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(54) **Titre : CATALYSEUR DE SYNTHESE DE FISCHER-TROPSCH A BASE DE COBALT REVETU DE SUBSTANCES MESOPOREUSES ET SON PROCEDE DE PREPARATION**
(54) **Title: COBALT-BASED FISCHER-TROPSCH SYNTHESIS CATALYST COATED WITH MESOPOROUS MATERIALS AND PREPARATION METHOD THEREFOR**

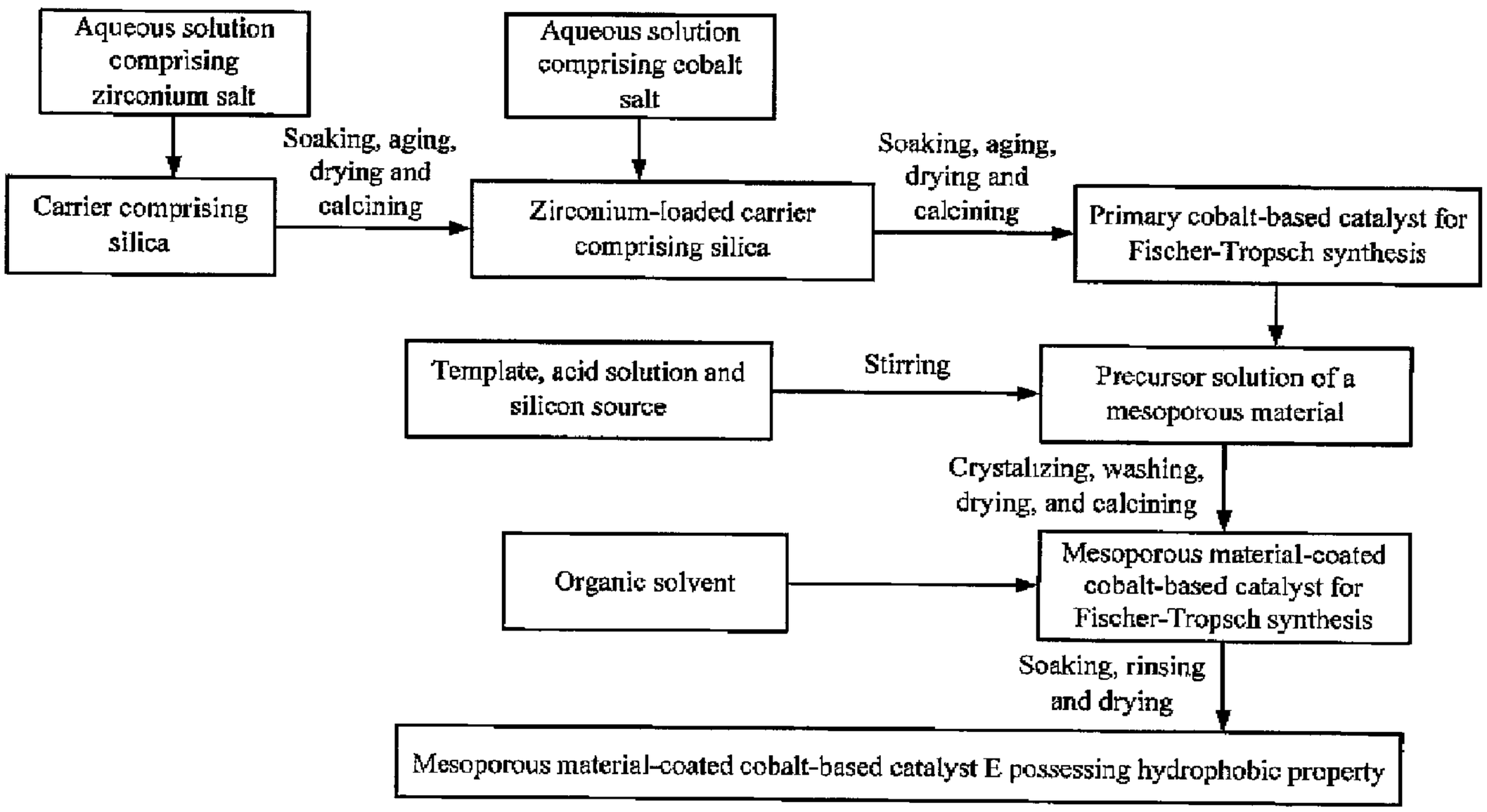

FIG. 1

(57) **Abrégé/Abstract:**
A cobalt-based Fischer-Tropsch synthesis catalyst coated with mesoporous materials and preparation method therefor are disclosed. The catalyst comprises a silica carrier surface-loaded with an active component of cobalt and a selective promoter of

(21) **2 946 638**

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(57) **Abrégé(suite)/Abstract(continued):**
zirconium; the outside of the active component of cobalt and the selective promoter of zirconium is coated with a mesoporous material shell layer. The preparation method comprises preparing silica carrier loaded with zirconium, preparing an initial cobalt-based Fischer-Tropsch synthesis catalyst on the silica carrier base, formulating a precursor solution of mesoporous materials, then dipping, crystallizing, washing, drying and calcining to obtain the cobalt-based Fischer-Tropsch synthesis catalyst coated with mesoporous materials. The active component is coated and protected by the mesoporous material shell layer, the thickness of the shell layer is controllable, the catalyst has long service life, high reactivity and good stability. The pore structure of mesoporous materials provides a channel for diffusing CO and H_2, the selectivity of C_5^+ is high and the selectivity of methane is low. The catalyst is specially applicable to slurry bubble column reactors or continuously stirred tank reactors.

ABSTRACT

A cobalt-based Fischer-Tropsch synthesis catalyst coated with mesoporous materials and preparation method therefor are disclosed. The catalyst comprises a silica carrier surface-loaded with an active component of cobalt and a selective promoter of zirconium; the outside of the active component of cobalt and the selective promoter of zirconium is coated with a mesoporous material shell layer. The preparation method comprises preparing silica carrier loaded with zirconium, preparing an initial cobalt-based Fischer-Tropsch synthesis catalyst on the silica carrier base, formulating a precursor solution of mesoporous materials, then dipping, crystallizing, washing, drying and calcining to obtain the cobalt-based Fischer-Tropsch synthesis catalyst coated with mesoporous materials. The active component is coated and protected by the mesoporous material shell layer, the thickness of the shell layer is controllable, the catalyst has long service life, high reactivity and good stability. The pore structure of mesoporous materials provides a channel for diffusing CO and H2, the selectivity of C5 + is high and the selectivity of methane is low. The catalyst is specially applicable to slurry bubble column reactors or continuously stirred tank reactors.

COBALT-BASED FISCHER-TROPSCH SYNTHESIS CATALYST COATED WITH MESOPOROUS MATERIALS AND PREPARATION METHOD THEREFOR

FIELD OF THE INVENTION

[0001] The invention belongs to the field of the industrially catalyzed Fischer Tropsch synthesis, and particularly relates to a mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis and a method for preparing the same.

BACKGROUND OF THE INVENTION

[0002] Coal, petroleum, and natural gas are important energies on which the existence and development of the human civilization are dependent, and are the safeguard for the national economic sustainable development and security and stability. With the continuous exploit of such energies, the energy crisis becomes serious, and therefore it is an urgent problem for scientists to seek renewable energy. China is a big agricultural country and has a great quantity of different kinds of renewable biomass. It is an important route to substitute the fossil energy by the renewable biomass energy for solving the energy crisis.

[0003] Fischer Tropsch synthesis is a process including gasification the biomass into synthetic gas and transformation of the synthetic gas ($CO+H_2$) into the hydrocarbon in the presence of the catalyst. The route of transforming the biomass into the synthetic gas and producing different kinds of oils by the Fischer Tropsch synthesis is able to effectively solve the energy crisis.

[0004] A basic reaction for the Fischer Tropsch synthesis is $CO+2H_2 \rightarrow (—CH_2—)+H_2O$. As water is produced along with the production of the hydrocarbon, the water concentration may reaches very high in some reactors adopting post mixing, such as the slurry reactor. Currently, the most widely applied industrialized catalyst for the Fischer Tropsch synthesis adopts iron and cobalt as the active components. For the cobalt-based

catalyst for the Fischer Tropsch synthesis, the metal cobalt is the active component of the catalyst and is probably oxidized and deactivated by the product water, which accounts for 50 wt. % of the total products. In addition, the higher the conversion of CO, the deactivation is more serious. For example, Bertole, et al., (J.Catal., 2002, 210: 84-96) has reported that water deactivates the unsupported Co-based catalyst, because that the high water pressure (>0.4 MPa) easily leads to sintering of the catalyst, the specific area of cobalt is reduced, and the activity of the metal is reduced or the absorption of CO on the surface of the catalyst is reduced. Batholomew (Appl. Catal. A, 2001, 212.17-60) also holds the opinion that the water vapor increases the sintering rate of the unsupported catalyst. As the cobalt-based catalyst has relatively high production cost, the catalyst is highly required on the stability, activity, and selectivity, and therefore it is very necessary to prepare water-insensitive catalyst.

