

METHOD FOR PREPARING HIGH-PURITY COBALT NITRATE CRYSTALS FROM CO/SiO₂ WASTE CATALYSTS

FIELD OF THE INVENTION

[0001] The invention relates to the preparation of organic substances, and more particularly to a method for preparation of high purity of a crystal of cobalt nitrate from a spent catalyst of Co/SiO₂.

BACKGROUND OF THE INVENTION

[0002] With the increasingly serious environmental pollution and the gradual depletion of oil resources, the development of non-polluting, renewable energy has become a new focus of research. Biomass is the most abundant and cheapest renewable resource, the global yield of lignocelluloses biomass produced from the photosynthesis reaches 150 billion tons each year, of which, approximately 90% have not been utilized by humans. The biomass is used to produce syngas, and the syngas is transformed into synthetic oil by Fischer-Tropsch synthesis reaction. The synthetic oil is conducted with subsequent process and distillation to obtain super clean gasoline and diesel oil that are superior to the European V standard.

[0003] Silica supported cobalt-based Co/SiO₂ catalyst is highly active in catalytic hydrogenation. The reaction rate is not affected by the water pressure, carbon is not prone to be accumulated and intoxication is avoided. The catalyst has low selectivity to CO₂ and high selectivity to long chain hydrocarbon, and the products contain a relatively small amount of oxygenated compounds. Thus, the silica supported cobalt-based

Co/SiO₂ catalyst is a relatively good and extensively studied catalyst system. The cobalt mineral resource in China is very scarce, and the currently detected exploitation quantity is less than 2% of the total exploitation quantity of the world, but the usage thereof in China each year accounts for 25% of the total consumption of the world. Thus, the cobalt mineral resource in China is seriously relied on import, which results in high price and further leading to high production costs of the catalyst. Cobalt is recovered from a spent catalyst in the cobalt-based Fischer-Tropsch synthesis reaction to reproduce the cobalt-based catalyst, which not only decreases the environmental pollution of the waste catalyst and improves the utilization of the cobalt resources, but also largely decreases the production cost of the cobalt catalyst, thereby being environmental friendly and having economic benefit.

[0004] Chinese Patent Application No. 200810055107.0 has disclosed a method for recovering cobalt from cobalt-based Fischer-Tropsch synthesis catalyst, and the method includes: adding deionized water and the spent cobalt-based Fischer-Tropsch catalyst (spent cobalt-based catalyst containing carriers of SiO₂, Al₂O₃, ZrO₂, and TiO₂) to a reactor in a weight ratio of 1-5:1, introducing CO into the reactor, and heating the reactor to a constant temperature to carry out the reaction; decreasing the temperature and discharging CO from the reactor, and discharging a liquid containing cobalt from the reactor; adding an alkali solution to the liquid containing cobalt to allow the cobalt to precipitate in the form of Co(OH)₂; dissolving the precipitate by adding nitric acid, and evaporating a resulting solution to crystallize Co(NO₃)_{2.6}H₂O. In the above method, Co(OH)₂ is first precipitated and is then dissolved by nitric acid to obtain Co(NO₃)_{2.6}H₂O, and the purity of Co(NO₃)_{2.6}H₂O is only 98% below. Chinese Patent Application No. 200910272794.6 discloses a method for preparing highly purified cobalt nitrate using a alumina supported cobalt based spent catalyst in Fischer-Tropsch synthesis, and the method includes: grinding, dissolving by concentrated hydrochloric acid, precipitating

cobalt by sodium sulfide, precipitating cobalt by dicarboxyl, calcinating, dissolving by nitric acid, and evaporating and crystallizing. A final product $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has a purity of 99% above. However, an intermediate CoS produced in the process of reproduction and recover of the spent catalyst has fine granules, which is difficult to filter and easily results in cobalt loss, thereby decreasing the recovery rate of cobalt to approximately 92%.

SUMMARY OF THE INVENTION

[0005] In view of the above-described problems, it is one objective of the invention to provide a method for preparing high purity of a crystal of cobalt nitrate from a spent catalyst of Co/SiO₂. The method features a high recovery rate and high product purity.

