PROCESS FOR THE COMPREHENSIVE RECOVERY OF METAL COBALT, RUTHENIUM AND ALUMINUM FROM WASTE CATALYST CO-RU/AL_2O_3 IN FISCHER-TROPSCH SYNTHESIS

FIELD OF THE INVENTION

[0001] This invention relates to techniques of recovering metals from catalysts and waste catalysts, more particularly, to a method for recovering metal cobalt, ruthenium, and aluminum from waste Co-Ru/Al_2O_3catalysts for FIscher-Tropsch synthesis.

BACKGROUND OF THE INVENTION

[0002] To solve the problems of approaching oil depletion and increased environmental pollution, development of clean, renewable alternative liquid fuels becomes an essential topic. FIscher-Tropsch synthesis converts synthesis gas prepared from gasification of carbon-containing substances such as natural gas, coal, and biomassinto liquid fuel (as called synthetic oil) with the aid of Fischer–Tropsch catalysts. This synthetic oil is a clean, renewable fuel that can be converted into widely used gasoline or dieselthat meet the Euro 5 standard by consequent treatment such as distillation.

[0003] The main metal active components of Fischer–Tropsch catalysts include the metal elements of Group VIII,such as Fe, Co, Ni, and Ru. In particular, the cobalt-based catalyst is a hot topics in research and application of Fischer–Tropsch catalysts due to its outstanding catalytic ability. Though Ru has the highest catalytic activity, its application is limited by its scarcity and high price and is usually used as a promoter to improve the selectivity and activity of a

catalyst. There are many patentson Fischer–Tropsch catalysts using cobalt as the main active componentand ruthenium as the promoter, e.g., US Pat. No. 4,822,824, CN Pat. No. 1617292A, and CN Pat. No. 101698152A.

[0004] Aluminum oxide has a high melting point, excellent thermal stability, and good wear resistance. It is widely used as a carrier for Fischer–Tropsch catalysts. Specially, the weight percentage amount of aluminum oxide in the Fischer–Tropsch catalysts used in slurry bed is more than 50%. However, up to now, there is still no report on recovering aluminum oxide from Fischer–Tropsch catalysts.

[0005] The reserves of cobalt and ruthenium in China are scare and mostly rely on expensive imports. This causes increased costs of the catalysts. Though China has a large reserve of bauxite, the increasing consumption of aluminum leads to a deficiency of the aluminum production capacity. Therefore, recovery of cobalt, ruthenium, and aluminum from deactivated Fischer–Tropsch catalysts and recycling them into metal salts or oxides that can be used in preparation of catalystsis a method to reduce environmental pollution as well as production cost of the catalyst.

[0006] The prior patents on recovery of cobalt from cobalt-based catalysts carried on aluminum oxide includes CN Pat. No. 101270420 and CN Pat.No. 101700913A.In CN Pat. No. 101270420A, first, CO is introduced into a reactor containing deionized water and waste Fischer–Tropsch catalysts containing cobalt (including waste cobalt-based catalyst containing SiO_2, Al_2O_3, ZrO_2, or TiO_2 as carriers) and heated at a constant temperature. Next, the reactor is cooled down and the CO is released therefrom. After that, the solution containing cobalt is released from the reactor and a lye is added into the solution to precipitate the cobalt as $Co(OH)_2$. Nitric acid is added into the precipitation to dissolve it. After

crystallization by evaporation, $Co(NO_3)_2 \cdot 6H_2O$ is obtained. The $Co(NO_3)_2 \cdot 6H_2O$ obtained by this method has a purity lower than 99% and cannot be directly used in preparation of cobalt-based catalyst. In CN Pat. No. 101700913A, waste cobalt-based catalyst on aluminum oxide carrier is ground, dissolved in concentrated hydrochloric acid, precipitated by sodium sulfide, precipitated by oxalic acid, calcined, dissolved in nitric acid, and crystallized by evaporationso as to obtain $Co(NO_3)_2 \cdot 6H_2O$ having a purity higher than 99%. However, because the waste catalysts are not reduced and because the intermediate CoSin the recovery process has very tiny particle sizes, loss of cobalt is likely to happen during filtration, which leads to a low cobalt recovery rate around 92%.

[0007] Among the known methods for recovering ruthenium from waste catalysts, the most widely used one is distillation. For example, CN Pat. No. 100387344C recites analkali fusion-oxidization distillation method for recovery of ruthenium-based catalysts on activated carbon carrier. In this method, the ruthenium-based catalyst is calcined at 600 – 1000°C to remove the activated carbon carrier, and then is mixed with KOH and KNO_3 and heated at 300 – 900°C for 1 – 5 hours to carry out analkali fusion reaction. After cooling, analkali fusion product is obtained. The alkali fusion product is dissolved in hot water of 50 – 90°C to obtain a K_2RuO_4 solution. Then, sodium hypochlorite and concentrated sulfuric acid is added into the solution and distilled at 50 – 90°C for 2 – 4 hours to produce RuO_4 gas. The RuO_4 gas is absorbed witha strong acid solution and then distilled under atmospheric pressure or a reduced pressure to obtain a corresponding ruthenium salt. This method has disadvantages summarized as follows: RuO_4 produced in distillation process is a strong oxidizer. Since it explodes when meeting organic molecules of light molecular weight and is highly toxic, the reactions must be performed in a closed fume hood. Furthermore, the

procedure of this method is complex and long. In CN Pat. No. 102108444, a method for recovering ruthenium from ruthenium-based catalysts on carriers is recited. In this method, the catalyst is calcined at a high temperature under nitrogen for removal of organic substances and activation of the catalyst. Then the melted black catalyst solid is oxidized into RuO_4 gas at 100 – 300°C and 1 – 3 MPa under O_2/O_3. The RuO_4 gas is introduced into dilute hydrochloric acid and reduced to red-brown $RuCl_3$ solution. β-$RuCl_3 \cdot xH_2O$ is obtained after vacuum distillation of the $RuCl_3$ solution. This method has a disadvantage of low ruthenium recovery rate.

[0008] CN Pat. No. 101331240 recites a method for recovering ruthenium from used catalysts containing ruthenium oxide. This catalyst contains ruthenium existing in an oxide form loaded on a carrier which is difficult to be dissolved in inorganic acids. In this method, first, the catalyst containing ruthenium oxide is treated with hydrogen flow so that the ruthenium oxide on the carrier is reduced to ruthenium metal. Then it is treated with heated hydrochloric acid under a gas containing oxygen to dissolve the ruthenium metal on the carrier in a form of ruthenium(III). Then the obtained ruthenium(III) chloride solution is obtained is recovered for further treatment. This method has a low ruthenium recovery rate and is not suitable for recovery of catalysts containing ruthenium oxide which uses γ-Al_2O_3 as the carrier.

[0009] The aforementioned patents are focused on recovery of a single metal. There is no reports on recovery of the three metals Co, Ru, and Al in one method. Due to the different properties the metals, the recovery rate and purity of the metals changes dramatically in accordance with the recovery method.

SUMMARY OF INVENTION

[0010] It is an object of the present invention to provide a safe, efficient method for recovering metal cobalt, ruthenium, and aluminum from waste Co-Ru/Al_2O_3 catalysts for FIscher-Tropsch synthesis.

