochloric solution, and completely dissolving the RuO_4 gas to obtain an H_3RuCl_6 solution;

[0043] 5) slowly introducing 0.72 g (which is 1.2 times of the theoretical weight that is required for complete reaction) oxidant KClO_3 powder into the H_3RuCl_6 solution, stirring the H_3RuCl_6 solution for 1 hour to completely oxidize the H_3RuCl_6 solution to generate H_2RuCl_6 , introducing 4.77 g NH_4Cl (which is 1.5 times of the theoretical weight of the NH_4Cl that is required for complete reaction) into the H_2RuCl_6 solution, heating the H_2RuCl_6 solution to 80°C , stirring the H_2RuCl_6 solution for 1.5 hours at 200 r/min to obtain a $(\text{NH}_4)_2\text{RuCl}_6$ precipitate, filtering the H_2RuCl_6 solution to obtain a filter cake, washing the filter cake by an ethanol solution to remove the impurities and the muriatic acid on the filter cake, and drying the filter cake to obtain an $(\text{NH}_4)_2\text{RuCl}_6$ solid; and

[0044] 6) reducing the $(\text{NH}_4)_2\text{RuCl}_6$ solid at a temperature of 800°C using a mixed gas of hydrogen and nitrogen to obtain metal ruthenium, the volume fraction of the hydrogen in the mixed gas being 10%, the weight of the metal ruthenium being measured to be 2.976 g.

[0045] In this embodiment, the recovering rate of the ruthenium is 99.2%.

Example 3

[0046] A method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium, the method comprising:

[0047] 1) weighing 90 g of waste catalyst of aluminum oxide loaded with ruthenium (in which the weight percentage of the ruthenium is 5.0%) and putting the waste catalyst into a crucible, placing the crucible inside a muffle, purging the muffle with nitrogen, drying waste catalyst of aluminum oxide loaded with ruthenium at 100-150°C in a nitrogen atmosphere for 1-2 hours, calcining the waste catalyst of aluminum oxide loaded with ruthenium at 300-500°C for 2-4 hours for removing the residual organic substance in the waste catalyst, cooling to room temperature to obtain 81.2 g black solid, and grinding the black solid into black solid powder;

[0048] 2) placing 60 g of the obtained black powder inside a fluidized bed reactor, purging the fluidized bed reactor with nitrogen for 40 minutes and then purging the fluidized bed reactor with hydrogen, and reducing the black powder to obtain a powder comprising metal ruthenium at a temperature of 400°C at a pressure of 2.0 MPa for 2.5 hours;

[0049] 3) purging the fluidized bed reactor with nitrogen for 40 minutes, and then introducing a mixed gas of oxygen and ozone to oxidize the powder comprising ruthenium for obtaining RuO₄ gas at a temperature of 650°C at a pressure of 2 MPa for 5 hours, in which the space rate of the mixed gas of oxygen and ozone is 4000 h⁻¹ and the volume fraction of the ozone in the mixed gas of oxygen and ozone is 15%;

[0050] 4) introducing the RuO₄ gas into 5 mol/L hydrochloric solution, and completely dissolving the RuO₄ gas to obtain an H₃RuCl₆ solution;

[0051] 5) slowly introducing 1.13 g (which is 1.2 times of the theoretical weight that is required for complete reaction) oxidant $\text{Mg}(\text{ClO}_3)_2$ powder into the H_3RuCl_6 solution, stirring the H_3RuCl_6 solution for 1.5 hours to completely oxidize the H_3RuCl_6 solution to generate H_2RuCl_6 , introducing 6.36 g NH_4Cl (which is 2 times of the theoretical weight of the NH_4Cl that is required for complete reaction) into the H_2RuCl_6 solution, heating the H_2RuCl_6 solution to 90°C , stirring the H_2RuCl_6 solution for 2.5 hours at 100 r/min to obtain a $(\text{NH}_4)_2\text{RuCl}_6$ precipitate, filtering the H_2RuCl_6 solution to obtain a filter cake, washing the filter cake by an ethanol solution to remove the impurities and the muriatic acid on the filter cake, and drying the filter cake to obtain an $(\text{NH}_4)_2\text{RuCl}_6$ solid; and

[0052] 6) reducing the $(\text{NH}_4)_2\text{RuCl}_6$ solid at a temperature of 650°C using a mixed gas of hydrogen and nitrogen to obtain metal ruthenium, the volume fraction of the hydrogen in the mixed gas being 15%, the weight of the metal ruthenium being measured to be 2.946 g.

[0053] In this embodiment, the recovering rate of the ruthenium is 98.2%.

Example 4

[0054] A method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium, the method comprising:

[0055] 1) weighing 90 g of waste catalyst of aluminum oxide loaded with ruthenium (in which the weight percentage of the ruthenium is 5.0%) and putting the waste catalyst into a crucible, placing the crucible inside a muffle, purging the muffle with nitrogen, drying

waste catalyst of aluminum oxide loaded with ruthenium loaded with ruthenium at 100-150°C in a nitrogen atmosphere for 1-2 hours, calcining the waste catalyst of aluminum oxide loaded with ruthenium at 300-500°C for 2-4 hours for removing the residual organic substance in the waste catalyst, cooling to room temperature to obtain 81.2 g black solid, and grinding the black solid into black solid powder;

[0056] 2) placing 60 g of the obtained black powder inside a fluidized bed reactor, purging the fluidized bed reactor with nitrogen for 25 minutes and then purging the fluidized bed reactor with hydrogen, and reducing the black powder to obtain a powder comprising metal ruthenium at a temperature of 350°C at a pressure of 2.0 MPa for 3 hours;