[0006] To achieve the above objective, in accordance with one embodiment of the invention, there is provided a method for preparing a crystal of cobalt nitrate from a spent catalyst of Co/SiO₂, the method comprises the following steps:

[0007] 1) calcining a spent catalyst of Co/SiO₂ in the presence of air for between 3 and 6 hours at a temperature of between 350 and 500°C, cooling to room temperature, and grinding the spent catalyst of Co/SiO₂ to yield a powder;

[0008] 2) introducing the powder to a fluidized bed reactor, allowing the powder to be reduced for between 8 and 12 hours in the presence of a mixed gas of H₂ and N₂, a volume ratio of H₂ and N₂ in the mixed gas being between 1: 1 and 4: 1;

[0009] 3) adding a reduced spent catalyst to an excessive dilute nitric acid solution for dissolution, filtering, and collecting a cobalt nitrate solution;

[0010] 4) adjusting a pH value of the cobalt nitrate solution using an alkali solution to be

1.5, adding a preheated oxalic acid solution having a temperature of between 25 and 80°C and a pH value of 1.5 to the cobalt nitrate solution in the presence of a water bath of between 25 and 80°C, adjusting a pH value of a resulting solution using a dilute alkali solution to be 1.5, immediately filtering the resulting solution to yield a precipitate of cobalt oxalate, washing the precipitate of cobalt oxalate using deionized water to yield a neutral filtrate, wherein, a mole number of oxalic acid in the oxalic acid solution is controlled to be between 2 and 3 times a mole number of cobalt in the cobalt nitrate solution;

[0011] 5) drying the precipitate of cobalt oxalate and calcining for between 4 and 8 hours at a temperature of between 550 and 650°C, to yield cobalt oxide;

[0012] 6) dissolving the cobalt oxide with a dilute nitric acid solution to yield a second cobalt nitrate solution; and

[0013] 7) evaporating and crystallizing the second cobalt nitrate solution to yield a crystal of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

[0014] In step 2), a flow rate of the mixed gas is between 1000 and 4000 h^{-1} , a pressure of the fluidized bed reactor is between 0.1 and 1 MPa, and a reaction temperature is between 350 and 750°C.

[0015] In step 3), the dilute nitric acid solution has a concentration of 1 and 3 mol/L.

[0016] In step 6), the dilute nitric acid solution has a concentration of 1 and 3 mol/L.

[0017] In step 4), the water bath has a temperature of 70°C, the oxalic acid solution is preheated to 70°C, and the deionized water is preheated to 70°C.

[0018] Advantages of the present disclosure are summarized as follows. The invention employs a spent catalyst of Co/SiO_2 from Fischer-Tropsch process to prepare a high

purity of a crystal of cobalt nitrate. Heavy hydrocarbons on the surface of the catalyst are removed through aerobic calcination. The spent catalyst is reduced by a reducing mixed gas comprising more than 50 vol. % of hydrogen to yield cobalt. The reduction product is dissolved in the excessive dilute nitric acid to yield the cobalt nitrate solution, which is allowed to react with an oxalic acid solution to produce a precipitate of cobalt oxalate. The oxalic acid solution is excessively added so as to facilitate the precipitation of cobalt thereby improving the conversion of cobalt. In addition, the pH value is controlled at 1.5, to ensure the complete precipitation of cobalt to form cobalt oxalate. The temperature is controlled at between 25 and 80°C, particularly at 70°C. Too much low temperature results in the obtained cobalt oxalate granules are too much fine, which cause a great loss in the next filtering and washing. In the process of precipitating cobalt oxalate, the released hydrogen ions decreases the pH value of the mixture, so, for the benefit of the complete precipitation of cobalt, the pH value at the reaction end should be adjusted to be 1.5. Thereafter, the cobalt oxalate is decomposed under high temperature to yield cobalt oxide, and the latter is added to dilute nitric acid to yield a solution of cobalt nitrate. The solution is evaporated and crystallized to yield high purity of a crystal of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

[0019] The process conditions are strictly controlled in the present disclosure, so that the resulting product has high recovery rate and high purity, and can be directly used for the industrial applications. The method of the present disclosure has simple operation, short flow path, and low requirements on devices and process condition, and thus is suitable for large-scale applications.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0020] For further illustrating the invention, experiments detailing a method for preparing

a crystal of cobalt nitrate from a spent catalyst of Co/SiO₂ are described below. It should be noted that the following examples are intended to describe and not to limit the invention.