[0011] The method for recovering metal cobalt, ruthenium, and aluminum from waste Co-Ru/Al_2O_3 catalysts for FIscher-Tropsch synthesisdescribed in this present invention comprises the following steps:

[0012] 1) putting loose particles of a waste Co-Ru/Al_2O_3 catalyst into a muffle furnace, then introducing air into the muffle furnace and calcining the loose particles at 350 – 500°C for 3 – 6 hours to remove the heavy hydrocarbons on the surface of the catalyst particles; then cooling the particles down to room temperature;

[0013] 2) grinding the particles obtained in step 1) into uniform powders and putting them into a fluidized bed reactor; purging the reactor with nitrogen for 0.5 hour and then reducing the particles in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 1: 1 – 4: 1 at a space velocity of 1000 – 4000 h^{-1}, a pressure of 0.1 – 1 MPa, and a temperature of 350 – 800°C for 8 – 12 hours;

[0014] 3) putting the reduced waste catalysts obtained in step 2) and alkali fusing agents into a crucible layer by layer, then putting the crucible into a muffle furnace; heating the muffle furnace and keeping it at 200°C for 1 hour, then increasing the temperature of the muffle furnace by 3°C/min to 900 – 1000°Cusing a temperature program to carry out an alkali fusion reaction for 2 – 4 hours; then cooling the muffle furnace to room temperature to obtain the alkali fusion product;

[0015] 4) leaching the alkali fusion product obtained in step 3) in deionized water having a temperature of 90 – 100°Cin a solid-to-liquid ratio from 1: 2 to 1: 4 for 0.5 – 1 hour to dissolve the water-soluble K_2RuO_4 and $KAlO_2$ or Na_2RuO_4 and $NaAlO_2$,

then filtering to obtain a residue;

[0016] 5) washing the residue obtained in step 4) to neutrality, then adding excess dilute nitric acid to dissolve the cobalt metal and cobalt oxide to obtain a cobalt nitrate solution;

[0017] 6) adjusting the cobalt nitrate solution obtained in step 5) to a Co^{2+} concentration of 20 g/L, a pH of 1.5, and a temperature of 70°C; adding oxalic acid solution or ammonium oxalate solution having a pH of 1.5 and a temperature of 70°C to precipitate cobalt ions as cobalt oxalate, in which the molar amount of the oxalic acid in the oxalic acid solution or ammonium oxalate in the ammonium oxalate solution is 3 – 4 times the molar amount of the cobalt; hot-filtering and washing the residue with deionized water having a temperature of 65 – 80°C; dehydrating the residue with absolute ethanol to obtain a pink cobalt oxalate precipitate; the reaction occurring in this step is:

$$Co(NO_3)_2 + H_2C_2O_4 + 2H_2O = CoC_2O_4 \cdot 2H_2O \downarrow + 2HNO_3;\ \text{or}$$

$$Co(NO_3)_2 + (NH_4)_2C_2O_4 + 2H_2O = CoC_2O_4 \cdot 2H_2O \downarrow + 2NH_4NO_3.$$

[0018]7) drying the pink cobalt oxalate obtained in step 6) in a dryer at 80 – 110°C, then putting the cobalt oxalate to a fluidized bed reactor; purging the fluidized bed reactor with nitrogen for 0.5 hour, then reducing the cobalt oxalate in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratioof 1: 1 – 4: 1 at a temperature of 400 –560°C, a pressure of 0.1 – 1 MPa, a space velocity of 1000 – 4000 h^{-1} for 2–4 hours to obtain cobalt metal; the reaction occurring in this step is:

$$CoC_2O_4 \cdot 2H_2O = Co + 2CO_2 + 2H_2O.$$

[0019] 8) adding dilute nitric acid to the cobalt metal obtained in step 7) until the cobalt metal just completely dissolves, then evaporating to obtain crystallized $Co(NO_3)_2 \cdot 6H_2O$.

[0020] 9) mixing the filtrate of step 4) and the effluent of step 5), and then dropping reducing agent of absolute ethanol to the mixture and stirring to covert pink ruthenium salt to black ruthenium hydroxide precipitate; then filtering the precipitate and washing itwith deionized water having a temperature of 65 – 80°Cuntil the effluent becomes neutral or contains no potassium or sodium ions; then washing the precipitate with absolute ethanol for three times; the reactions occurring in this step are:

$$K_2RuO_4 + 2CH_3CH_2OH \xrightarrow{OH^-} Ru(OH)_4\downarrow + 2CH_3CHO + 2KOH;\ \text{or}$$

$$Na_2RuO_4 + 2CH_3CH_2OH \xrightarrow{OH^-} Ru(OH)_4\downarrow + 2CH_3CHO + 2NaOH.$$

[0021] 10) putting the black ruthenium hydroxide obtained in step 9) to a three-necked flask having stirring and refluxing devices; adding concentrated hydrochloric acid to the three-necked flask and stirring at 91 – 95°C for 1 – 2 hours; then adding hydroxylammonium chloride to completely dissolve the black ruthenium hydroxide, allowing the obtained solution to stand, and then putting the solution to a distilling flask and vacuum-distilling at a vacuum degree of 40 ± 1 KPa until the solution is converted into a paste; then stopping heating to let the liquid evaporate spontaneously to obtainβ-$RuCl_3 \cdot xH_2O$ crystal;the reactions occurring in this step are:

$$Ru(OH)_4 + 4HCl = RuCl_4 + 4H_2O;$$

$$2RuCl_4 + 2NH_2OH \cdot HCl = 2RuCl_3 + N_2\uparrow + 4HCl + 2H_2O.$$

[0022] 11) mixing the filtrate obtained in filtration of the ruthenium hydroxide precipitate and the effluentobtained from washing the precipitate in step 9), introducing CO_2 having a purity higher than 99.0% to the mixed liquid and stirring, controlling a reaction temperature at 25 – 95°C to produce white aluminum hydroxide precipitate, whereinthe reaction is completed when the pH of the

solution reaches 10.0; filtering and then washing the precipitate with deionized water having a temperature of 65 – 80°C until the effluent becomes neutral or contains no potassium or sodium ions; then washing the precipitate with absolute ethanol for three times; the reaction occurring in this step is:

$2KAlO_2 + CO_2 + 3H_2O = K_2CO_3 + 2Al(OH)_3\downarrow$; or

$2NaAlO_2 + CO_2 + 3\ H_2O = Na_2CO_3 + 2Al(OH)_3\downarrow$.

[0023] 12) drying the aluminum hydroxide at 80 – 130°C, then calcining at 500 – 750°C to obtain aluminum oxide; the reaction occurring in this step is:

$2Al(OH)_3 = Al_2O_3 + 3H_2O$.

[0024] In a class of this embodiment, the alkali fusing agents in step 3) areKOH and KNO_3, or NaOH and $NaNO_3$. The reactions occurring in step 3) are

$RuO_2 + 2KOH + KNO_3 = K_2RuO_4 + KNO_2 + H_2O$;

$Ru + 2KOH + 3KNO_3 = K_2RuO_4 + 3KNO_2 + H_2O$;

$Al_2O_3 + 2KOH = 2KAlO_2 + H_2O$;

or

$RuO_2 + 2NaOH + NaNO_3 = Na_2RuO_4 + NaNO_2 + H_2O$;

$Ru + 2NaOH + 3NaNO_3 = Na_2RuO_4 + 3NaNO_2 + H_2O$;

$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$;

The amount of the alkali fusing agents used is 2.5 times the theoretical amount thereof.

[0025] In a class of this embodiment, in step 3), the alkali fusion is layered alkali fusion containing four layers. From the bottom of the crucible upward, 2/3 of the total amount of KOH, waste catalysts, 1/3 of the total amount of KOH, and KNO_3

are disposed layer by layer; or 2/3 of the total amount of NaOH, waste catalysts, 1/3 of the total amount of NaOH, and $NaNO_3$ are disposed layer by layer. Layered alkali fusion avoids sintering and evaporation of RuO_4 so as to reduce loss of ruthenium.

[0026] In a class of this embodiment, in step 3), the temperature of alkali fusion is 950 – 1000°C for achieving complete reaction of ruthenium and aluminum oxide with the alkali fusing agents.