[0057] 3) purging the fluidized bed reactor with nitrogen for 35 minutes, and then introducing a mixed gas of oxygen and ozone to oxidize the powder comprising ruthenium for obtaining RuO₄ gas at a temperature of 600°C at a pressure of 2 MPa for 6 hours, in which the space rate of the mixed gas of oxygen and ozone is 4000 h⁻¹ and the volume fraction of the ozone in the mixed gas of oxygen and ozone is 5%;

[0058] 4) introducing the RuO₄ gas into 6 mol/L hydrochloric solution, and completely dissolving the RuO₄ gas to obtain an H₃RuCl₆ solution;

[0059] 5) slowly introducing 0.63 g (which is 1.2 times of the theoretical weight that is required for complete reaction) oxidant NaClO₃ powder into the H₃RuCl₆ solution, stirring the H₃RuCl₆ solution for 1.5 hours to completely oxidize the H₃RuCl₆ solution to generate H₂RuCl₆, introducing 7.94 g NH₄Cl (which is 2.5 times of the theoretical weight of the NH₄Cl that is required for complete reaction) into the H₂RuCl₆ solution, heating the H₂RuCl₆ solution to 70°C, stirring the H₂RuCl₆ solution for 1 hour at 400 r/min to

obtain a $(\text{NH}_4)_2\text{RuCl}_6$ precipitate, filtering the H_2RuCl_6 solution to obtain a filter cake, washing the filter cake by an ethanol solution to remove the impurities and the muriatic acid on the filter cake, and drying the filter cake to obtain an $(\text{NH}_4)_2\text{RuCl}_6$ solid; and

[0060] 6) reducing the $(\text{NH}_4)_2\text{RuCl}_6$ solid at a temperature of 800°C using a mixed gas of hydrogen and nitrogen to obtain metal ruthenium, the volume fraction of the hydrogen in the mixed gas being 15%, the weight of the metal ruthenium being measured to be 2.901 g.

[0061] In this embodiment, the recovering rate of the ruthenium is 96.7%.

CLAIMS

1. A method for recovering ruthenium from waste catalyst of aluminum oxide loaded with ruthenium, the method comprising:
 - 1) drying waste catalyst of aluminum oxide loaded with ruthenium loaded with ruthenium at 100-150°C in a nitrogen atmosphere for 1-2 hours, calcining the waste catalyst of aluminum oxide loaded with ruthenium at 300-500°C for 2-4 hours, cooling the waste catalyst of aluminum oxide loaded with ruthenium to room temperature, and grinding the waste catalyst of aluminum oxide loaded with ruthenium into black powder comprising ruthenium oxide;
 - 2) placing the black powder inside a fluidized bed reactor, purging the fluidized bed reactor with nitrogen for 20-40 minutes and then purging the fluidized bed reactor with hydrogen, and reducing the black powder to obtain a powder comprising ruthenium at a temperature of 200-400°C at a pressure of 1-2 MPa for 2-3 hours;
 - 3) purging the fluidized bed reactor with nitrogen for 20-40 minutes, and then introducing a mixed gas of oxygen and ozone to oxidize the powder comprising ruthenium for obtaining RuO_4 gas at a temperature of 500-750°C at a pressure of 1-2 MPa for 1-8 hours;
 - 4) introducing the RuO_4 gas into a 3-8 mol/L hydrochloric solution, and completely dissolving the RuO_4 gas to obtain an H_3RuCl_6 solution;
 - 5) slowly introducing excess oxidant into the H_3RuCl_6 solution, stirring the H_3RuCl_6 solution for 0.5-1.5 hours to completely oxidize the H_3RuCl_6 solution to

generate H_2RuCl_6 , introducing excess NH_4Cl into the H_2RuCl_6 solution, heating the H_2RuCl_6 solution to 60-90°C, stirring the H_2RuCl_6 solution for 1-3 hours, filtering the H_2RuCl_6 solution to obtain a filter cake, and washing the filter cake to obtain an $(\text{NH}_4)_2\text{RuCl}_6$ solid, wherein the oxidant is soluble chlorate; and

6) reducing the $(\text{NH}_4)_2\text{RuCl}_6$ solid at a temperature of 450-800°C using a mixed gas of hydrogen and nitrogen to obtain ruthenium, wherein a volume fraction of the hydrogen in the mixed gas is 1-15%.

2. The method of claim 1, wherein in step 3) the space rate of the mixed gas of oxygen and ozone is 1000-4000 h^{-1} .
3. The method of claim 1 or 2, wherein in step 3), the volume fraction of the ozone in the mixed gas of oxygen and ozone is 1-20%.
4. The method of claim 1 or 2, wherein in step 4) the concentration of the hydrochloric solution is 6 mol/L.
5. The method of claim 1 or 2, wherein in step 5) the weight of the NH_4Cl is 1.2-2.5 times of the theoretical weight of the NH_4Cl that is required to completely react with the H_2RuCl_6 solution.
6. The method of claim 1 or 2, wherein in step 5) the oxidant is one or more of the following: ammonium chlorate, potassium chlorate, sodium chlorate, and magnesium chlorate.

7. The method of claim 1 or 2, wherein in step 5) the filter cake is washed by an ethanol solution.
8. The method of claim 1 or 2, wherein in step 5) the H_2RuCl_6 solution is stirred at 100-400 r/min for 1-3 hours.
9. The method of claim 8, wherein in step 5) the H_2RuCl_6 solution is stirred at 200 r/min for 1.5-2.5 hours.