Example 1

[0021] 1) 20.01 g of a spent catalyst of Co/SiO₂ comprising 12.1 wt. % of cobalt was collected. The spent catalyst was added to a muffle furnace, air was charged, and the temperature was increased from room temperature to 350°C, and was allowed to keep for 6 hours for removal of heavy hydrocarbons on the surface of the catalyst. The muffle furnace was cooled to room temperature and a resulting product was uniformly ground to yield a powder.

[0022] 2) The powder was introduced to a fluidized bed reactor, and reduced in the presence of a mixed gas of H₂ and N₂ (a volume ratio of H₂ and N₂ in the mixed gas was 1:1) at 400°C and 1 MPa for 10 hours, and the flow rate of the mixed gas is 4000 h⁻¹.

[0023] 3) The reduced spent catalyst was added to 200 mL of a dilute nitric acid solution having a concentration of 3 mol/L. The mixture was stirred, and filtered to collect a filtrate being a cobalt nitrate solution.

[0024] 4) The pH value of the cobalt nitrate solution was adjusted to be 1.5 by saturated NaOH solution. 12.95 g of an oxalic acid solid (H₂C₂O₄·2H₂O) was dissolved in deionized water, and the pH value thereof was adjusted to be 1.5 using 1 wt. % of NaOH solution, whereby yielding an oxalic acid solution. The oxalic acid solution was preheated to 70°C, added dropwise (0.01 mL/s) to the cobalt nitrate solution in the presence of a water bath of 70°C, and stirred for 15 min. The pH value of a resulting solution was adjusted to be 1.5 using 5 wt. % NaOH solution, and the solution was filtered immediately to yield a precipitate of CoC₂O₄. The precipitate of CoC₂O₄ was washed with deionized

water (70°C) to yield a neutral filtrate.

[0025] 5) The precipitate of CoC_2O_4 was dried and calcined in a muffle furnace at 550°C for 5 hours to yield cobalt oxide (Co_2O_3).

[0026] 6) The cobalt oxide was dissolved in 3 mol/L of a nitric acid solution to yield a second cobalt nitrate solution.

[0027] 7) The second cobalt nitrate solution was evaporated in a 70°C water bath. Crystalline films were constantly formed and collected. The crystalline films were dried to a constant weight to yield 11.57 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

[0028] According to the measurement method provided in GBT 15898-1995, the purity of the product of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was 99.40%, and the recovery percent of cobalt in this example was 96.18%.

Example 2

[0029] 1) 10.24 g of a spent catalyst of Co/SiO_2 comprising 18.36 wt. % of cobalt was collected. The spent catalyst was added to a muffle furnace, air was charged, and the temperature was increased from room temperature to 400°C, and was allowed to keep for 4 hours for removal of heavy hydrocarbons on the surface of the catalyst. The muffle furnace was cooled to room temperature and a resulting product was uniformly ground to yield a powder.

[0030] 2) The powder was introduced to a fluidized bed reactor, and reduced in the presence of a mixed gas of H_2 and N_2 (a volume ratio of H_2 and N_2 in the mixed gas was 3:1) at 750°C and 0.5 MPa for 8 hours, and the flow rate of the mixed gas is 3000 h^{-1} .

[0031] 3) The reduced spent catalyst was added to 160 mL of a dilute nitric acid solution having a concentration of 2 mol/L. The mixture was stirred, and filtered to collect a filtrate being a cobalt nitrate solution.

[0032] 4) The pH value of the cobalt nitrate solution was adjusted to be 1.5 by saturated NaOH solution. 10.05 g of an oxalic acid solid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) was dissolved in deionized water, and the pH value thereof was adjusted to be 1.5 using 1 wt. % of NaOH solution, whereby yielding an oxalic acid solution. The oxalic acid solution was preheated to 70°C, added dropwise (0.01 mL/s) to the cobalt nitrate solution in the presence of a water bath of 70°C, and stirred for 15 min. The pH value of a resulting solution was adjusted to be 1.5 using 5 wt. % NaOH solution, and the solution was filtered immediately to yield a precipitate of CoC_2O_4 . The precipitate of CoC_2O_4 was washed with deionized water (70°C) to yield a neutral filtrate.

[0033] 5) The precipitate of CoC_2O_4 was dried and calcined in a muffle furnace at 650°C for 4 hours to yield cobalt oxide (Co_2O_3).

[0034] 6) The cobalt oxide was dissolved in 3 mol/L of a nitric acid solution to yield a second cobalt nitrate solution.