[0027] In a class of this embodiment, in step 3), the reaction time of alkali fusion is 3 hours.

[0028] In a class of this embodiment, in step 4), the alkali fusion product is leached in deionized water having a temperature of 96– 100°C to ensure the ruthenate and, more importantly, the aluminate to be complete leached;

[0029] In a class of this embodiment, in step 4), the solid-to-liquid ratio is 3.

[0030] In a class of this embodiment, the concentration of the dilute nitric acid in steps 5) and 8) is 1 – 3 mol/L.

[0031] In a class of this embodiment, in step 6), the oxalic acid solution or ammonium oxalate solution is slowly dropped into the cobalt nitrate solution while 5% ammonium water is added to keep the pH of the solution at 1.5 – 1.7 so that the cobalt in the solution is completely precipitated to achieve a high recovery rate thereof.

[0032] In a class of this embodiment, the temperature for reducing cobalt oxalate in step 7) is 400 – 480°C.

[0033] In a class of this embodiment, in step 9), the reducing agent of ethanol is excess so as to complete convert ruthenate into ruthenium hydroxide precipitate. The molar ratio of the ruthenium in the waste ruthenium-based catalysts to the

absolute ethanol is 1: 3 – 1: 5.

[0034]In a class of this embodiment, the concentrated hydrochloric acid in step 10) has a mass fraction of 36 – 38%.

[0035] In a class of this embodiment,in step 10), the molar ratio of the hydroxylammonium chloride to ruthenium element is 1: 1, which helps to achieve β-$RuCl_3 \cdot xH_2O$ with a high purity.

[0036] In a class of this embodiment, in step 11), in order to produced aluminum hydroxide with a large particle size that can be easily filtered, the reaction temperature is preferable to be 65 – 85°C.

[0037] In a class of this embodiment, in step 11), the flow rate of the CO_2 is 500 – 1500 mL/min.

[0038] The advantages of the invention is summarized as follows:

[0039] 1) The method of the invention can effectively separate and recover cobalt, ruthenium, and aluminum from waste Co-Ru/Al_2O_3 catalysts for FIscher-Tropsch synthesis.

[0040] 2) The waste catalyst is treated by removal of hydrocarbon and reduction. The residue containing cobalt is separated in alkali fusion step, and then is leached in acids. Then via precipitation of cobalt by oxalic acid or ammonium oxalate, reduction of cobalt oxalate, and dissolution of cobalt metal in nitric acid, $Co(NO_3) \cdot 6H_2O$ with a purity higher than 99% is obtained. The obtained $Co(NO_3) \cdot 6H_2O$ does not contain ions, such as chloride and sulfide ions,which cause catalyst poisoning during Fischer–Tropsch process. Therefore, it can be directly used to prepare Fischer–Tropsch catalysts.

[0041] 3) Theβ-$RuCl_3 \cdot xH_2O$ obtained via alkali fusion, leaching of ruthenate

with deionized water, reduction by ethanol, dissolution by concentrated hydrochloric acid, and vacuum distillation has a high purity. Furthermore, this is a safe process since it does not produce toxic, explosive RuO_4 gas.

[0042] 4) Via CO_2carbonation which is performed at a controlled temperature and CO_2 flow rate and endsata controlled pH, aluminum hydroxide is prepared from aluminate solution. Aluminum oxide obtained by calcining the aluminum hydroxide meets the national standardof first grade alumina. The preparation process is economic and environmentally friendly.

[0043] 5)The method of the invention achieves high metal recovery rate. Specifically, the cobalt recovery rate is higher than 97%;the ruthenium recovery rate is higher than 95%; and the aluminum recovery rate is higher than 92%.

[0044] 6) The method of the invention is safe and simple. The equipment and material used therein is cheap and easy to get, leading to low cost and rendering the method suitable for industrial production.

BRIEF DESCRIPTION OF THE DRAWINGS

[0045] Figure 1 is a flow diagram according to one embodiment of the invention.

DETAILED DESCRIPTON OF THE INVENTION

[0046] The invention is explained in further detail below. It should be noted that the following examples are intended to describe and not to limit the invention.

Example 1

[0047] 1) 20.23 g of loose particles of waste Co-Ru/Al_2O_3 catalyst is provided. Elemental analysis determines that the catalyst contains Co 30.05%, Ru 4.83%, and Al 27.90%. The loose particles of waste Co-Ru/Al_2O_3 catalyst isput into a muffle furnace and air is introduced into the muffle furnace. The catalyst particlesarecalcined at 500°C for 3 hours to remove the heavy hydrocarbons on the surface thereof and then cooled down to room temperature.

[0048] 2) Thewaste catalyst obtained in step 1) is ground into uniform powders and then put into a fluidized bed reactor. The powders are reduced in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2volume ratio of 4: 1 at a space velocity of 1000 h^{-1}, a pressure of 1 MPa, and a temperature of 800°C for 10 hours.

[0049] 3) The reduced waste catalyst obtained in step 2) and alkali fusing agents are put into a crucible layer by layer. The layers disposed from the bottom of the crucible upward contain 21.31 g of KOH, the waste catalyst, 10.65 g of KOH, and 7.32 g of KNO_3, respectively. The crucible is then put into a muffle furnace. The muffle furnace is then heated and kept at 200°C for 1 hour. After that, the temperature of the muffle furnaceis increased by 3°C/min to 950°C using a temperature program to carry out alkali fusion reaction for 3 hours. Next, the muffle furnace is cooled down to room temperature to obtain the alkali fusion product.

[0050] 4) The alkali fusion product obtained in step 3) is leached in deionized water having a temperature of 90°C (in a solid-to-liquid ratioof 1: 2) for 1 hour to completely dissolve the water-soluble K_2RuO_4 and $KAlO_2$, and then filtered to obtain a residue.

[0051] 5) The residue obtained in step 4) is washed to neutrality.Next, 300 mL of 3 mol/L dilute nitric acid is added to completely dissolve the cobalt metal and cobalt oxidein the residue to obtain a cobalt nitrate solution.

[0052] 6) The cobalt nitrate solution obtained in step 5) is adjusted to a Co^{2+} concentration of 20 g/L. The pH of the solution is adjusted to 1.5 by using ammonium water with a mass fraction of 10%, and the temperature of the solution is adjusted to 70°C. Then, the cobalt nitrate solution is slowly mixed with an oxalic acid solution having a pH of 1.5 and a temperature of 70°C to precipitate cobalt ions as cobalt oxalate while ammonium water with a mass fraction of 5% is added to the solution to maintain the pH thereof at 1.5 – 1.7. After precipitation is completed, the mixture is hot-filtered and the precipitate is washed with deionized water having a temperature of 65 – 80°C to neutrality. The washed precipitate is dehydrated with absolute ethanol to obtain a pink cobalt oxalate precipitate. The oxalic acid solution used is prepared by: adding deionized water until 39.01 g of solid oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) just dissolves, and adding 5% ammonium water to adjust the solution's pH to 1.5.

[0053] 7) The cobalt oxalate obtained in step 6) is dried in a dryer at 80°C, then putinto a fluidized bed reactor and reduced in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2volume ratio of 3: 1 at 560°C, 0.5 MPa, and a space velocity of 4000 h^{-1} for 2 hours to obtain cobalt metal.

[0054] 8) The cobalt metal obtained in step 7) is dissolved in a sufficient amount of 3 mol/L dilute nitric acid. The obtained mixture is evaporated to obtain crystallized $Co(NO_3)_2 \cdot 6H_2O$. The crystallized $Co(NO_3)_2 \cdot 6H_2O$ is cooled in a dryer and then weighed. The obtained $Co(NO_3)_2 \cdot 6H_2O$ is 29.52 g, the purity of which measured by GBT 15898-1995 method is 99.41%. The recovery rate of cobalt is 97.75%.