[0005] Chinese patent publication number CN101203304A has disclosed a cobalt-based catalyst including oxidized carrier. The oxidized carrier includes aluminum and between 0.01 and 20 wt. % of lithium, in which, lithium exists in the form of lithium aluminate. Such the lithium aluminate-contained carrier has improved water resistance, reduces the formation of dialuminium cobalt tetraoxide, and possesses high activity and selectivity of C_5^+. However, the preparation of the carrier is difficult and requires to be calcined at between 700 and 1000°C for a long time.

[0006] Chinese patent publication number CN1785515A has disclosed a catalyst for synthesizing middle distillate by syngas. The catalyst adopts mesoporous zirconium dioxide as the carrier. The catalyst contains between 5 and 35 wt. % of the metal cobalt, between 0 and 2 wt. % of a noble metal, and between 0 and 10 wt. % of non-noble metallic oxide. The catalyst has high activity, good stability, high selectivity of hydrocarbons containing between 11 and 20 carbons, and good mechanical property. However, the preparation of the mesoporous zirconium dioxide is complicate and costly.

SUMMARY OF THE INVENTION

[0007] In view of the above-described problems, it is one objective of the invention to provide a mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis

and a method for preparing the same. The catalyst has long service life, good stability, and controllable thickness of shell layer.

[0008] To achieve the above objective, in accordance with one embodiment of the invention, there is provided a mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis. The catalyst comprises a silica carrier. A surface of the silica carrier is loaded with an active component cobalt and a selective promoter zirconium. An external of the active component cobalt and the selective promoter zirconium is coated with a shell layer of a mesoporous material.

[0009] The catalyst of the invention is prepared by firstly loading the active component on the surface of the silica carrier by impregnation, and coating the mesoporous material possessing regular pore channels outside the active component, during which, a thickness of the shell layer of the mesoporous material is controllable by changing parameters. The thickness of the shell layer of the mesoporous material is designed to be between 1.8 and 13 μm, and preferably between 2.0 and 6.0 μm. Thus, the shell layer of the mesoporous material encapsulates the active component inside the pore channels to avoid the aggregation and shedding of the active component, and in the meanwhile, the regular pore channel of the mesoporous material provides mass transfer channel for CO and H_2 to ensure the high reactivity of the catalyst.

[0010] Preferably, to avoid the decrease in the activity of the catalyst because of the shedding of the active component in the reaction process or the transfer process, and to prevent the active metal Co from being oxidized and deactivated by water produced in the reaction, the shell layer of the mesoporous material is coated with a hydrophobic layer of an organic compound.

[0011] Preferably, the silica carrier is an inorganic silica gel.

[0012] Preferably, the inorganic silica gel has a specific area of between 150 and 350 m^2/g, an average pore size of between 3 and 50 nm, a pore volume of between 0.7 and 1.7 mL/g, and a particle size of between 20 and 200 μm.

[0013] Preferably, the specific area of the inorganic silica gel is between 200 and 300 m^2/g, the average pore size of the inorganic silica gel is between 8 and 13 nm, the pore

volume of the inorganic silica gel is between 0.75 and 1.3 mL/g, and the particle size of the of the inorganic silica gel is between 40 and 150 μm.

[0014] Preferably, a content of the active component cobalt accounts for between 10 and 25 wt. % of a total weight of the catalyst; and a content of the selective promoter zirconium accounts for between 5 and 10 wt. % of the total weight of the catalyst.

[0015] Preferably, the content of the active component cobalt accounts for between 15 and 20 wt. % of the total weight of the catalyst; and the content of the selective promoter zirconium accounts for between 5 and 8 wt. % of the total weight of the catalyst.

[0016] Preferably, the content of the active component cobalt accounts for between 20 and 25 wt. % of the total weight of the catalyst; and the content of the selective promoter zirconium accounts for between 8 and 10 wt. % of the total weight of the catalyst.

[0017] Preferably, the catalyst has a specific area of between 150 and 400 m^2/g, an average pore size of between 2 and 40 nm, and a pore volume of between 0.5 and 1.4 mL/g.

[0018] Preferably, the catalyst has the specific area of between 250 and 350 m^2/g, the average pore size of between 3 and 9 nm, and the pore volume of between 0.6 and 1.0 mL/g.

[0019] A method for preparing the above catalyst is also provided. The method comprises:

[0020] 1) impregnating the silica carrier into an aqueous solution of a zirconium salt, aging a resulting first mixture for between 12 and 24 hrs, drying the first mixture at a temperature of between 70 and 120°C for between 8 and 24 hrs, calcining the first mixture at a temperature of between 400 and 500°C for between 3 and 12 hrs to yield a zirconium-loaded silica carrier;

[0021] 2) impregnating the zirconium-loaded silica carrier into an aqueous solution of a cobalt salt, aging a resulting second mixture for between 12 and 24 hrs, drying the second mixture at a temperature of between 70 and 120°C for between 8 and 24 hrs, calcining the

second mixture at a temperature of between 400 and 500°C for between 3 and 12 hrs to yield a primary cobalt-based catalyst for Fischer Tropsch synthesis;

[0022] 3) dissolving a template P123 into a nitric acid solution, uniformly stirring a resulting third mixture, adding tetraethyl orthosilicate to the third mixture and continuing stirring for between 12 and 30 hrs to yield a precursor solution of a mesoporous material;

[0023] 4) impregnating the primary cobalt-based catalyst for Fischer Tropsch synthesis into the precursor solution of the mesoporous material to yield a fourth mixture; and crystalizing, washing, drying, and calcining the fourth mixture to yield the mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis.

[0024] Preferably, the method further comprises: 5) impregnating the mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis into a hydrophobic organic solution, sealing a resulting fifth mixture for between 3 and 12 hrs, and selecting an organic solvent to rinse the fifth mixture, drying the fifth mixture at a temperature of between 60 and 90°C for between 3 and 8 hrs to yield a mesoporous material-coated cobalt-based catalyst possessing hydrophobic property.

[0025] Preferably, the zirconium salt of 1) is zirconium nitrate or zirconyl nitrate, and preferably zirconyl nitrate.

[0026] Preferably, the cobalt salt of 2) is cobalt carbonate or cobalt nitrate, and preferably cobalt nitrate.

[0027] Preferably, in 3), a concentration of the nitric acid solution is between 1 and 2 mol/L; the third mixture is stirred at a temperature of between 25 and 45°C until a clarified solution is yielded. Tetraethyl orthosilicate is added to the clarified solution and continued stirring for between 12 and 24 hrs to yield the precursor solution of the mesoporous material.

[0028] The template P123 adopts a known triblock copolymer, i. e., polyoxyethylene-polyoxypropylene-polyoxyethylene, having a molecular formula of PEO-PPO-PEO and a general formula of $EO_{20}PO_{70}EO_{20}$.

[0029] Preferably, in 4), the crystallization is performed at a temperature of between 80 and 130°C for between 20 and 100 hrs at a rotational speed of between 7 and 20 rpm. The washing is performed using deionized water until the fourth mixture is neutral. The drying is performed at a temperature of between 80 and 120°C for between 10 and 20 hrs. The calcination is performed at a temperature of between 400 and 550°C for between 5 and 12 hrs.

[0030] Preferably, in 4), the crystallization is performed at the temperature of between 90 and 120°C for between 30 and 80 hrs at a rotational speed of between 7 and 15 rpm.

[0031] Preferably, in 5), the hydrophobic organic solution is one selected from the group consisting of a polymethyltriethoxysilane, γ-aminopropyltriethoxysilane, and trimethylchlorosilane.

[0032] Preferably, in 5), the hydrophobic organic solution is one selected from the group consisting of n-hexane, acetone, and ethanol.

[0033] Preferably, in 5), the mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis is impregnated into the hydrophobic organic solution and sealed for between 3 and 8 hrs, and then rinsed by the organic solvent for between 2 and 3 times.

