

FISCHER-TROPSCH SYNTHESIS COBALT NANO-CATALYST BASED ON POROUS MATERIAL CONFINEMENT, AND PREPARATION METHOD THEREFOR

FIELD OF THE INVENTION

[0001] The invention relates to the application field of catalytic synthesis and nano-material, and more particularly to a Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement and a preparation method therefore.

BACKGROUND OF THE INVENTION

[0002] Researches and technological development on substitute for petroleum have been making progress with shrinking petroleum resources and increasing prices in recent years. What has received great attentions is the process converting the syngas ($\text{CO}+\text{H}_2$) made from coal, petroleum gas and biomass into hydrocarbon by gasification through Fischer-Tropsch synthesis, which is a variety of chemical reactions that produce hydrocarbons from syngas ($\text{CO}+\text{H}_2$) using catalyst. The products are mainly heavy hydrocarbons (C_{5+}) having a relatively high carbon number.

High-quality diesel and jet fuel can be made from paraffin through refining and splitting, which are very clean motor fuel with little sulfide and nitride. This synthesis process invented by German chemists Grans Fischeer and Hans Tropsch in 1923 is one of the most effective ways to increase the supply of liquid fuel, which is expected to become one of the main methods to produce engine fuel with great economical significance and commercial value.

[0003] The factors related to reaction mechanism of Fischer-Tropsch synthesis include the effect of type, size, dispersity and reducibility of active metal particles on reactivity, channeling effect of carrier (confinement effect and shape-selective effect, etc.) and promotion effect of assistant, which will influence the detailed process of reaction mechanism, and then effect the reactivity and the product type and distribution. A lot of researches have shown that catalytic material

construction, including dispersity of active constituent, active center structure, microenvironment, location, channeling structure of carrier, etc. will have a great effect on the activity and selectivity in conversion reaction of syngas. Sun Yuhan and other people prepared catalyst $\text{Co}_3\text{O}_4@\text{MCM-41}$ having a core-shell structure and stable activity that is easy to reduce. First, they prepared Co_3O_4 particle, then designed and prepared core-shell structured cobalt-base catalyst with mesoporous-silicon-coated Co_3O_4 particle using PVP as the amphiphilic reagent. This catalyst can depress the agglomeration of cobalt active center. But this is a complicated process with single metal component in catalytic material and a low CO conversion rate, and the products are mainly light hydrocarbon with high methane selectivity. (Sun Yuhan, Chemical Industry and Engineering Progress, 2010, 380)

[0004] The Patent CN 101698152A has disclosed a Fischer-Tropsch synthesized cobalt-base catalyst and its preparation and application. The catalyst consists of metal components and a carrier which is spherical alumina powder; and the first metal component is Co, the second metal component is Ce, La or Zr, and the third metal component is Pt, Ru, Rh or Re. The catalyst is suitable for slurry bubble column reactor and continuous-stirred slurry reactor, but is very expensive and its active center is easy to agglomerate and inactivate.

[0005] Micro-capsular reactor is a new concept in nano-assembly and catalyst in recent years, which addresses the problem in traditional catalyst of being difficult to recycle as well as poor stability and selectivity, etc. For this reactor, not only guest molecules can go into the capsular space selectively to go through catalytic reaction with reactive species in the capsule, but also its products can selectively disperse out of the reactor.

SUMMARY OF THE INVENTION

[0006] It is one objective of the invention to combine the advantage of the catalyst preparation using a microcapsule reactor and the advantage of the nano-catalyst based on porous material confinement to provide a Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material

confinement and a preparation method therefore. The preparation method of the catalyst is simple, the production costs are lowered, the selectivity for methane is low, the activity of the catalytic reaction is high, and the selectivity for C₅₊ is good. The diesel and the paraffin are the main products.

[0007] Technical scheme of the invention is as follows: a Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement, the catalyst is prepared by a sol-gel method using an organogel as a template. The catalyst uses a metal component as a core and a porous material as a shell. The metal component comprises: a first metal component being Co, a second metal component being selected from Ce, La, and Zr, and a third metal component being selected from Pt, Ru, Rh, and Re. A finished catalyst comprises: between 10 and 35 wt. % of a first metal component, between 0.5 and 10 wt. % of a second metal component, and between 0.02 and 2 wt. % of a third metal component, and a carrier. The carrier is a porous material, a component thereof is a nano silica or alumina; the porous material is in the shape of a spheroid; the porous material has a pore size of between 1 and 20 nm and a specific area of between 300 and 500 m²/g. An active component has a particle size of between 0.5 and 20 nm.