[0055] 9) The filtrate of step 4) and the effluent of step 5) are mixed, and then 30

mL of absolute ethanol is slowly droppedinto the mixture and stirred to covert pink ruthenate to black ruthenium hydroxide precipitate.Then the precipitate is filtered and washed with deionized water having a temperature of 65 – 80°C until the effluent becomes neutraland contains no potassium ions. After that, the precipitate is washed with absolute ethanol for three times.

[0056] 10) The black ruthenium hydroxide obtained in step 9) is putinto a three-necked flask having stirring and refluxing devices. Concentrated hydrochloric acid with a mass fraction of 36 – 38°C is added to the three-necked flask. The mixture is stirred at 91 – 95°C for 2 hours. Then 0.67 g of hydroxylammonium chloride is added to completely dissolve the black ruthenium hydroxide. The obtained solution is allowed to stand for a while, andthen is putinto a distilling flask and vacuum-distilled at a vacuum degree of 40 ± 1 KPa until the solution is converted into a paste. Next, heating is stopped to let the liquid evaporate spontaneously to obtain 2.415 g of β-$RuCl_3 \cdot xH_2O$ crystal. ICP-AES method determines that the β-$RuCl_3 \cdot xH_2O$ has a ruthenium content of 38.58%. The recovery rate of ruthenium is 95.36%.

[0057] 11) The filtrate obtained from the filtration of the ruthenium hydroxide precipitateand the effluentobtained from washing the precipitate in step 9) are mixed together.The mixture is heated to 95°C, and CO_2 having a purity higher than 99.0% in introduced into the mixtureat a flow rate of 1500 mL/min and stirred to produce white aluminum hydroxide precipitate.The reaction is completed when the pH of the solution reaches 10.0.The precipitate is filtered and then washed with deionized water until the effluent becomes neutraland contains no potassium ions.After that, the precipitate is washed with absolute ethanol for three times.

[0058] 12) The aluminum hydroxide is dried at 120°C, then calcined at 500°C to obtain 10.04 g of aluminum oxide having a purity of 99.31%. The recovery rate of

aluminum is 93.47%.

Example 2

[0059] 1) 20.74 g of loose particles of waste Co-Ru/Al_2O_3 catalyst is provided. Elemental analysis determines that the catalyst contains Co 25.33%, Ru 3.07%, and Al 32.53%. The loose particles of waste Co-Ru/Al_2O_3 catalyst is put into a muffle furnace and air is introduced into the muffle furnace. The catalyst particles are calcined at 350°C for 6 hours to remove the heavy hydrocarbons on the surface thereof and then cooled down to room temperature.

[0060] 2) The waste catalyst obtained in step 1) is ground into uniform powders and then put into a fluidized bed reactor. The powders are reduced in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 2: 1 at a space velocity of 3000 h^{-1}, a pressure of 0.8 MPa, and a temperature of 700°C for 11 hours.

[0061] 3) The reduced waste catalyst obtained in step 2) and alkali fusing agents are put into a crucible layer by layer. The layers disposed from the bottom of the crucible upward contain 17.50 g of NaOH, the waste catalyst, 8.75 g of NaOH, and 4.02 g of $NaNO_3$, respectively. The crucible is then put into a muffle furnace. The muffle furnace is then heated and kept at 200°C for 1 hour. After that, the temperature of the muffle furnace is increased by 3°C/min to 900°C using a temperature program to carry out alkali fusion reaction for 4 hours. Next, the muffle furnace is cooled down to room temperature to obtain the alkali fusion product.

[0062] 4) The alkali fusion product obtained in step 3) is leached in deionized water having a temperature of 95°C (in a solid-to-liquid ratio of 1: 3) for 0.5 hour to

completely dissolve the water-soluble Na_2RuO_4 and $NaAlO_2$, and then filtered to obtain a residue.

[0063] 5) The residue obtained in step 4) is washed to neutrality. Next, 360 mL of 2mol/L dilute nitric acid is added to completely dissolve the cobalt metal and cobalt oxide in the residue to obtain a cobalt nitrate solution.

[0064] 6) The cobalt nitrate solution obtained in step 5) is adjusted to a Co^{2+} concentration of 20 g/L. The pH of the solution is adjusted to 1.5 by using ammonium water with a mass fraction of 10%, and the temperature of the solution is adjusted to 70°C. Then, the cobalt nitrate solution is slowly mixed with an ammonium oxalate solution having a pH of 1.5 and a temperature of 70°C to precipitate cobalt ions as cobalt oxalate while ammonium water with a mass fraction of 5% is added to the solution to maintain the pH thereof at 1.5 – 1.7. After precipitation is completed, the mixture is hot-filtered and the precipitate is washed with deionized water having a temperature of 65 – 80°C to neutrality. The washed precipitate is dehydrated with absolute ethanol to obtain a pink cobalt oxalate precipitate. The ammonium oxalate solution used is prepared by: adding deionized water until 44.30 g of solid ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$) just dissolves, and adding 5% ammonium water to adjust the solution's pH to 1.5.

[0065] 7) The cobalt oxalate obtained in step 6) is dried in a dryer at 90°C, then put into a fluidized bed reactor and reduced in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 2: 1 at 500°C, 0.8 MPa, and a space velocity of 3000 h^{-1} for 3 hours to obtain cobalt metal.

[0066] 8) The cobalt metal obtained in step 7) is dissolved in a sufficient amount of 2mol/L dilute nitric acid. The obtained mixture is evaporated to obtain crystallized $Co(NO_3)_2 \cdot 6H_2O$. The crystallized $Co(NO_3)_2 \cdot 6H_2O$ is cooled in a dryer and then weighed. The obtained $Co(NO_3)_2 \cdot 6H_2O$ is 25.59 g, the purity of which measured

by GBT 15898-1995 method is 99.26%. The recovery rate of cobalt is 97.90%.

[0067] 9) The filtrate of step 4) and the effluent of step 5) are mixed, and then 20 mL of absolute ethanol is slowly dropped into the mixture and stirred to covert pink ruthenate to black ruthenium hydroxide precipitate. Then the precipitate is filtered and washed with deionized water having a temperature of 65 – 80°C until the effluent becomes neutral and contains no sodium ions. After that, the precipitate is washed with absolute ethanol for three times.

[0068] 10) The black ruthenium hydroxide obtained in step 9) is put into a three-necked flask having stirring and refluxing devices. Concentrated hydrochloric acid with a mass fraction of 36 – 38°C is added to the three-necked flask. The mixture is stirred at 91 – 95°C for 1.5 hours. Then 0.44 g of hydroxylammonium chloride is added to completely dissolve the black ruthenium hydroxide. The obtained solution is allowed to stand for a while, and then is put into a distilling flask and vacuum-distilled at a vacuum degree of 40 ± 1 KPa until the solution is converted into a paste. Next, heating is stopped to let the liquid evaporate spontaneously to obtain 1.603 g of β-$RuCl_3 \cdot xH_2O$ crystal. ICP-AES method determines that the β-$RuCl_3 \cdot xH_2O$ has a ruthenium content of 37.96%. The recovery rate of ruthenium is 95.59%.

[0069] 11) The filtrate obtained from the filtration of the ruthenium hydroxide precipitate and the effluentobtained from washing the precipitate in step 9) are mixed together. The mixture is heated to 65°C, and CO_2 having a purity higher than 99.0% in introduced into the mixture at a flow rate of 1200 mL/min and stirred to produce white aluminum hydroxide precipitate. The reaction is completed when the pH of the solution reaches 10.0. The precipitate is filtered and then washed with deionized water until the effluent becomes neutral and contains no sodium ions. After that, the precipitate is washed with absolute ethanol for three times.