[0034] Advantages of the mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis and the method for preparing the same according to embodiments of the invention are summarized as follows:

[0035] The cobalt-based catalyst for the Fischer Tropsch synthesis prepared in the invention overcomes the limitation of the conventional cobalt-based catalyst and the eggshell type catalyst. By firstly coating the shell layer of the mesoporous material on the surface of the catalyst and controlling the thickness of the shell layer by process parameters, the active component of the catalyst is protected, and in the meanwhile the structure of the pore channels of the mesoporous material provides the channels for diffusion of CO and H_2. Furthermore, the introduction of the superhydrophobic organic molecules into the shell layer of the mesoporous material is able to effectively stop the water molecules from inside the channels.

[0036] Not only is the shedding of the active component prevented during the friction, activation, or transfer process of the catalyst, but also the influence of the vapor on the catalyst is avoided in the reaction. Thus, the stability of the catalyst is greatly improved, the service life of the catalyst is effectively prolonged, and the industrial application prospect of the catalyst is good. The Co-based catalyst of the invention possesses long service life, high reactivity, good stability, high selectivity of C_5^+, and low selectivity of methane, and therefore particularly adaptable to bubble column slurry reactor or continuous stirred slurry reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0037] The invention is described hereinbelow with reference to the accompanying drawings, in which:

[0038] FIG. **1** is a flow chart showing a process for preparing a mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis;

[0039] FIG. **2** is a TEM picture showing a thickness of a shell layer of a catalyst B;

[0040] FIG. **3** is a TEM picture showing a thickness of a shell layer of a catalyst C;

[0041] FIG. **4** is a TEM picture showing a thickness of a shell layer of a catalyst D;

[0042] FIG. **5** is a TEM picture showing a thickness of a shell layer of a catalyst E;

[0043] FIG. **6** is a TEM picture showing a thickness of a shell layer of a catalyst F; and

[0044] FIG. **7** is a TEM picture showing a thickness of a shell layer of a catalyst G.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0045] For further illustrating the invention, experiments detailing a mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis are described below. It should be noted that the following examples are intended to describe and not to limit the invention.

Example 1 Preparation of catalyst B

[0046] The catalyst B comprises: an inorganic silica gel as a carrier, Co as an active component, Zr as a promoter, and a shell layer of a mesoporous material. A content of Zr is 5 wt. %, and a content of Co is 20 wt. %.

[0047] Preparation of the catalyst B is as follows:

[0048] 1) 30 g of the inorganic silica gel carrier having a specific area of 280 m^2/g, a pore volume of 1.25 mL/g, an average pore size of 13.6 nm, and a particle size of 40 μm was impregnated into 45 mL of an aqueous solution comprising 5.07 g of $ZrO(NO_3)_2$ to yield a first mixture. The first mixture was then aged in air for 16 hrs, dried at 110°C for 8 hrs, and calcined in a muffle furnace at 450°C for 10 hrs to yield a zirconium-loaded inorganic silica gel carrier.

[0049] 2) The zirconium-loaded inorganic silica gel carrier was impregnated into 63 mL of an aqueous solution comprising 39.43 g of $Co(NO_3)_3 \cdot 6H_2O$ to yield a second mixture. Thereafter, the second mixture was aged in air for 16 hrs, dried at 110°C for 8 hrs, and calcined in the muffle furnace at 450°C for 10 hrs to yield a primary cobalt-based catalyst for Fischer Tropsch synthesis.

[0050] 3) 4 g of a template P123 is dissolved into 140 mL of a nitric acid solution having a concentration of 2 mol/L to yield a third mixture. The third mixture was thereafter stirred at 35°C until a clarified solution was yielded. 8.4 g of tetraethyl orthosilicate was added to the clarified solution and continued stirring for 24 hrs to yield a precursor solution of a mesoporous material.

[0051] 4) The precursor solution of the mesoporous material was transferred to a clean teflon reactor. 10 g of the primary cobalt-based catalyst for Fischer Tropsch synthesis was impregnated into the precursor solution of the mesoporous material to yield a fourth mixture. The fourth mixture was then fixed in a device for hydrothermal synthesis, crystalized at 130°C for 20 hrs at a rotational speed of 7 rpm. The fourth mixture was then washed by deionized water to be neutral, dried at 100°C for 12 hrs, and calcined at 550°C for 5 hrs to yield the catalyst B, i. e., a mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis.

[0052] It was found from detection that the catalyst B has a specific area of 291 m^2/g, a pore volume of 1.16 mL/g, an average pore size of 10.6 nm, and a thickness of the shell layer of 1.8 μm. The thickness of the shell layer of the catalyst B was illustrated in a TEM picture as shown in FIG. 2.

Example 2 Preparation of catalyst C

[0053] The catalyst C comprises: an inorganic silica gel as a carrier, Co as an active component, Zr as a promoter, and the shell layer of the mesoporous material as illustrated in Example 1. A content of Zr is 5 wt. %, and a content of Co is 20 wt. %.

[0054] The preparation of the catalyst C is basically the same as that of Example 1 except that the time for the crystallization in 3) herein was 60 hrs.

[0055] It was found from detection that the catalyst C has a specific area of 301 m^2/g, a pore volume of 0.98 mL/g, an average pore size of 9.5 nm, and a thickness of the shell layer of 5 μm. The thickness of the shell layer of the catalyst C was illustrated in a TEM picture as shown in FIG. 3.

Example 3 Preparation of catalyst D

[0056] The catalyst D comprises: an inorganic silica gel as a carrier, Co as an active component, Zr as a promoter, and the shell layer of the mesoporous material as illustrated in Example 1. A content of Zr is 5 wt. %, and a content of Co is 20 wt. %. The catalyst D has a specific area of 320 m^2/g, a pore volume of 1.02 mL/g, an average pore size of 8.9 nm, and a thickness of the shell layer of 13 μm.

[0057] The preparation of the catalyst D is basically the same as that of Example 1 except that the time for the crystallization in 3) herein was 100 hrs. The thickness of the shell layer of the catalyst D was illustrated in a TEM picture as shown in FIG. 4.

Example 4 Preparation of catalyst E

[0058] The catalyst E comprises: an inorganic silica gel as a carrier, Co as an active component, Zr as a promoter, a shell layer of a mesoporous material, and a hydrophobic organic compound layer of trimethylchlorosilane. A content of Zr is 5 wt. %, and a content of Co is 20 wt. %.

[0059] Preparation of the catalyst E is as follows:

[0060] 1) 30 g of the inorganic silica gel carrier having a specific area of 280 m^2/g, a pore volume of 1.25 mL/g, an average pore size of 13.6 nm, and a particle size of 40 μm was impregnated into 45 mL of an aqueous solution comprising 5.07 g of $ZrO(NO_3)_2$ to yield a first mixture. The first mixture was then aged in air for 16 hrs, dried at 110°C for 8 hrs, and calcined in a muffle furnace at 450°C for 10 hrs to yield a zirconium-loaded inorganic silica gel carrier.

[0061] 2) The zirconium-loaded inorganic silica gel carrier was impregnated into 63 mL of an aqueous solution comprising 39.43 g of $Co(NO_3)_3 \cdot 6H_2O$ to yield a second mixture. Thereafter, the second mixture was aged in air for 16 hrs, dried at 110°C for 8 hrs, and calcined in the muffle furnace at 450°C for 10 hrs to yield a primary cobalt-based catalyst for Fischer Tropsch synthesis.

[0062] 3) coating of the shell layer of the mesoporous material: 4 g of a template P123 is dissolved into 140 mL of a nitric acid solution having a concentration of 2 mol/L to yield a third mixture. The third mixture was thereafter stirred at 35°C until a clarified solution was yielded. 8.4 g of tetraethyl orthosilicate was added to the clarified solution and continued stirring for 24 hrs to yield a precursor solution of a mesoporous material.

[0063] 4) The precursor solution of the mesoporous material was transferred to a clean teflon reactor. 10 g of the primary cobalt-based catalyst for Fischer Tropsch synthesis was impregnated into the precursor solution of the mesoporous material to yield a fourth mixture. The fourth mixture was then fixed in a device for hydrothermal synthesis, crystalized at 130°C for 20 hrs at a rotational speed of 7 rpm. The fourth mixture was then washed by deionized water to be neutral, dried at 100°C for 12 hrs, and calcined at 550°C for 5 hrs to yield a mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis.

[0064] 5) The mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis was impregnated into 200 mL of a trimethylchlorosilane solution, and sealed for 8 hrs. A resulting fifth mixture was then rinsed by anhydrous ethanol for 2 times, dried at 80°C for 8 hrs to yield the catalyst E, i,.e., a mesoporous material-coated cobalt-based catalyst possessing hydrophobic property.