[0008] Preferably, the catalyst comprises: between 15 and 30 wt. % of a first metal component, between 1 and 5 wt. % of a second metal component, and between 0.05 and 2 wt. % of a third metal component, and a carrier.

[0009] In order to obtain a product primarily comprising a light hydrocarbon, the carrier is the porous material having the pore size of between 1 and 10 nm and the specific area of between 300 and 400 m²/g; and the active component has the particle size of between 0.5 and 5 nm.

[0010] In order to obtain a product primarily comprising a middle distillate (C₅-C₁₈), the carrier is the porous material having the pore size of between 10 and 15 nm, and the specific area of between 400 and 500 m²/g; and the active component has the particle size of between 6 and 15 nm.

[0011] In order to obtain a product comprising a relatively high content of C₁₈₊, the carrier is the

porous material having the pore size of between 10 and 20 nm and the specific area of between 400 and 500 m²/g; and the active component has the particle size of between 16 and 20 nm

[0012] A method for preparing the Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement, the method comprises the following steps:

[0013] 1) selecting raw materials: collecting tetraethyl orthosilicate (TEOS) or aluminum nitrate, a water-soluble salt containing the first metal component Co, and a nitrate or a nitrosyl nitrate containing the second metal component, and a nitrate or a nitrosyl nitrate containing the third metal component according to the corresponding weight percents of each component; and providing a gel template agent;

[0014] 2) dissolving the gel template agent in a polar solvent to yield a first solution, adding an aqueous solution containing the metal salts to the first solution at a constant temperature, adding an adequate amount of ammonia to adjust the pH value to between 8 and 10, and stirring at the constant temperature of between 0.1 and 3 hr to yield a second solution;

[0015] 3) adding TEOS or aluminum nitrate to the second solution and continuing stirring for between 3 and 24 hr at the constant temperature to yield a mixture;

[0016] 4) spray drying the mixture at the temperature of between 90 and 150°C, whereby obtaining an organic-inorganic hybrid material in the form of powder; and

[0017] 5) transferring the powder after the spray drying to a muffle furnace, calcining the powder at a temperature of between 300 and 753°C for between 3 and 12 hr, whereby yielding the finished catalyst.

[0018] Preferably, in step 4), the gel prepared by the sol-gel template method is spray dried at the temperature of between 110 and 150°C to yield the organic-inorganic hybrid material.

[0019] Preferably, in step 5), the powder after the spray drying is transferred to the muffle furnace and calcined at the temperature of between 350 and 753°C for between 5 and 10 hr for yielding the finished catalyst.

[0020] Preferably, the gel template agent is a linear amphiphilic polymer containing an amino group.

[0021] Preferably, in preparation of the aqueous solution, water-soluble salt containing the first metal component Co is cobalt nitrate, cobalt acetate, or cobalt carbonate. The salt containing the second metal component is a nitrate thereof. The salt containing the third metal component is a nitrate thereof.

[0022] Advantages of the invention are summarized as follows:

[0023] 1. Co is an active metal making major catalysis in this Fischer-Tropsch synthesized catalyst. Theoretically, with the same dispersity, the higher the Co content is, the more active the catalyst will be. However, factors such as specific surface area, pore diameter and channel will restrain the maximum load of Co; and if Co is overloaded, it will be easy to agglomerate, then to reduce catalyst activity on the contrary. Thus, skilled persons in the art have been attempting to add assistant to improve the dispersity of Co on catalyst carrier to improve Co catalysis as much as possible. In the present invention, nanoporous catalyst whose shape, particle diameter and pore diameter are controllable can be obtained by choosing proper organogel template, reaction time and reactant weight. Because active components will disperse evenly in the porous material, they cannot be agglomerated, thereby improving the activity of the catalyst and the selectivity of the reaction product. Meanwhile, the activity and selectivity of the catalyst are further improved by adding the assistant. In this way, the content of active components will be reduced so as to decrease the production costs of the catalyst. This catalyst is suitable for slurry bubble column reactor and continuous stirred slurry reactor.