[0070] 12) The aluminum hydroxide is dried at 80°C, then calcined at 600°C to obtain 11.93 g of aluminum oxide having a purity of 98.95%. The recovery rate of aluminum is 92.64%.

Example 3

[0071] 1) 19.96 g of loose particles of waste Co-Ru/Al_2O_3 catalyst is provided. Elemental analysis determines that the catalyst contains Co 18.94%, Ru 2.11%, and Al 37.80%. The loose particles of waste Co-Ru/Al_2O_3 catalyst is put into a muffle furnace and air is introduced into the muffle furnace. The catalyst particles are calcined at 400°C for 5 hours to remove the heavy hydrocarbons on the surface thereof and then cooled down to room temperature.

[0072] 2) The waste catalyst obtained in step 1) is ground into uniform powders and then put into a fluidized bed reactor. The powders are reduced in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 3: 1 at a space velocity of 2000 h^{-1}, a pressure of 0.5 MPa, and a temperature of 350°C for 12 hours.

[0073] 3) The reduced waste catalyst obtained in step 2) and alkali fusing agents are put into a crucible layer by layer. The layers disposed from the bottom of the crucible upward contain 19.19 g of NaOH, the waste catalyst, 9.59 g of NaOH, and 2.66 g of $NaNO_3$, respectively. The crucible is then put into a muffle furnace. The muffle furnace is then heated and kept at 200°C for 1 hour. After that, the temperature of the muffle furnace is increased by 3°C/min to 1000°C using a temperature program to carry out alkali fusion reaction for 2 hours. Next, the muffle furnace is cooled down to room temperature to obtain the alkali fusion product.

[0074] 4) The alkali fusion product obtained in step 3) is leached in deionized water having a temperature of 100°C (in a solid-to-liquid ratio of 1: 4) for 0.5 hour to completely dissolve the water-soluble Na_2RuO_4 and $NaAlO_2$, and then filtered to obtain a residue.

[0075] 5) The residue obtained in step 4) is washed to neutrality. Next, 390 mL of 1mol/L dilute nitric acid is added to completely dissolve the cobalt metal and cobalt oxide in the residue to obtain a cobalt nitrate solution.

[0076] 6) The cobalt nitrate solution obtained in step 5) is adjusted to a Co^{2+} concentration of 20 g/L. The pH of the solution is adjusted to 1.5 by using ammonium water with a mass fraction of 10%, and the temperature of the solution is adjusted to 70°C. Then, the cobalt nitrate solution is slowly mixed with an oxalic acid solution having a pH of 1.5 and a temperature of 70°C to precipitate cobalt ions as cobalt oxalate while ammonium water with a mass fraction of 5% is added to the solution to maintain the pH thereof at 1.5 – 1.7. After precipitation is completed, the mixture is hot-filtered and the precipitate is washed with deionized water having a temperature of 65 – 80°C to neutrality. The washed precipitate is dehydrated with absolute ethanol to obtain a pink cobalt oxalate precipitate. The oxalic acid solution used is prepared by: adding deionized water until 28.29 g of solid oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) just dissolves, and adding 5% ammonium water to adjust the solution's pH to 1.5.

[0077] 7) The cobalt oxalate obtained in step 6) is dried in a dryer at 100°C, then put into a fluidized bed reactor and reduced in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 1: 1 at 400°C, 1 MPa, and a space velocity of 4000 h^{-1} for 4 hours to obtain cobalt metal.

[0078] 8) The cobalt metal obtained in step 7) is dissolved in a sufficient amount of 1mol/L dilute nitric acid. The obtained mixture is evaporated to obtain crystallized

$Co(NO_3)_2 \cdot 6H_2O$. The crystallized $Co(NO_3)_2 \cdot 6H_2O$ is cooled in a dryer and then weighed. The obtained $Co(NO_3)_2 \cdot 6H_2O$ is 18.44 g, the purity of which measured by GBT 15898-1995 method is 99.18%. The recovery rate of cobalt is 97.96%.

[0079] 9) The filtrate of step 4) and the effluent of step 5) are mixed, and then 11 mL of absolute ethanol is slowly dropped into the mixture and stirred to covert pink ruthenate to black ruthenium hydroxide precipitate. Then the precipitate is filtered and washed with deionized water having a temperature of 65 – 80°C until the effluent becomes neutral and contains no sodium ions. After that, the precipitate is washed with absolute ethanol for three times.

[0080] 10) The black ruthenium hydroxide obtained in step 9) is put into a three-necked flask having stirring and refluxing devices. Concentrated hydrochloric acid with a mass fraction of 36 – 38°C is added to the three-necked flask. The mixture is stirred at 91 – 95°C for 1.5 hours. Then 0.29 g of hydroxylammonium chloride is added to completely dissolve the black ruthenium hydroxide. The obtained solution is allowed to stand for a while, and then is put into a distilling flask and vacuum-distilled at a vacuum degree of 40 ± 1 KPa until the solution is converted into a paste. Next, heating is stopped to let the liquid evaporate spontaneously to obtain 1.097 g of β-$RuCl_3 \cdot xH_2O$ crystal. ICP-AES method determines that the β-$RuCl_3 \cdot xH_2O$ has a ruthenium content of 37.06%. The recovery rate of ruthenium is 96.52%.

[0081] 11) The filtrate obtained from the filtration of the ruthenium hydroxide precipitate and the effluentobtained from washing the precipitate in step 9) are mixed together. The mixture is heated to 40°C, and CO_2 having a purity higher than 99.0% in introduced into the mixture at a flow rate of 800 mL/min and stirred to produce white aluminum hydroxide precipitate. The reaction is completed when the pH of the solution reaches 10.0. The precipitate is filtered and then washed

with deionized water until the effluent becomes neutral and contains no sodium ions. After that, the precipitate is washed with absolute ethanol for three times.

[0082] 12) The aluminum hydroxide is dried at 100°C, then calcined at 700°C to obtain 13.56 g of aluminum oxide having a purity of 99.07%. The recovery rate of aluminum is 94.26%.

Example 4

[0083] 1) 20.18 g of loose particles of waste Co-Ru/Al_2O_3 catalyst is provided. Elemental analysis determines that the catalyst contains Co 11.66%, Ru 0.96%, and Al 43.85%. The loose particles of waste Co-Ru/Al_2O_3 catalyst is put into a muffle furnace and air is introduced into the muffle furnace. The catalyst particles are calcined at 450°C for 4 hours to remove the heavy hydrocarbons on the surface thereof and then cooled down to room temperature.

[0084] 2) The waste catalyst obtained in step 1) is ground into uniform powders and then put into a fluidized bed reactor. The powders are reduced in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 1: 1 at a space velocity of 4000 h^{-1}, a pressure of 0.4 MPa, and a temperature of 500°C for 8 hours.

[0085] 3) The reduced waste catalyst obtained in step 2) and alkali fusing agents are put into a crucible layer by layer. The layers disposed from the bottom of the crucible upward contain 30.95 g of KOH, the waste catalyst, 15.47 g of KOH, and 1.45 g of KNO_3, respectively. The crucible is then put into a muffle furnace. The muffle furnace is then heated and kept at 200°C for 1 hour. After that, the temperature of the muffle furnace is increased by 3°C/min to 960°C using a temperature program to carry out alkali fusion reaction for 4 hours. Next, the

muffle furnace is cooled down to room temperature to obtain the alkali fusion product.

[0086] 4) The alkali fusion product obtained in step 3) is leached in deionized water having a temperature of 98°C (in a solid-to-liquid ratio of 1: 3) for 1 hour to completely dissolve the water-soluble K_2RuO_4 and $KAlO_2$, and then filtered to obtain a residue.