[0065] It was found from detection that the catalyst E has a specific area of 279 m^2/g, a pore volume of 0.86 mL/g, an average pore size of 8.2 nm, and a thickness of the shell layer of 2.5 μm. The thickness of the shell layer of the catalyst E was illustrated in a TEM picture as shown in FIG. 5.

Example 5 Preparation of catalyst F

[0066] The catalyst F comprises: an inorganic silica gel as a carrier, Co as an active component, Zr as a promoter, and a shell layer of the mesoporous material, and a hydrophobic organic compound layer of a polymethyltriethoxysilane. A content of Zr is 5 wt. %, and a content of Co is 20 wt. %.

[0067] The preparation of the catalyst F is basically the same as that of Example 4 except that the polymethyltriethoxysilane is adopted to substitute trimethylchlorosilane of Example 4 as the material for the hydrophobic organic compound layer.

[0068] It was found from detection that the catalyst F has a specific area of 282 m^2/g, a pore volume of 0.91 mL/g, an average pore size of 7.9 nm, and a thickness of the shell layer of 2.1 μm. The thickness of the shell layer of the catalyst F was illustrated in a TEM picture as shown in FIG. 6.

Example 6 Preparation of catalyst G

[0069] The catalyst G comprises: an inorganic silica gel as a carrier, Co as an active component, Zr as a promoter, and a shell layer of the mesoporous material, and a hydrophobic organic compound layer of γ-aminopropyltriethoxysilane. A content of Zr is 5 wt. %, and a content of Co is 20 wt. %.

[0070] The preparation of the catalyst G is basically the same as that of Example **4** except that γ-aminopropyltriethoxysilane is adopted to substitute trimethylchlorosilane of Example **4** as the material for the hydrophobic organic compound layer.

[0071] It was found from detection that the catalyst G has a specific area of 280 m^2/g, a pore volume of 0.83 mL/g, an average pore size of 8.5 nm, and a thickness of the shell layer of 2.3 μm. The thickness of the shell layer of the catalyst G was illustrated in a TEM picture as shown in FIG. 7.

Example 7 Preparation of catalyst H

[0072] The catalyst H comprises: an inorganic silica gel as a carrier, Co as an active component, Zr as a promoter, a shell layer of a mesoporous material, and a hydrophobic organic compound layer of γ-aminopropyltriethoxysilane. A content of Zr is 8 wt. %, and a content of Co is 25 wt. %.

[0073] Preparation of the catalyst H is as follows:

[0074] 1) 30 g of the inorganic silica gel carrier having a specific area of 150 m^2/g, a pore volume of 1.3 mL/g, an average pore size of 8 nm, and a particle size of 90 μm was impregnated into 45 mL of an aqueous solution comprising 16.74 g of $Zr(NO_3)_4 \cdot 5H_2O$ to yield a first mixture. The first mixture was then aged in air for 24 hrs, dried at 120°C for 10 hrs, and calcined in a muffle furnace at 500°C for 3 hrs to yield a zirconium-loaded inorganic silica gel carrier.

[0075] 2) The zirconium-loaded inorganic silica gel carrier was impregnated into 63 mL of an aqueous solution comprising 22.5 g of $CoCO_3$ to yield a second mixture. Thereafter, the second mixture was aged in air for 24 hrs, dried at 120°C for 10 hrs, and calcined in the muffle furnace at 500°C for 3 hrs to yield a primary cobalt-based catalyst for Fischer Tropsch synthesis.

[0076] 3) Coating of the shell layer of the mesoporous material: 4 g of a template P123 is dissolved into 140 mL of a nitric acid solution having a concentration of 1 mol/L to yield a third mixture. The third mixture was thereafter stirred at 45°C until a clarified

solution was yielded. 8.4 g of tetraethyl orthosilicate was added to the clarified solution and continued stirring for 12 hrs to yield a precursor solution of a mesoporous material.

[0077] 4) The precursor solution of the mesoporous material was transferred to a clean teflon reactor. 10 g of the primary cobalt-based catalyst for Fischer Tropsch synthesis was impregnated into the precursor solution of the mesoporous material to yield a fourth mixture. The fourth mixture was then fixed in a device for hydrothermal synthesis, crystalized at 100°C for 24 hrs at a rotational speed of 10 rpm. The fourth mixture was then washed by deionized water to be neutral, dried at 80°C for 20 hrs, and calcined at 400°C for 12 hrs to yield a mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis.

[0078] 5) The mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis was impregnated into 200 mL of a γ-aminopropyltriethoxysilane solution, and sealed for 3 hrs. A resulting fifth mixture was then rinsed by n-hexane for 3 times, dried at 60°C for 3 hrs to yield the catalyst H, i,.e., a mesoporous material-coated cobalt-based catalyst possessing hydrophobic property.

[0079] It was found from detection that the catalyst H has a specific area of 200 m^2/g, a pore volume of 1.0 mL/g, an average pore size of 4.0 nm, and a thickness of the shell layer of 2.0 μm.

Example 8 Preparation of catalyst I

[0080] The catalyst I comprises: an inorganic silica gel as a carrier, Co as an active component, Zr as a promoter, a shell layer of a mesoporous material, and a hydrophobic organic compound layer of γ-aminopropyltriethoxysilane. A content of Zr is 10 wt. %, and a content of Co is 10 wt. %.

[0081] Preparation of the catalyst I is as follows:

[0082] 1) 30 g of the inorganic silica gel carrier having a specific area of 300 m^2/g, a pore volume of 0.75 mL/g, an average pore size of 13 nm, and a particle size of 150 μm was impregnated into 45 mL of an aqueous solution comprising 9.5 g of zirconyl nitrate

to yield a first mixture. The first mixture was then aged in air for 12 hrs, dried at 70°C for 24 hrs, and calcined in a muffle furnace at 400°C for 12 hrs to yield a zirconium-loaded inorganic silica gel carrier.

[0083] 2) The zirconium-loaded inorganic silica gel carrier was impregnated into 63 mL of an aqueous solution comprising 7.55 g of $CoCO_3$ to yield a second mixture. Thereafter, the second mixture was aged in air for 12 hrs, dried at 70°C for 24 hrs, and calcined in the muffle furnace at 400°C for 12 hrs to yield a primary cobalt-based catalyst for Fischer Tropsch synthesis.

[0084] 3) Coating of the shell layer of the mesoporous material: 4 g of a template P123 is dissolved into 140 mL of a nitric acid solution having a concentration of 2 mol/L to yield a third mixture. The third mixture was thereafter stirred at 25°C until a clarified solution was yielded. 8.4 g of tetraethyl orthosilicate was added to the clarified solution and continued stirring for 30 hrs to yield a precursor solution of a mesoporous material.

[0085] 4) The precursor solution of the mesoporous material was transferred to a clean teflon reactor. 10 g of the primary cobalt-based catalyst for Fischer Tropsch synthesis was impregnated into the precursor solution of the mesoporous material to yield a fourth mixture. The fourth mixture was then fixed in a device for hydrothermal synthesis, crystalized at 80°C for 70 hrs at a rotational speed of 15 rpm. The fourth mixture was then washed by distilled water to be neutral, dried at 120°C for 10 hrs, and calcined at 500°C for 8 hrs to yield a mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis.

[0086] 5) The mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis was impregnated into 200 mL of a γ-aminopropyltriethoxysilane solution, and sealed for 15 hrs. A resulting fifth mixture was then rinsed by acetone for 2 times, dried at 90°C for 5 hrs to yield the catalyst I, i,.e., a mesoporous material-coated cobalt-based catalyst possessing hydrophobic property.

[0087] It was found from detection that the catalyst I has a specific area of 350 m^2/g, a pore volume of 0.6 mL/g, an average pore size of 9 nm, and a thickness of the shell layer of 6 μm.

Comparative example 1 Conventional catalyst A

[0088] The conventional catalyst A comprises: an inorganic silica gel as a carrier, Co as an active component, and Zr as a promoter. A content of Zr is 5 wt. %, and a content of Co is 20 wt. %.

[0089] Preparation of the catalyst A is as follows:

[0090] 1) 30 g of the inorganic silica gel carrier having a specific area of 280 m^2/g, a pore volume of 1.25 mL/g, an average pore size of 13.6 nm, and a particle size of 40 μm was impregnated into 45 mL of an aqueous solution comprising 5.07 g of $ZrO(NO_3)_2$ to yield a first mixture. The first mixture was then aged in air for 16 hrs, dried at 110°C for 8 hrs, and calcined in a muffle furnace at 450°C for 10 hrs to yield a zirconium-loaded inorganic silica gel carrier.