[0024] 2. The range of Fischer-Tropsch synthesis products is wide from methane to paraffin with high molecular weight, so poor selectivity is a defect in this process. The activity and product selectivity of Fischer-Tropsch synthesis are significantly changed by the cobalt particle size in the catalytic material. The product distribution is modified in the invention by selecting the porous material having the specific pore diameter and the specific surface area as the carrier, and the

diesel and paraffin in the products have higher selectivity. According to our study, the core in core-shell structured nano-catalyst is active in catalysis, while the shell makes the core stable. And the closed space of the shell forms a microenvironment where the reactant can accumulate to achieve high local concentration to promote efficient reaction so as to improve overall activity of the catalyst and product selectivity, and to enhance the property of anti-carbon, anti-sintering and hydrothermal stability, etc. When the particle diameter is between 0.5 and 20nm, and the specific surface area is between 300 and 500m²/g, it is easier to produce diesel and paraffin.

[0025] 3. The cobalt-based nano-catalyst confined by porous material in the invention is in-situ synthesized by sol gel process, so the active components of the catalyst and the porous material used as carrier can be synthesized simultaneously, thereby simplifying the preparation process, being convenient for operation and applicable for industrial production.

[0026] The new catalyst in the invention combines the advantages of the catalyst preparation process in micro-capsular reactor and of the nano-catalyst confined by porous material. It uses organic gel as the complete, on the surface of which the active components grow. The core-shell structured cobalt-based porous catalyst designed and prepared has high activity, with low selectivity for methane, and its main products are diesel and paraffin. Compared to the patent CN 101698152A, it is easier for the active components in the catalyst to evenly disperse on the porous carrier so as to achieve high material activity, CO conversion rate and low methane selectivity. At the same time, the high catalysis can be realized by adding only a small amount of precious metal assistant, thereby decreasing the production cost.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] FIG. 1 is a flow chart for a method for preparing Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0028] A Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement, the catalyst is prepared by a sol-gel method using an organogel as a template. The catalyst uses a metal component as a core and a porous material as a shell. The metal component comprises: a first metal component being Co, a second metal component being selected from Ce, La, and Zr, and a third metal component being selected from Pt, Ru, Rh, and Re. A finished catalyst comprises: between 10 and 35 wt. % of a first metal component, between 0.5 and 10 wt. % of a second metal component, and between 0.02 and 2 wt. % of a third metal component, and a carrier. The carrier is a porous material, a component thereof is a nano silica or alumina; the porous material is in the shape of a spheroid; the porous material has a pore size of between 1 and 20 nm and a specific area of between 300 and 500 m²/g. An active component has a particle size of between 0.5 and 20 nm.

[0029] Preferably, the catalyst comprises: between 15 and 30 wt. % of a first metal component, between 1 and 5 wt. % of a second metal component, and between 0.05 and 2 wt. % of a third metal component, and a carrier.

[0030] Preferably, in order to obtain a product primarily comprising a light hydrocarbon, the carrier is the porous material having the pore size of between 1 and 10 nm and the specific area of between 300 and 400 m²/g; and the active component has the particle size of between 0.5 and 5 nm.

[0031] Preferably, in order to obtain a product primarily comprising a middle distillate (C₅-C₁₈), the carrier is the porous material having the pore size of between 10 and 15 nm, and the specific area of between 400 and 500 m²/g; and the active component has the particle size of between 6 and 15 nm.

[0032] Preferably, in order to obtain a product with a relatively high content of C₁₈₊, the carrier is the porous material having the pore size of between 10 and 20 nm and the specific area of

between 400 and 500 m²/g; and the active component has the particle size of between 16 and 20 nm.

[0033] A method for preparing the Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement, the method comprises the following steps:

[0034] 1) selecting raw materials: collecting tetraethyl orthosilicate (TEOS) or aluminum nitrate, a water-soluble salt containing the first metal component Co, and a nitrate or a nitrosyl nitrate containing the second metal component, and a nitrate or a nitrosyl nitrate containing the third metal component according to the corresponding weight percents of each component; and providing a gel template agent;

[0035] 2) dissolving the gel template agent in a polar solvent to yield a first solution, adding an aqueous solution containing the metal salts to the first solution at a constant temperature, adding adequate amount of ammonia to adjust the pH value to between 8 and 10, and stirring at the constant temperature of between 0.1 and 3 hr to yield a second solution;

[0036] 3) adding TEOS or aluminum nitrate to the second solution and continuing stirring for between 3 and 24 hr at the constant temperature to yield a mixture;

[0037] 4) spray drying the mixture at the temperature of between 90 and 150°C, whereby obtaining an organic-inorganic hybrid material in the form of powder; and

[0038] 5) transferring the powder after the spray drying to a muffle furnace, calcining the powder at a temperature of between 300 and 753°C for between 3 and 12 hr, whereby yielding the finished catalyst.