[0087] 5) The residue obtained in step 4) is washed to neutrality. Next, 320 mL of 1mol/L dilute nitric acid is added to completely dissolve the cobalt metal and cobalt oxide in the residue to obtain a cobalt nitrate solution.

[0088] 6) The cobalt nitrate solution obtained in step 5) is adjusted to a Co^{2+} concentration of 20 g/L. The pH of the solution is adjusted to 1.5 by using ammonium water with a mass fraction of 10%, and the temperature of the solution is adjusted to 70°C. Then, the cobalt nitrate solution is slowly mixed with an ammonium oxalate solution having a pH of 1.5 and a temperature of 70°C to precipitate cobalt ions as cobalt oxalate while ammonium water with a mass fraction of 5% is added to the solution to maintain the pH thereof at 1.5 – 1.7. After precipitation is completed, the mixture is hot-filtered and the precipitate is washed with deionized water having a temperature of 65 – 80°C to neutrality. The washed precipitate is dehydrated with absolute ethanol to obtain a pink cobalt oxalate precipitate. The ammonium oxalate solution used is prepared by: adding deionized water until 22.68 g of solid ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$) just dissolves, and adding 5% ammonium water to adjust the solution's pH to 1.5.

[0089] 7) The cobalt oxalate obtained in step 6) is dried in a dryer at 110°C, then put into a fluidized bed reactor and reduced in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 4: 1 at 480°C, 0.8 MPa, and a space velocity of 1000 h^{-1} for 3 hours to obtain cobalt metal.

[0090] 8) The cobalt metal obtained in step 7) is dissolved in a sufficient amount of 1mol/L dilute nitric acid. The obtained mixture is evaporated to obtain crystallized $Co(NO_3)_2 \cdot 6H_2O$. The crystallized $Co(NO_3)_2 \cdot 6H_2O$ is cooled in a dryer and then weighed. The obtained $Co(NO_3)_2 \cdot 6H_2O$ is 11.36 g, the purity of which measured by GBT 15898-1995 method is 99.72%. The recovery rate of cobalt is 97.48%.

[0091] 9) The filtrate of step 4) and the effluent of step 5) are mixed, and then 12 mL of absolute ethanol is slowly dropped into the mixture and stirred to covert pink ruthenate to black ruthenium hydroxide precipitate. Then the precipitate is filtered and washed with deionized water having a temperature of 65 – 80°C until the effluent becomes neutral and contains no potassium ions. After that, the precipitate is washed with absolute ethanol for three times.

[0092] 10) The black ruthenium hydroxide obtained in step 9) is put into a three-necked flask having stirring and refluxing devices. Concentrated hydrochloric acid with a mass fraction of 36 – 38°C is added to the three-necked flask. The mixture is stirred at 91 – 95°C for 1 hour. Then 0.13 g of hydroxylammonium chloride is added to completely dissolve the black ruthenium hydroxide. The obtained solution is allowed to stand for a while, and then is put into a distilling flask and vacuum-distilled at a vacuum degree of 40 ± 1 KPa until the solution is converted into a paste. Next, heating is stopped to let the liquid evaporate spontaneously to obtain 0.497 g of β-$RuCl_3 \cdot xH_2O$ crystal. ICP-AES method determines that the β-$RuCl_3 \cdot xH_2O$ has a ruthenium content of 37.39%. The recovery rate of ruthenium is 95.87%.

[0093] 11) The filtrate obtained from the filtration of the ruthenium hydroxide precipitate and the effluentobtained from washing the precipitate in step 9) are mixed together. The mixture is heated to 25°C, and CO_2 having a purity higher than 99.0% in introduced into the mixture at a flow rate of 500 mL/min and stirred

to produce white aluminum hydroxide precipitate. The reaction is completed when the pH of the solution reaches 10.0. The precipitate is filtered and then washed with deionized water until the effluent becomes neutral and contains no potassium ions. After that, the precipitate is washed with absolute ethanol for three times.

[0094] 12) The aluminum hydroxide is dried at 130°C, then calcined at 750°C to obtain 15.76 g of aluminum oxide having a purity of 99.21%. The recovery rate of aluminum is 93.53%.

Examples 5-8

[0095] The recovery processes of Examples 5-8 are identical to that of Example 4, except for that the temperatures of the alkali fusion reactions are 951°C, 970°C, 980°C, and 990°C, respectively. The recovery results are listed in Table 1.

Table 1Co, Ru, and Al recovery at differentalkali fusion temperatures

Example		5	6	7	8
Alkali fusion temperature		951°C	970°C	980°C	990°C
$Co(NO_3)_2·6H_2O$	Weight	11.56 g	11.51 g	11.33 g	11.43 g
	Purity	99.02%	99.38%	99.65%	99.23%
	Recovery rate	98.50%	98.43%	97.16%	97.60%
β-$RuCl_3·xH_2O$	Weight	0.501 g	0.499 g	0.490 g	0.497 g
	Ru content	37.27%	37.18%	38.04%	37.82%
	Recovery rate	96.48%	95.79%	96.26%	97.03%

Aluminum oxide	Weight	15.63 g	15.78 g	15.75 g	16.00 g
	Purity	99.27%	99.51%	99.36%	99.78%
	Recovery rate	92.77%	93.89%	93.62%	94.92%

[0096] The data of Examples 1-8 indicates that when the temperature of the alkali fusion reaction is 900 – 1000°C, the purity of recovered $Co(NO_3)_2 \cdot 6H_2O$ is higher than 99%, and the recovery rates and purities of β-$RuCl_3 \cdot xH_2O$ and aluminum oxide are relatively high. Table 1 indicates that limiting the temperature of the alkali fusion reaction in the range of 900 – 1000°C leads to a complete fusion of the ruthenium,the oxide thereof, and aluminum oxide with the alkali fusing agents. In this way, the complete separation of ruthenium and aluminum from cobalt is fulfilled. This is necessary for achieve ideal recovery results.

Comparative example 1

[0097] To explain the importance of the method for the alkali fusion and the temperature thereof, in this comparative example, the mixing alkali fusion method of the prior art is carried out and the temperature of this method is controlled outside of the temperature range used in this invention.

[0098] *20.04 g of waste Co-Ru/Al_2O_3 catalyst is provided. Elemental analysis* determines that the catalyst contains Co 30.05%, Ru 4.83%, and Al 27.90%.The recovery process is identical to that of Example 1, expect for that step 3) is changed to: The reduced waste catalyst obtained in step 2) and alkali fusing agents (KOH 31.67 g, KNO_3 7.25 g) are mixed uniformly and put into a crucible. The crucible is then put into a muffle furnace. The muffle furnace is then heated

and kept at 200°C for 1 hour to allow the sufficient contact between the reactants.After that, the temperature of the muffle furnace is elevated by 3°C/min to 650°C using a temperature program to carry out alkali fusion reaction for 4 hours. Next, the muffle furnace is cooled down to room temperature to obtain the alkali fusion product. The amount of alkali fusing agents used is 2.5 times the theoretical amount thereof. The other steps are not changed. The obtained $Co(NO_3)_2 \cdot 6H_2O$ is 31.13 g, the purity of which measured by GBT 15898-1995 method is 94.34%. The recovery rate of cobalt is 98.75%. The obtained β-$RuCl_3 \cdot xH_2O$ crystal is 2.248 g. ICP-AES method determines that the β-$RuCl_3 \cdot xH_2O$ has a ruthenium content of 37.22%. The recovery rate of ruthenium is 86.43%. The obtained aluminum oxide is 9.45 g and has anAl_2O_3 content of 99.17%. The recovery rate of aluminum is 88.72%.