[0091] 2) The zirconium-loaded inorganic silica gel carrier was impregnated into 63 mL of an aqueous solution comprising 39.43 g of $Co(NO_3)_3 \cdot 6H_2O$ to yield a second mixture. Thereafter, the second mixture was aged in air for 16 hrs, dried at 110°C for 8 hrs, and calcined in the muffle furnace at 450°C for 10 hrs to yield a cobalt-based catalyst A for Fischer Tropsch synthesis.

[0092] Evaluation results of the synthesis of the liquid hydrocarbon using biomass respectively in the presence of the catalysts B-I and the conventional catalyst A are compared in Table 1.

[0093] It was known from Table 1 that when the conventional catalyst is coated with a shell layer of the mesoporous material, the conversion of CO is not visibly changes and approximately between 55 and 65 wt. %. This is primarily because that although the shell layer of the mesoporous material has a certain thickness, the particle size of the catalyst is relatively small, the mass transfer resistance is also relatively small, and the shell layer of the mesoporous material provides mass transfer channels for H_2 and CO. While the selectivity of the liquid hydrocarbon is slightly improved and the selectivity of methane is slightly decreased, which may be because that the shell layer of the mesoporous material is capable of preventing the active component from shedding as a result of friction in the process of activation and transfer. In addition, the shell layer of the mesoporous material

is capable of stopping water of the bulk from directly contacting the active center. After hydrophobic organic modification of the surface of the shell layer, the selectivity of the liquid hydrocarbon increases, and the selectivity of the methane is obviously decreased, which indicates that the introduction of the hydrophobic substance into the shell layer of the mesoporous material is capable of effectively preventing the catalyst from being oxidized by water and deactivated. Once the small molecule water is produced, it is blew out of the shell layer along with the hydrophobic organic compound layer. Thus, the Cobalt-based catalyst prepared in the invention has relatively high reactivity, high selectivity of C_5^+, and low selectivity of methane.

[0094] Particularly after the introduction of the hydrophobic substance into the shell layer of the mesoporous material, the selectivity of the liquid hydrocarbon is much greatly improved. Because the molecular structure of the organic compound in the modified catalyst F is relatively smaller, the hydrophobicity of the modified catalyst F is relatively poor than those of the catalysts E and G. The price of the organic compound in the modified catalyst E is higher than the modified catalyst G, and has easy volatilization and strong corrosivity. The catalyst H has relatively small specific area and pore size, and the activity thereof and the selectivity of the hydrocarbon are slightly reduced. The catalyst I has relatively large particle size and thick shell layer, a certain mass transfer resistance, and reduced conversion of CO, but the crystallization time of the catalyst I is relatively long. Based on the above ground, the catalyst G is superior than the catalysts E, F, H, and I.

Table 1 Comparison of activities and selectivities among catalysts A-I

Catalyst	X_{CO}/%	S(CH_4)/%	S(C_2-C_4)%	S(C_5^+)/%	S(CO_2)/%
A	60.3	14.5	7.1	76.9	1.5
B	61.0	10.6	7.1	81.1	1.2
C	60.5	10.2	7.5	81.0	1.3
D	60.0	10.7	7.0	80.9	1.4
E	62.4	5.5	6.3	87.2	1.0
F	63.1	9.2	6.9	82.9	1.0
G	64.5	5.2	6.3	87.5	0.9
H	60.0	7.6	7.1	84.3	1.0

I	55.3	7.8	7.5	83.8	0.9

[0095] For better explaining the advantage of the invention, long-term stabilities of the conventional catalyst A and the catalysts B and G of the invention are studied, results of which are listed in Table 2 and 3.

Table 2 Comparison of conversions of CO among catalysts after long-term operation

Catalyst	t=500h	t=800h	t=1000h	t=1500h	t=2000h	t=2500h
A	60.3%	58.6%	50.4%	40.3%	31.8%	25.8%
B	61.0%	60.9%	59.9%	56.9%	50.2%	40.1%
G	64.5%	64.4%	64.3%	63.9%	62.2%	60.1%

Table 3 Comparison of selectivities of liquid hydrocarbon (C_5+) among catalysts after long-term operation

Catalyst	t=500h	t=800h	t=1000h	t=1500h	t=2000h	t=2500h
A	76.9%	76.8%	71.3%	63.5%	58.1%	53.5%
B	81.0%	81.1%	79.5%	76.4%	70.6%	67.8%
G	87.4%	87.5%	87.5%	86.5%	85.9%	84.9%

[0096] It is known from Table 2 and 3 that when the reaction time of the conventional catalyst A in the absence of any modification reaches 800 hrs, the activity of the conventional catalyst A begins to decrease, which may because Co on the surface of the catalyst is shed off under the action of friction after long-term stirring, and water produced from the reaction make the catalyst oxidized and deactivated. When the conventional catalyst is coated with the shell layer of the mesoporous material to yield the catalysts B and G, the reaction time is prolonged to 1500 hrs and the conversion of CO still remains 55% above. This is probably because the shell layer of the catalyst is able to protect the active center of the catalyst and prevent the metal part of the catalyst from being shed off under the friction. Particularly for the catalyst G modified by the hydrophobic organic substances, when the reaction operates for 2500 hrs, the activity of the catalyst is still high, and the conversion of CO still remains approximately 60%, and the selectivity of the liquid hydrocarbon is approximately 85%, which indicates that the

service life of the catalyst is obviously prolonged. This is because the introduction of the hydrophobic group into the shell layer of the mesoporous material is able to effective prevent the metal part from being shed off the catalyst, and effectively prevent water from contacting with the active center, which may otherwise make the catalyst deactivated. In summary, the Co-based catalyst prepared in the invention has great stability and effectively prolonged service life.

CLAIMS

1. A mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis, the catalyst comprising a silica carrier, **characterized in that**

a surface of the silica carrier is loaded with an active component cobalt and a selective promoter zirconium; and

an external of the active component cobalt and the selective promoter zirconium is coated with a shell layer of a mesoporous material.

2. The catalyst of claim 1, **characterized in that** the shell layer of the mesoporous material is coated with a hydrophobic layer of an organic compound.

3. The catalyst of claim 1 or 2, **characterized in that** the silica carrier is an inorganic silica gel.

4. The catalyst of claim 3, **characterized in that** the inorganic silica gel has a specific area of between 150 and 350 m^2/g, an average pore size of between 3 and 50 nm, a pore volume of between 0.7 and 1.7 mL/g, and a particle size of between 20 and 200 μm.

5. The catalyst of claim 4, **characterized in that** the specific area of the inorganic silica gel is between 200 and 300 m^2/g, the average pore size of the inorganic silica gel is between 8 and 13 nm, the pore volume of the inorganic silica gel is between 0.75 and 1.3 mL/g, and the particle size of the of the inorganic silica gel is between 40 and 150 μm.

6. The catalyst of claim 1 or 2, **characterized in that** a content of the active

component cobalt accounts for between 10 and 25 wt. % of a total weight of the catalyst; and a content of the selective promoter zirconium accounts for between 5 and 10 wt. % of the total weight of the catalyst.

7. The catalyst of claim 6, **characterized in that** the content of the active component cobalt accounts for between 15 and 20 wt. % of the total weight of the catalyst; and the content of the selective promoter zirconium accounts for between 5 and 8 wt. % of the total weight of the catalyst.

8. The catalyst of claim 6, **characterized in that** the content of the active component cobalt accounts for between 20 and 25 wt. % of the total weight of the catalyst; and the content of the selective promoter zirconium accounts for between 8 and 10 wt. % of the total weight of the catalyst.

9. The catalyst of claim 1 or 2, **characterized in that** a thickness of the shell layer of the mesoporous material is between 1.8 and 13 μm.

10. The catalyst of claim 9, **characterized in that** the thickness of the shell layer of the mesoporous material is between 2.0 and 6.0 μm.

11. The catalyst of claim 1 or 2, **characterized in that** the catalyst has a specific area of between 150 and 400 m^2/g, an average pore size of between 2 and 40 nm, and a pore volume of between 0.5 and 1.4 mL/g.

12. The catalyst of claim 11, **characterized in that** the catalyst has the specific area of between 250 and 350 m^2/g, the average pore size of between 3 and 9 nm, and the pore volume of between 0.6 and 1.0 mL/g.