[0039] Preferably, in step 4), the gel prepared by the sol-gel template method is spray dried at the temperature of between 110 and 150°C to yield the organic-inorganic hybrid material.

[0040] Preferably, in step 5), the powder after the spray drying is transferred to the muffle furnace and calcined at the temperature of between 350 and 753°C for between 5 and 10 hr for yielding the finished catalyst.

[0041] Preferably, the gel template agent is a linear amphiphilic polymer containing an amino group.

[0042] Preferably, in preparation of the aqueous solution, water-soluble salt containing the first metal component Co is cobalt nitrate, cobalt acetate, or cobalt carbonate. The salt containing the second metal component is a nitrate thereof. The salt containing the third metal component is a nitrate thereof.

[0043] To specifically illustrate the invention, the main content of the invention is further explained combined with FIG. 1 and the following examples, but the content of the invention is not limited by the these examples.

Example 1

[0044] 20 g of polyethyleneimine (PEI) was collected and dissolved in 100 mL of ethanol at the temperature of 80°C to yield a solvent. Thereafter, to 100 mL of deionized water, 93.8 g of cobalt nitrate hexahydrate, 39.1 g of lanthanum nitrate hexahydrate, and 2.32 g of platinum nitrate were added and stirred for dissolving thereof to yield an aqueous solution. The aqueous solution and the solvent were then evenly mixed, added with 5 mL of ammonia, and stirred at the constant temperature for 2 hr to yield a reaction solution. TEOS of a calculated amount was added to the reaction solution and stirred at the room temperature overnight to yield a mixture. After that, the mixture was spray dried to yield powder. The powder was then transferred to a muffled furnace and dried for 6 hr after the temperature slowly climbed to 400°C, whereby yielding a Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement. Components of the nano-catalyst were as follows: Co: La: Pt: SiO₂=15: 10:0.5: 74.5.

[0045] Activation of the nano-catalyst was performed in a pressurized fixed bed reactor as follows: 100 g of the nano-catalyst was placed in the reactor. Pure H₂ (the purity > 99.9 %) was used as a reducing gas and a volume velocity thereof was controlled at 1000 h⁻¹; a heating rate was

controlled at 2°C/min, an activation temperature was controlled at 350°C, an activation pressure was controlled at 0.5 megapascal, and an activation time was 4 hr.

[0046] Catalytic reaction was performed in a slurry bed reactor as follows: 50 g of the activated catalyst was transferred to the slurry bed reactor in an anhydrous oxygen-free condition. Polyolefin was used as a reaction medium. A synthesis gas was introduced, in which, $H_2 : CO = 1.5$. A flow rate of the synthesis gas was controlled to allow the volume velocity thereof to be $1000 h^{-1}$, and the pressure in the reactor was controlled to be 3.0 megapascal. A heating program was set to increase the reaction temperature at a rate of 3°C/min to 150°C and then continue increasing the reaction temperature at a rate of 2°C/min until 220°C, where the reaction was performed. Selectivity (wt. %) of the product was as follows: C_1 , 6.1; C_{2-4} , 7.3; C_{5-11} , 32.2; C_{12-18} , 29.5; C_{18+} , 24.9. Conversion rate of CO reached 81.5.

Example 2

[0047] 20 g of PEI was collected and dissolved in 100 mL of ethanol at the temperature of 80°C to yield a solvent. Thereafter, to 100 mL of deionized water, 53.6 g of cobalt nitrate hexahydrate, 1.7 g of cerium nitrate hexahydrate, and 5.9 g of ruthenium nitrosyl nitrate were added and stirred for dissolving thereof to yield an aqueous solution. The aqueous solution and the solvent were then evenly mixed and stirred at the constant temperature for 2 hr to yield a reaction solution. Aluminum nitrate of a calculated amount was added to the reaction solution and stirred at the room temperature overnight to yield a mixture. After that, the mixture was spray dried to yield powder. The powder was then transferred to a muffled furnace and dried for 3 hr after the temperature slowly climbed to 550°C, whereby yielding a Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement. Components of the catalyst were as follows: Co: Ce: Ru: Al_2O_3 = 10: 0.5: 1.5: 88.