[0035] 7) The second cobalt nitrate solution was evaporated in a 70°C water bath. Crystalline films were constantly formed and collected. The crystalline films were dried to a constant weight to yield 9.04 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

[0036] According to the measurement method provided in GBT 15898-1995, the purity of the product of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was 99.57%, and the recovery percent of cobalt in this example was 96.94%.

Example 3

[0037] 1) 15.62 g of a spent catalyst of Co/SiO₂ comprising 22.64 wt. % of cobalt was collected. The spent catalyst was added to a muffle furnace, air was charged, and the temperature was increased from room temperature to 500°C, and was allowed to keep for 3 hours for removal of heavy hydrocarbons on the surface of the catalyst. The muffle

furnace was cooled to room temperature and a resulting product was uniformly ground to yield a powder.

[0038] 2) The powder was introduced to a fluidized bed reactor, and reduced in the presence of a mixed gas of H_2 and N_2 (a volume ratio of H_2 and N_2 in the mixed gas was 4:1) at $600^\circ C$ and 0.1 MPa for 12 hours, and the flow rate of the mixed gas is 1000 h^{-1} .

[0039] 3) The reduced spent catalyst was added to 300 mL of a dilute nitric acid solution having a concentration of 3 mol/L. The mixture was stirred, and filtered to collect a filtrate being a cobalt nitrate solution.

[0040] 4) The pH value of the cobalt nitrate solution was adjusted to be 1.5 by saturated NaOH solution. 18.91 g of an oxalic acid solid ($H_2C_2O_4 \cdot 2H_2O$) was dissolved in deionized water, and the pH value thereof was adjusted to be 1.5 using 1 wt. % of NaOH solution, whereby yielding an oxalic acid solution. The oxalic acid solution was preheated to $70^\circ C$, added dropwise (0.01 mL/s) to the cobalt nitrate solution in the presence of a water bath of $70^\circ C$, and stirred for 15 min. The pH value of a resulting solution was adjusted to be 1.5 using 5 wt. % NaOH solution, and the solution was filtered immediately to yield a precipitate of CoC_2O_4 . The precipitate of CoC_2O_4 was washed with deionized water ($70^\circ C$) to yield a neutral filtrate.

[0041] 5) The precipitate of CoC_2O_4 was dried and calcined in a muffle furnace at $600^\circ C$ for 8 hours to yield cobalt oxide (Co_2O_3).

[0042] 6) The cobalt oxide was dissolved in 1 mol/L of a nitric acid solution to yield a second cobalt nitrate solution.

[0043] 7) The second cobalt nitrate solution was evaporated in a $70^\circ C$ water bath. Crystalline films were constantly formed and collected. The crystalline films were dried to a constant weight to yield 16.94 g of $Co(NO_3)_2 \cdot 6H_2O$.

[0044] According to the measurement method provided in GBT 15898-1995, the purity of

the product of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was 99.63%, and the recovery percent of cobalt in this example was 96.64%.

Example 4

[0045] 1) 15.62 g of a spent catalyst of Co/SiO_2 comprising 22.64 wt. % of cobalt was collected. The spent catalyst was added to a muffle furnace, air was charged, and the temperature was increased from room temperature to 450°C , and was allowed to keep for 5 hours for removal of heavy hydrocarbons on the surface of the catalyst. The muffle furnace was cooled to room temperature and a resulting product was uniformly ground to yield a powder.

[0046] 2) The powder was introduced to a fluidized bed reactor, and reduced in the presence of a mixed gas of H_2 and N_2 (a volume ratio of H_2 and N_2 in the mixed gas was 3:1) at 350°C and 0.3 MPa for 10 hours, and the flow rate of the mixed gas is 3000 h^{-1} .

[0047] 3) The reduced spent catalyst was added to 300 mL of a dilute nitric acid solution having a concentration of 1 mol/L. The mixture was stirred, and filtered to collect a filtrate being a cobalt nitrate solution.