13. A method for preparing the catalyst of claim 1, comprising:

1) impregnating the silica carrier into an aqueous solution of a zirconium salt, aging a resulting first mixture for between 12 and 24 hrs, drying the first mixture at a temperature of between 70 and 120°C for between 8 and 24 hrs, calcining the first mixture at a temperature of between 400 and 500°C for between 3 and 12 hrs to yield a zirconium-loaded silica carrier;

2) impregnating the zirconium-loaded silica carrier into an aqueous solution of a cobalt salt, aging a resulting second mixture for between 12 and 24 hrs, drying the second mixture at a temperature of between 70 and 120°C for between 8 and 24 hrs, calcining the second mixture at a temperature of between 400 and 500°C for between 3 and 12 hrs to yield a primary cobalt-based catalyst for Fischer Tropsch synthesis;

3) dissolving a template P123 into a nitric acid solution, uniformly stirring a resulting third mixture, adding tetraethyl orthosilicate to the third mixture and continuing stirring for between 12 and 30 hrs to yield a precursor solution of a mesoporous material;

4) impregnating the primary cobalt-based catalyst for Fischer Tropsch synthesis into the precursor solution of the mesoporous material to yield a fourth mixture; and crystalizing, washing, drying, and calcining the fourth mixture to yield the mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis.

14. The method of claim 13, further comprising: 5) impregnating the mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis into a hydrophobic organic solution, sealing a resulting fifth mixture for between 3 and 12 hrs, and selecting an organic solvent to rinse the fifth mixture, drying the fifth mixture at a temperature of between 60 and 90°C for between 3 and 8 hrs to yield a mesoporous material-coated cobalt-based catalyst possessing hydrophobic

property.

15. The method of claim 13 or 14, **characterized in that** the zirconium salt of 1) is zirconium nitrate or zirconyl nitrate.

16. The method of claim 13 or 14, **characterized in that** the cobalt salt of 2) is cobalt carbonate or cobalt nitrate.

17. The method of claim 13 or 14, **characterized in that** in 3), a concentration of the nitric acid solution is between 1 and 2 mol/L; the third mixture is stirred at a temperature of between 25 and 45°C until a clarified solution is yielded; and tetraethyl orthosilicate is added to the clarified solution and continued stirring for between 12 and 24 hrs to yield the precursor solution of the mesoporous material.

18. The method of claim 13 or 14, **characterized in that** in 4), the crystallization is performed at a temperature of between 80 and 130°C for between 20 and 100 hrs at a rotational speed of between 7 and 20 rpm; the washing is performed using deionized water until the fourth mixture is neutral; the drying is performed at a temperature of between 80 and 120°C for between 10 and 20 hrs; and the calcination is performed at a temperature of between 400 and 550°C for between 5 and 12 hrs.

19. The method of claim 18, **characterized in that** in 4), the crystallization is performed at the temperature of between 90 and 120°C for between 30 and 80 hrs at a rotational speed of between 7 and 15 rpm.

20. The method of claim 14, **characterized in that** in 5), the hydrophobic organic

solution is one selected from the group consisting of a polymethyltriethoxysilane, γ-aminopropyltriethoxysilane, and trimethylchlorosilane.

21. The method of claim 14, **characterized in that** in 5), the hydrophobic organic solution is one selected from the group consisting of n-hexane, acetone, and ethanol.

22. The method of claim 20, **characterized in that** in 5), the mesoporous material-coated cobalt-based catalyst for Fischer Tropsch synthesis is impregnated into the hydrophobic organic solution and sealed for between 3 and 8 hrs, and then rinsed by the organic solvent for between 2 and 3 times.

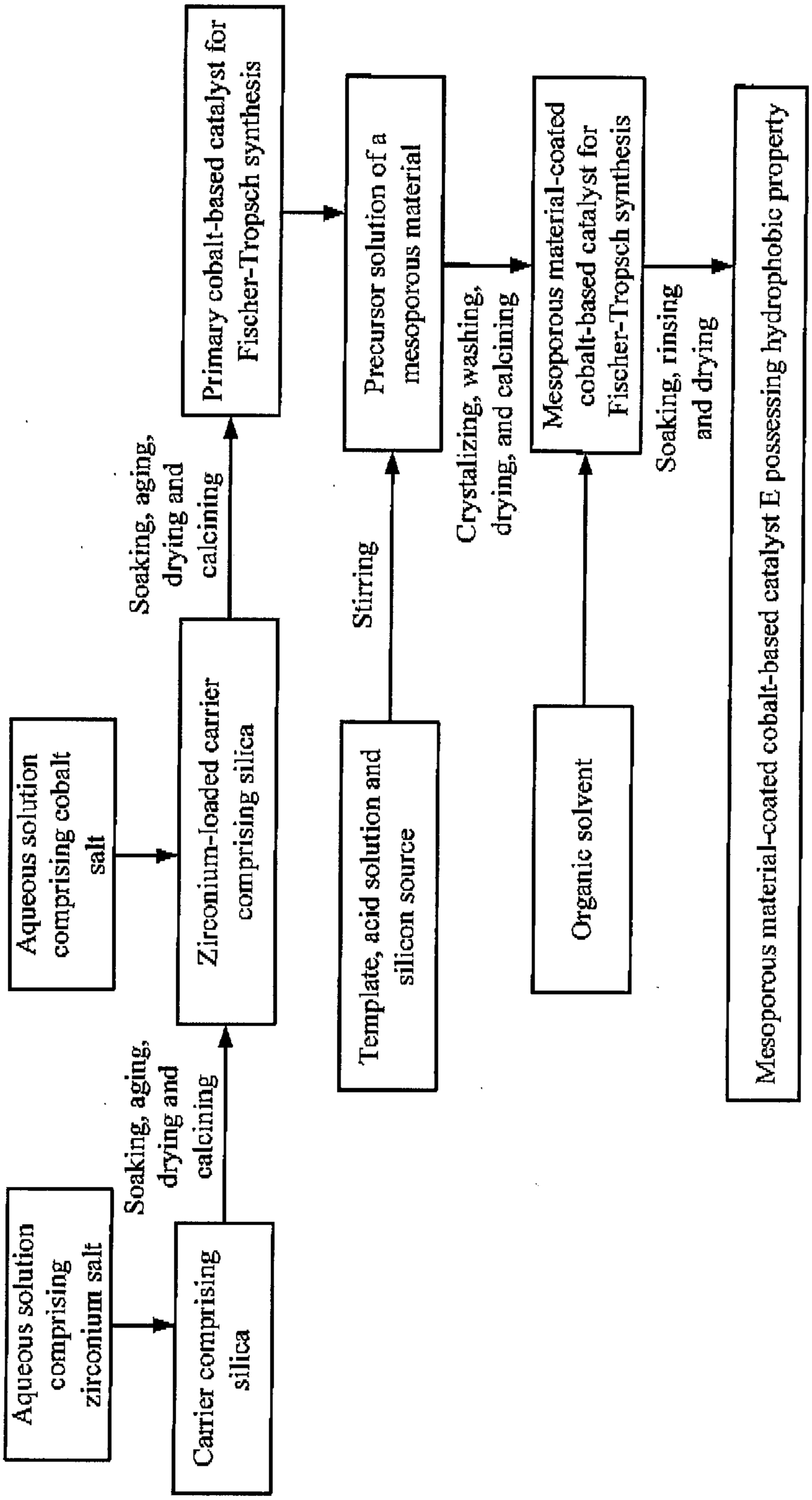
Aqueous solution comprising zirconium salt
Carrier comprising silica
Soaking, aging, drying and calcining
Aqueous solution comprising cobalt salt
Zirconium-loaded carrier comprising silica
Soaking, aging, drying and calcining
Primary cobalt-based catalyst for Fischer-Tropsch synthesis
Template, acid solution and silicon source
Stirring
Precursor solution of a mesoporous material
Crystalizing, washing, drying, and calcining
Organic solvent
Soaking, rinsing and drying
Mesoporous material-coated cobalt-based catalyst for Fischer-Tropsch synthesis
Mesoporous material-coated cobalt-based catalyst E possessing hydrophobic property