[0099] Comparative example 1 shows that the traditional mixing alkali fusion method and a relatively low temperature of alkali fusion lead to a low purity of $Co(NO_3)_2 \cdot 6H_2O$ and low recovery rates of ruthenium and aluminum. It indicates that the traditional mixing alkali fusion method and a relatively low temperature of alkali fusion result in incomplete alkali fusion and, therefore, cause a poor recovery efficiency.

Comparative example 2

[0100] To explain the importance of the temperature of the deionized water used for leaching the alkali fusion product, in this comparative example, the alkali fusion product is leached in deionized water having a temperature of 80°C.

[0101] 20.68 g of waste Co-Ru/Al_2O_3 catalyst is provided. Elemental analysis determines that the catalyst contains Co 25.33%, Ru 3.07%, and Al 32.53%. The

recovery process is identical to that of Example 2, expect for that the alkali fusion product obtained in step 3) is leached in deionized water having a temperature of 80°C (in a solid-to-liquid ratio of 1: 2) for 1 hour. The other steps are not changed. The obtained $Co(NO_3)_2 \cdot 6H_2O$ is 25.31 g, the purity of which measured by GBT 15898-1995 method is 99.14%. The recovery rate of cobalt is 96.99%. The obtained β-$RuCl_3 \cdot xH_2O$ crystal is 1.604 g. ICP-AES method determines that the β-$RuCl_3 \cdot xH_2O$ has a ruthenium content of 37.63%. The recovery rate of ruthenium is 95.09%. The obtained aluminum oxide is 10.34 g and has an Al_2O_3 content of 99.35%. The recovery rate of aluminum is 80.81%.

[0102] Comparative example 1 shows that leaching the alkali fusion product in deionized water having a temperature of 80°C leads to a low recovery rate of aluminum. It indicates that when the temperature of the deionized water used for leaching the alkali fusion product is lower than that in the invention, aluminate in the alkali fusion product cannot be completely leached.

Comparative example 3

[0103] To explain the importance of the parameters in addition of oxalic acid or ammonium oxalate, the temperature for reducing cobalt oxalate, and the parameters for determining the end of the carbonation reaction for separating aluminum hydroxide, in this comparative example, these parameters are controlled at values different from those in the invention.

[0104] 20.01 g of waste Co-Ru/Al_2O_3 catalyst is provided. Elemental analysis determines that the catalyst contains Co 18.94%, Ru 2.11%, and Al 37.80%.

[0105] Steps 1) – 5) are identical to those in Example 3.

[0106] In step 6), the cobalt nitrate solution obtained in step 5) is adjusted to a pH

of 1.5 by using ammonium water with a mass fraction of 10%, and the temperature of the solution is adjusted to 70°C. Then, an oxalic acid solution having a pH of 1.5 and a temperature of 70°C is added into the cobalt nitrate solution and continuously stirred, and the pH of the mixture is adjusted to 1.5 by using ammonium water with a mass fraction of 5%. Next, the mixture is hot-filtered and the precipitate is washed with deionized water having a temperature of 65 – 80°C to neutrality. The washed precipitate is dehydrated with absolute ethanol to obtain a pink cobalt oxalate precipitate. The oxalic acid solution used is prepared by: adding deionized water until 28.29 g of solid oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) just dissolves, and adding 5% ammonium water to adjust the solution's pH to 1.5.

[0107] In step 7), the cobalt oxalate obtained in step 6) is dried in a dryer at 100°C, then put into a fluidized bed reactor and reduced in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 1: 1 at 300°C, 1 MPa, and a space velocity of 4000 h^{-1} for 4 hours to obtain cobalt metal.

[0108] Steps 8) – 10) are identical to those of Example 3.

[0109] In step 11), the filtrate obtained from the filtration of the ruthenium hydroxide precipitate and the effluentobtained from washing the precipitate in step 9) are mixed together. The mixture is heated to 40°C, and CO_2 having a purity higher than 99.0% in introduced into the mixture at a flow rate of 800 mL/min and stirred to produce white aluminum hydroxide precipitate. The reaction is completed when the pH of the solution reaches 11.5. The precipitate is filtered and then washed with deionized water until the effluent becomes neutral and contains no sodium ions. After that, the precipitate is washed with absolute ethanol for three times.

[0110] Step 12) is identical to that of Example 3.

[0111] The obtained $Co(NO_3)_2 \cdot 6H_2O$ is 17.03 g, the purity of which measured by GBT 15898-1995 method is 99.09%. The recovery rate of cobalt is 90.16%. The obtained β-$RuCl_3 \cdot xH_2O$ crystal is 1.085 g. ICP-AES method determines that the β-$RuCl_3 \cdot xH_2O$ has a ruthenium content of 37.22%. The recovery rate of ruthenium is 95.61%. The obtained aluminum oxide is 11.47 g and has a purity of 99.04%. The recovery rate of aluminum is 79.47%.

[0112] Comparative example 3 shows that traditional method of adding oxalic acid or ammonium oxalate at a relatively low temperature leads to a low recovery rate of cobalt; and that if carbonation for separating aluminum hydroxide is ended unsuitably, an incomplete reaction occurs and the recovery rate of aluminum is dramatically reduced.

CLAIMS:

1. A method for recovering metal cobalt, ruthenium, and aluminum from waste Co-Ru/Al_2O_3 catalysts for FIscher-Tropsch synthesis, the method comprising:

1) putting loose particles of a waste Co-Ru/Al_2O_3 catalyst into a muffle furnace, then introducing air into the muffle furnace and calcining the loose particles at 350 – 500°C for 3 – 6 hours to remove heavy hydrocarbons on the surface of the loose particles, and then cooling the loose particles down to room temperature;

2) grinding the loose particles obtained in step 1) into uniform powders, then putting the ground powders into a fluidized bed reactor, then purging the reactor with nitrogen for 0.5 hour, and then reducing the ground powders in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 1: 1 – 4: 1 at a space velocity of 1000 – 4000 h^{-1}, a pressure of 0.1 – 1 MPa, and a temperature of 350 – 800°C for 8 – 12 hours;

3) putting the reduced waste catalysts obtained in step 2) and alkali fusing agents into a crucible layer by layer, then putting the crucible into a muffle furnace, then heating the muffle furnace and keeping it at 200°C for 1 hour, then increasing the temperature of the muffle furnace by 3°C/min to 900 – 1000°C using a temperature program to carry out an alkali fusion reaction for 2 – 4 hours; then cooling the muffle furnace to room temperature to obtain an alkali fusion product;

4) leaching the alkali fusion product obtained in step 3) in deionized

water having a temperature of 90 – 100°C in a solid-to-liquid ratio from 1: 2 to 1: 4 for 0.5 – 1 hour to dissolve water-soluble K_2RuO_4 and $KAlO_2$ or Na_2RuO_4 and $NaAlO_2$, then filtering to obtain a residue;

5) washing the residue obtained in step 4) to neutrality, then adding excess dilute nitric acid to dissolve cobalt metal and cobalt oxide in the residue to obtain a cobalt nitrate solution;

6) adjusting the cobalt nitrate solution obtained in step 5) to a Co^{2+} concentration of 20 g/L, a pH of 1.5, and a temperature of 70°C, then adding oxalic acid solution or ammonium oxalate solution having a pH of 1.5 and a temperature of 70°C to the cobalt nitrate solution to precipitate cobalt ion as cobalt oxalate, wherein the molar amount of the oxalic acid in the oxalic acid solution or ammonium oxalate in the ammonium oxalate solution is 3 – 4 times the molar amount of the cobalt ion; then hot-filtering and washing the residue with deionized water having a temperature of 65 – 80°C; and then dehydrating the residue with absolute ethanol to obtain a pink cobalt oxalate precipitate, wherein the reaction occurring in this step is:

$$Co(NO_3)_2 + H_2C_2O_4 + 2H_2O = CoC_2O_4 \cdot 2H_2O \downarrow + 2HNO_3;$$ or

$$Co(NO_3)_2 + (NH_4)_2C_2O_4 + 2H_2O = CoC_2O_4 \cdot 2H_2O \downarrow + 2NH_4NO_3;$$