[0048] 4) The pH value of the cobalt nitrate solution was adjusted to be 1.5 by saturated NaOH solution. 22.12 g of an oxalic acid solid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) was dissolved in deionized water, and the pH value thereof was adjusted to be 1.5 using 1 wt. % of NaOH solution, whereby yielding an oxalic acid solution. The oxalic acid solution was preheated to 80°C , added dropwise (0.01 mL/s) to the cobalt nitrate solution in the presence of a water bath of 80°C , and stirred for 15 min. The pH value of a resulting solution was adjusted to be 1.5 using 5 wt. % NaOH solution, and the solution was filtered immediately to yield a precipitate of CoC_2O_4 . The precipitate of CoC_2O_4 was washed with deionized water (70°C) to yield a neutral filtrate.

[0049] 5) The precipitate of CoC_2O_4 was dried and calcined in a muffle furnace at 600°C for 6 hours to yield cobalt oxide (Co_2O_3).

[0050] 6) The cobalt oxide was dissolved in 1 mol/L of a nitric acid solution to yield a second cobalt nitrate solution.

[0051] 7) The second cobalt nitrate solution was evaporated in a 70°C water bath.

Crystalline films were constantly formed and collected. The crystalline films were dried to a constant weight to yield 17.32 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

[0052] According to the measurement method provided in GB/T 15898-1995, the purity of the product of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was 99.55%, and the recovery percent of cobalt in this example was 97.04%.

CLAIMS

1. A method for preparing a crystal of cobalt nitrate from a spent catalyst of Co/SiO₂, the method comprising the following steps:
 - 1) calcining a spent catalyst of Co/SiO₂ in the presence of air for between 3 and 6 hours at a temperature of between 350 and 500°C, cooling to room temperature, and grinding the spent catalyst of Co/SiO₂ to yield a powder;
 - 2) introducing the powder to a fluidized bed reactor, allowing the powder to be reduced for between 8 and 12 hours in the presence of a mixed gas of H₂ and N₂, a volume ratio of H₂ and N₂ in the mixed gas being between 1: 1 and 4: 1;
 - 3) adding a reduced spent catalyst to an excessive dilute nitric acid solution for dissolution, filtering, and collecting a cobalt nitrate solution;
 - 4) adjusting a pH value of the cobalt nitrate solution using an alkali solution to be 1.5, adding a preheated oxalic acid solution having a temperature of between 25 and 80°C and a pH value of 1.5 to the cobalt nitrate solution in the presence of a water bath of between 25 and 80°C, adjusting a pH value of a resulting solution using a dilute alkali solution to be 1.5, immediately filtering the resulting solution to yield a precipitate of cobalt oxalate, washing the precipitate of cobalt oxalate using deionized water to yield a neutral filtrate, wherein, a mole number of oxalic acid in the oxalic acid solution is controlled to be between 2 and 3 times a mole number of cobalt in the cobalt nitrate solution;
 - 5) drying the precipitate of cobalt oxalate and calcining for between 4 and 8 hours at a temperature of between 550 and 650°C, to yield cobalt oxide;
 - 6) dissolving the cobalt oxide with a dilute nitric acid solution to yield a second cobalt nitrate solution; and

7) evaporating and crystallizing the second cobalt nitrate solution to yield a crystal of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

2. The method of claim 1, **characterized in that** in step 2), a flow rate of the mixed gas is between 1000 and 4000 h^{-1} , a pressure of the fluidized bed reactor is between 0.1 and 1 MPa, and a reaction temperature is between 350 and 750°C.
3. The method of claim 1 or 2, **characterized in that** in step 3), the dilute nitric acid solution has a concentration of 1 and 3 mol/L.
4. The method of claim 1 or 2, **characterized in that** in step 6), the dilute nitric acid solution has a concentration of 1 and 3 mol/L.
5. The method of claim 3, **characterized in that** in step 6), the dilute nitric acid solution has a concentration of 1 and 3 mol/L.
6. The method of claim 1 or 2, **characterized in that** in step 4), the water bath has a temperature of 70°C, the oxalic acid solution is preheated to 70°C, and the deionized water is preheated to 70°C.
7. The method of claim 3, **characterized in that** in step 4), the water bath has a temperature of 70°C, the oxalic acid solution is preheated to 70°C, and the deionized water is preheated to 70°C.
8. The method of claim 4, **characterized in that** in step 4), the water bath has a temperature of 70°C, the oxalic acid solution is preheated to 70°C, and the

deionized water is preheated to 70°C.

9. The method of claim 5, wherein in step 4), the water bath has a temperature of 70°C, the oxalic acid solution is preheated to 70°C, and the deionized water is preheated to 70°C.