FIG. 1

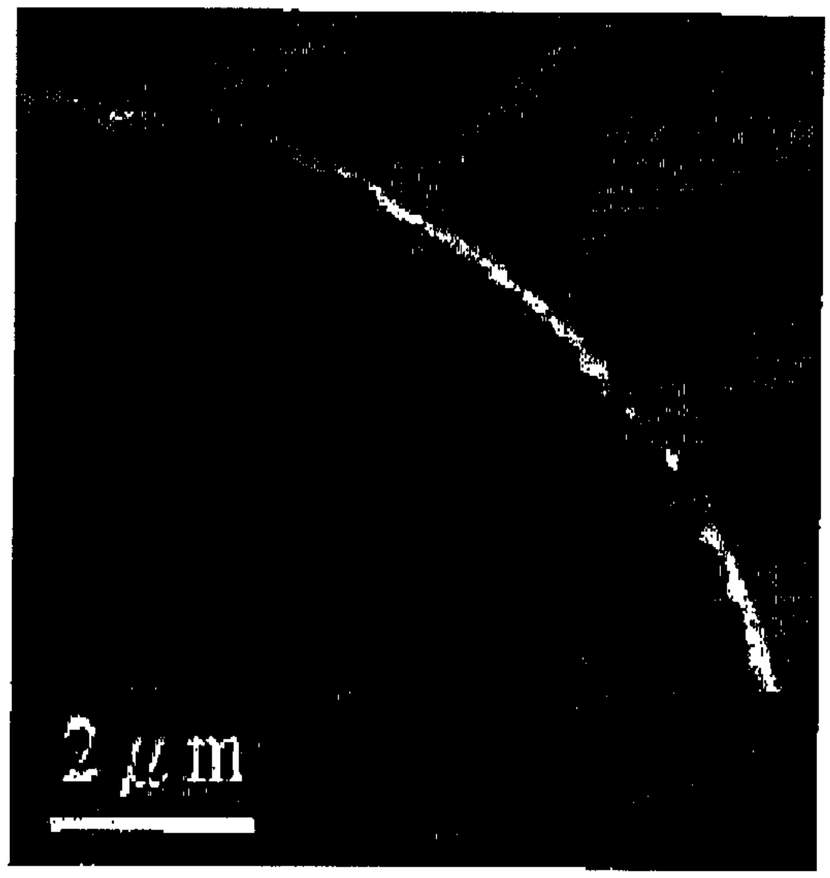

FIG. 2

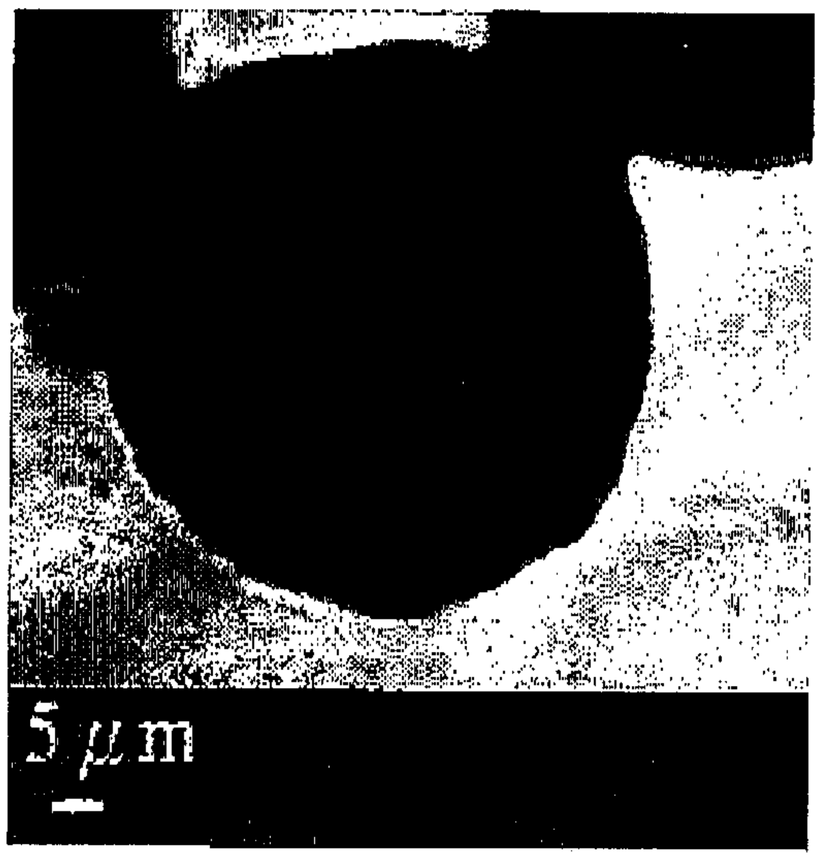

FIG. 3

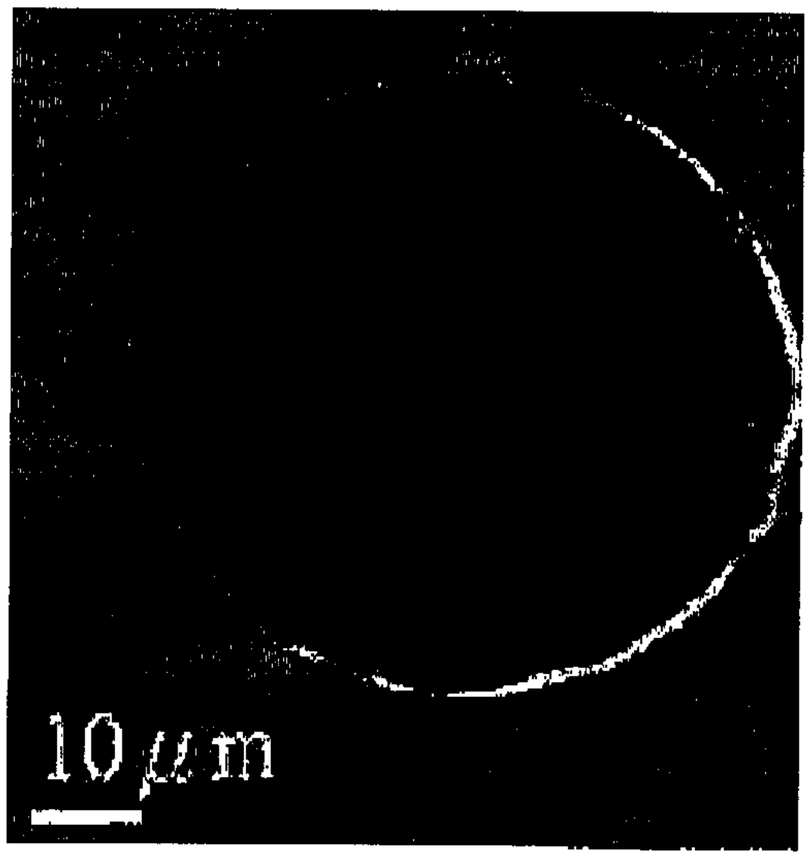

FIG. 4

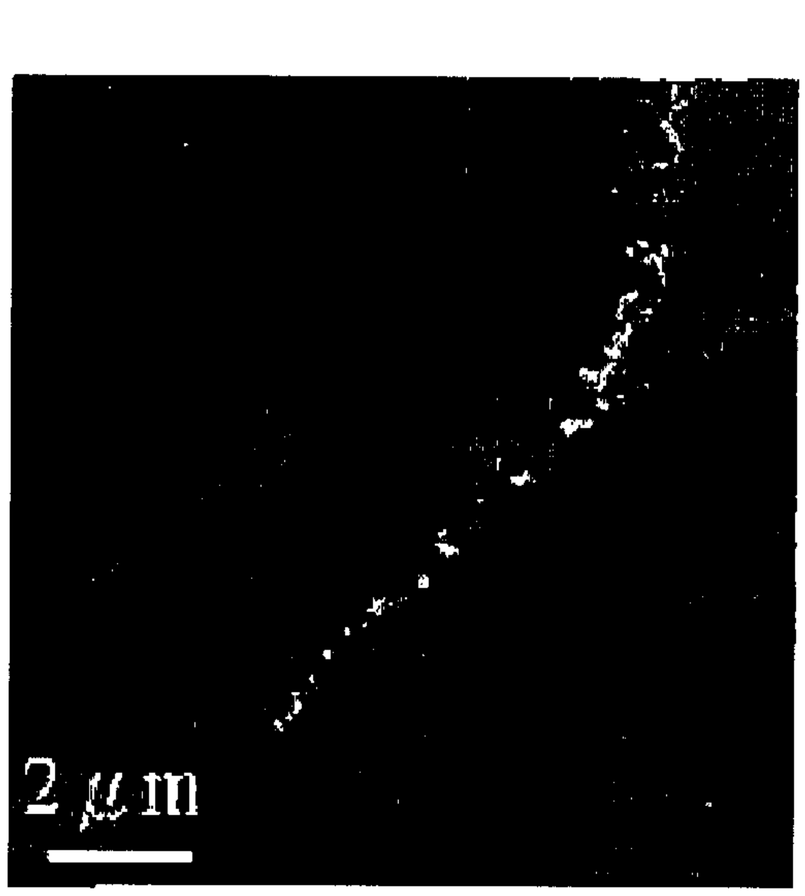

FIG. 5

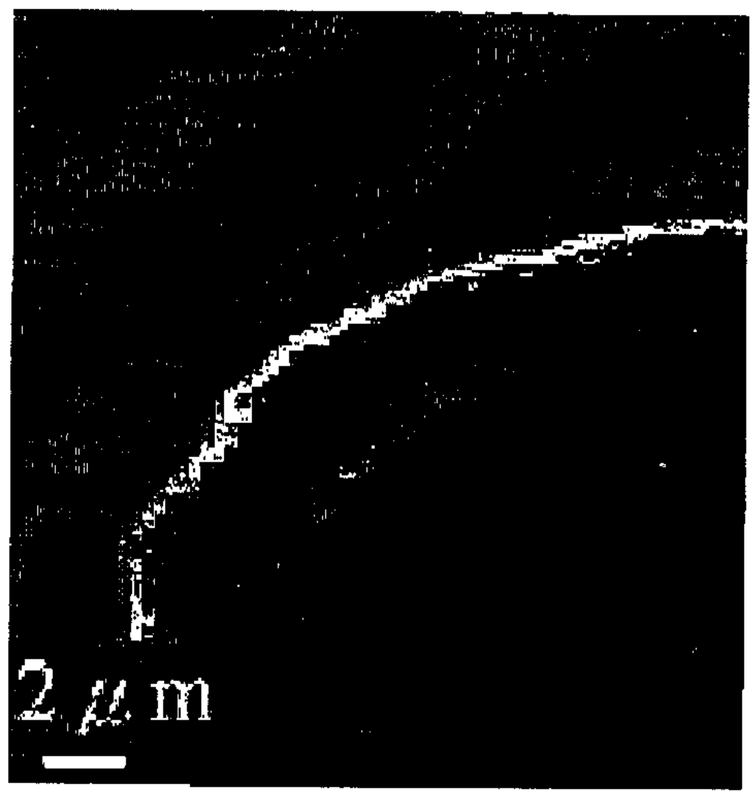

FIG. 6

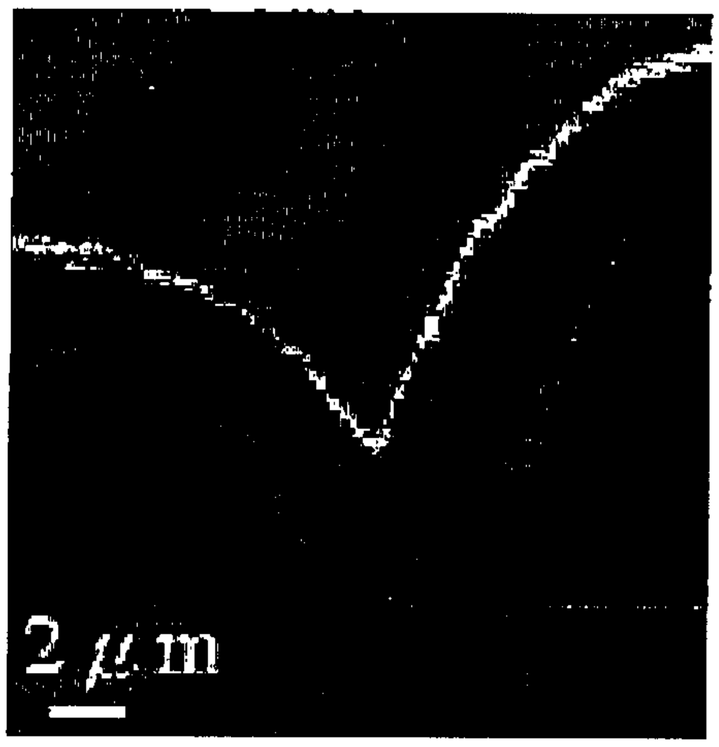

FIG. 7

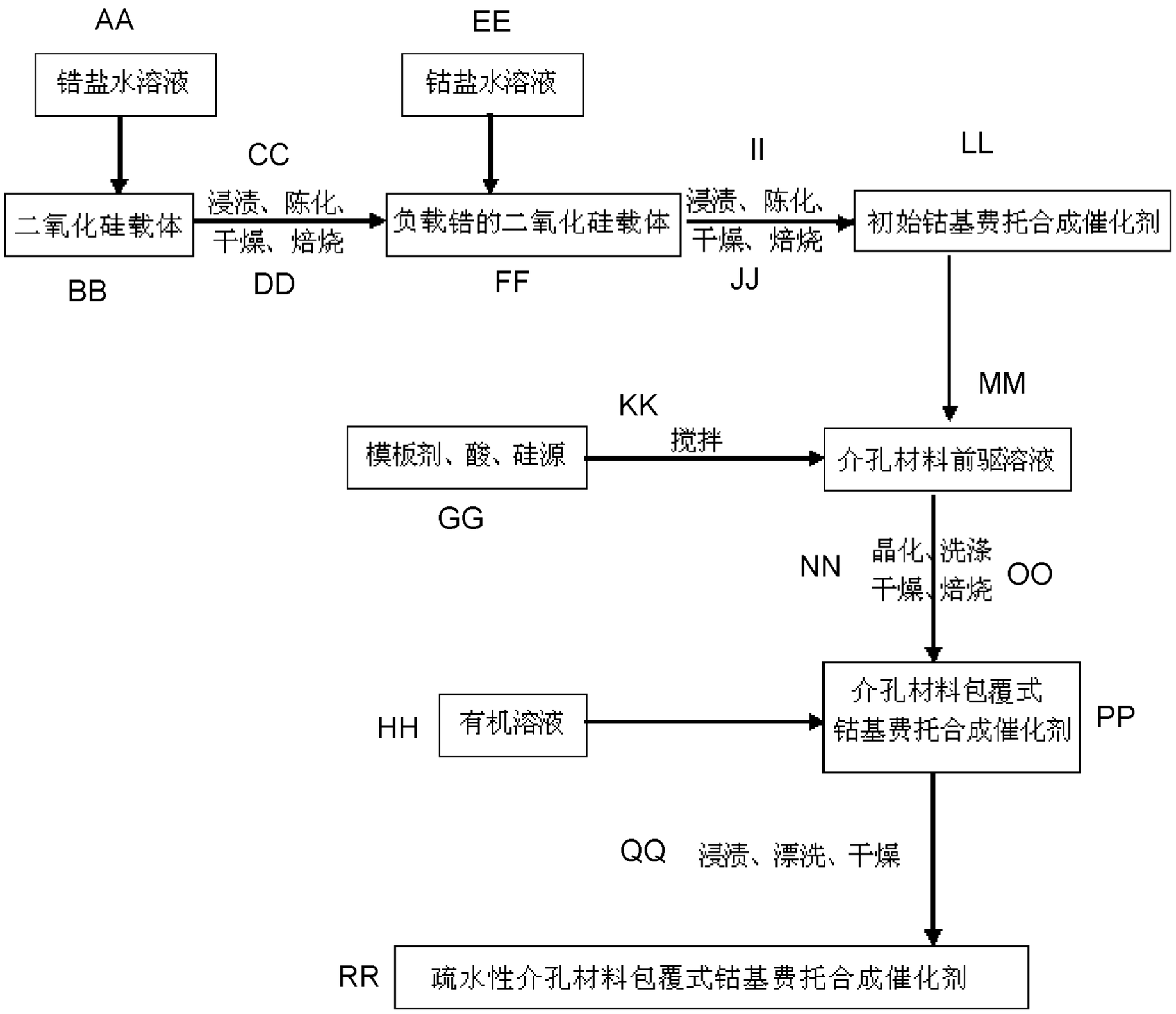

图 1 / FIG.1

AA AQUEOUS SOLUTION OF ZIRCONIUM SALTS
BB SILICA CARRIER
CC, II DIPPING AND AGING
DD, JJ DRYING AND CALCINING
EE AQUEOUS SOLUTION OF COBALT SALTS
FF SILICA CARRIER LOADED WITH ZIRCONIUM
GG TEMPLATING AGENTS, ACID AND SILICON SOURCE
HH ORGANIC SOLVENTS
KK STIRRING
LL INITIAL COBALT-BASED FISCHER-TROPSCH SYNTHESIS CATALYST
MM PRECURSOR SOLUTION OF MESOPOROUS MATERIALS
NN CRYSTALLIZING AND DRYING
OO WASHING AND CALCINING
PP COBALT-BASED FISCHER-TROPSCH SYNTHESIS CATALYST COATED WITH MESOPOROUS MATERIALS
QQ DIPPING, RINSING AND DRYING
RR HYDROPHOBIC COBALT-BASED FISCHER-TROPSCH SYNTHESIS CATALYST COATED WITH MESOPOROUS MATERIALS