7) drying the cobalt oxalate obtained in step 6) in a dryer at 80 – 110°C, then putting the cobalt oxalate to a fluidized bed reactor, then purging the fluidized bed reactor with nitrogen for 0.5 hour, and then reducing the cobalt oxalate in a mixed atmosphere containing H_2 and N_2 in a H_2-to-N_2 volume ratio of 1: 1 – 4: 1 at a temperature of 400 – 560°C, a pressure of 0.1 – 1 MPa, and a space velocity of 1000–4000 h^{-1} for 2 – 4

hours to obtain cobalt metal, wherein the reaction occurring in this step is:

$$CoC_2O_4 \cdot 2H_2O = Co + 2CO_2 + 2H_2O;$$

8) adding dilute nitric acid to the cobalt metal obtained in step 7) until the cobalt metal just completely dissolves, and then evaporating to obtain crystallized $Co(NO_3)_2 \cdot 6H_2O$;

9) mixing a filtrate of step 4) and a effluent of step 5), then dropping reducing agent of absolute ethanol into the mixture and stirring to covert pink ruthenium salt to black ruthenium hydroxide precipitate, then filtering the precipitate and washing the precipitate with deionized water having a temperature of 65 – 80°C until the effluent becomes neutral or contains no potassium or sodium ions, and then washing the precipitate with absolute ethanol for three times, wherein the reaction occurring in this step is:

$$K_2RuO_4 + 2CH_3CH_2OH \xrightarrow{OH^-} Ru(OH)_4\downarrow + 2CH_3CHO + 2KOH; \text{ or}$$

$$Na_2RuO_4 + 2CH_3CH_2OH \xrightarrow{OH^-} Ru(OH)_4\downarrow + 2CH_3CHO + 2NaOH;$$

10) putting the black ruthenium hydroxide obtained in step 9) to a three-necked flask having stirring and refluxing devices; then adding concentrated hydrochloric acid to the three-necked flask and stirring at 91 – 95°C for 1 – 2 hours; then adding hydroxylammonium chloride to completely dissolve the black ruthenium hydroxide; then allowing the obtained solution to stand; then putting the solution to a distilling flask and vacuum-distilling at a vacuum degree of 40 ± 1 KPa until the solution is converted into a paste; then stopping heating to let the liquid evaporate spontaneously to obtain β-$RuCl_3 \cdot xH_2O$ crystal, wherein the reactions occurring in this step are:

$$Ru(OH)_4 + 4HCl = RuCl_4 + 4H_2O;$$

$2RuCl_4 + 2NH_2OH \cdot HCl = 2RuCl_3 + N_2 \uparrow + 4HCl + 2H_2O$;

11) mixing the filtrate obtained in filtration of the ruthenium hydroxide precipitate and the effluentobtained from washing the precipitate in step 9), then introducing CO_2 having a purity higher than 99.0% to the mixed liquid and stirring at 25 – 95°C to produce white aluminum hydroxide precipitate,wherein the reaction is completed when the pH of the solution reaches 10.0; then filtering and washing the precipitate with deionized water having a temperature of 65 – 80°C until the effluent becomes neutral or contains no potassium or sodium ions; and then washing the precipitate with absolute ethanol for three times, wherein the reaction occurring in this step is:

$2KAlO_2 + CO_2 + 3H_2O = K_2CO_3 + 2Al(OH)_3\downarrow$; or

$2NaAlO_2 + CO_2 + 3\ H_2O = Na_2CO_3 + 2Al(OH)_3\downarrow$; and

12) drying the aluminum hydroxide at 80 – 130°C, and then calcining at 500 – 750°C to obtain aluminum oxide, wherein the reaction occurring in this step is:

$2Al(OH)_3 = Al_2O_3 + 3H_2O$.

2. The method of claim 1, wherein:

the alkali fusing agents in step 3) are KOH and KNO_3, or NaOH and $NaNO_3$;

the reactions occurring in step 3) are

$RuO_2 + 2KOH + KNO_3 = K_2RuO_4 + KNO_2 + H_2O$;

$Ru + 2KOH + 3KNO_3 = K_2RuO_4 + 3KNO_2 + H_2O$;

$Al_2O_3 + 2KOH = 2KAlO_2 + H_2O$;

or

$RuO_2 + 2NaOH + NaNO_3 = Na_2RuO_4 + NaNO_2 + H_2O$;

$Ru + 2NaOH + 3NaNO_3 = Na_2RuO_4 + 3NaNO_2 + H_2O$;

$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$; and

the amount of the alkali fusing agents used is 2.5 timesa theoretical amount thereof.

3. The method of claim 1 and 2, wherein:

the alkali fusion in step 3) is layered alkali fusion containing four layers;

from the bottom of the crucible upward, 2/3 of the total amount of KOH, waste catalysts, 1/3 of the total amount of KOH, and KNO_3 are disposed layer by layer; or 2/3 of the total amount of NaOH, waste catalysts, 1/3 of the total amount of NaOH, and $NaNO_3$ are disposed layer by layer; and

layered alkali fusion avoids sintering and evaporation of $RuO_4$for reducing loss of ruthenium.

4. *The method of claim 1 and 2, whereina temperature of alkali fusion in step* 3) is 950 – 1000°C for achieving complete reaction of ruthenium and aluminum oxide with the alkali fusing agents.

5. The method of claim 1 and 2, wherein a reaction time of alkali fusion in step 3) is 3 hours.

6. The method of claim 1 and 2, wherein in step 4), the alkali fusion product is leached in deionized water having a temperature of 96 – 100°C to ensure the ruthenate and, more importantly, the aluminate to be complete leached.

7. The method of claim 1 and 2, wherein in step 4), the solid-to-liquid ratio is 3.

8. The method of claim 1 and 2, wherein a concentration of the dilute nitric acid in steps 5) and 8) is 1 – 3 mol/L.

9. The method of claim 1 and 2, wherein in step 6), the oxalic acid solution or ammonium oxalate solution is slowly dropped into the cobalt nitrate solution while 5% ammonium water is added to keep the pH of the solution at 1.5 – 1.7 to completely precipitatecobalt in the solution to achieve a high recovery rate of cobalt.

10. The method of claim 1 and 2, wherein a temperature for reducing cobalt oxalate in step 7) is 400 – 480°C.

11. The method of claim 1 and 2, wherein in step 9):

the reducing agent of ethanol is excess to complete convert ruthenate into ruthenium hydroxide precipitate;and

a molar ratio of the ruthenium in the waste ruthenium-based catalysts to the absolute ethanol is 1: 3 – 1: 5.

12. The method of claim 1 and 2, wherein a concentrated hydrochloric acid in step 10) has a mass fraction of 36 – 38%.

13. The method of claim 1 and 2, wherein in step 10), a molar ratio of the hydroxylammonium chloride to ruthenium element is 1: 1 for obtainingβ-$RuCl_3 \cdot xH_2O$ having a high purity.

14. The method of claim 1 and 2, wherein in step 11), a reaction temperature is preferable to be 65 – 85°C to produced aluminum hydroxide having a large particle size that is able to be easily filtered.

15. The method of claim 1 and 2, wherein in step 11), a flow rate of the CO_2 is 500 – 1500 mL/min.