[0048] Activation of the catalyst was performed in a pressurized fixed bed reactor as follows: 100 g of the catalyst was placed in the reactor. Pure H_2 (the purity > 99.9 %) was used as a reducing gas

and a volume velocity thereof was controlled at 1000 h^{-1} ; a heating rate was controlled at $2^{\circ}\text{C}/\text{min}$, an activation temperature was controlled at 350°C , an activation pressure was controlled at 1.5 megapascal, and an activation time was 4 hr.

[0049] Catalytic reaction was performed in a slurry bed reactor as follows: 50 g of the activated catalyst was transferred to the slurry bed reactor in an anhydrous oxygen-free condition. Polyolefin was used as a reaction medium. A synthesis gas was introduced, in which, $\text{H}_2 : \text{CO} = 1.5$. A flow rate of the synthesis gas was controlled to allow the volume velocity to be 1000 h^{-1} , and the pressure in the reactor was controlled to be 3.0 megapascal. A heating program was set to increase the reaction temperature at a rate of $3^{\circ}\text{C}/\text{min}$ to 150°C and then continue increasing the reaction temperature at a rate of $2^{\circ}\text{C}/\text{min}$ until 220°C , where the reaction was performed. Selectivity (wt. %) of the product was as follows: C_1 , 6.8; C_{2-4} , 7.9; C_{5-11} , 27.2; C_{12-18} , 28.6; C_{18+} , 29.5. Conversion rate of CO reached 85.3.

Example 3

[0050] 20 g of PEI was collected and dissolved in 100 mL of ethanol at the temperature of 80°C to yield a solvent. Thereafter, to 100 mL of deionized water, 53.6 g of cobalt nitrate hexahydrate, 1.7 g of cerium nitrate hexahydrate, and 5.9 g of ruthenium nitrosyl nitrate were added and stirred for dissolving thereof to yield an aqueous solution. The aqueous solution and the solvent were then evenly mixed and stirred at the constant temperature for 2 hr to yield a reaction solution. TEOS of a calculated amount was added to the reaction solution and stirred at the room temperature overnight to yield a mixture. After that, the mixture was spray dried to yield powder. The powder was then transferred to a muffled furnace and dried for 3 hr after the temperature slowly climbed to 450°C , whereby yielding a Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement. Components of the catalyst were as follows: Co: Ce: Ru: $\text{SiO}_2 = 10: 0.5: 1.5: 88$.

[0051] Activation of the catalyst was performed in a pressurized fixed bed reactor as follows: 100

g of the catalyst was placed in the reactor. Pure H_2 (the purity > 99.9 %) was used as a reducing gas and a volume velocity thereof was controlled at 1000 h^{-1} ; a heating rate was controlled at $2^\circ\text{C}/\text{min}$, an activation temperature was controlled at 350°C , an activation pressure was controlled at 1.5 megapascal, and an activation time was 4 hr.

[0052] Catalytic reaction was performed in a slurry bed reactor as follows: 50 g of the activated catalyst was transferred to the slurry bed reactor in an anhydrous oxygen-free condition. Polyolefin was used as a reaction medium. A synthesis gas was introduced, in which, $H_2 : CO = 1.5$. A flow rate of the synthesis gas was controlled to allow the volume velocity to be 1000 h^{-1} , and the pressure in the reactor was controlled to be 3.0 megapascal. A heating program was set to increase the reaction temperature at a rate of $3^\circ\text{C}/\text{min}$ to 150°C and then continue increasing the reaction temperature at a rate of $2^\circ\text{C}/\text{min}$ until 220°C , where the reaction was performed. Selectivity (wt. %) of the product was as follows: C_1 , 5.6; C_{2-4} , 7.1; C_{5-11} , 23.9; C_{12-18} , 29.8; C_{18+} , 33.6. Conversion rate of CO reached 76.3.

Example 4

[0053] As a comparison, a method for preparing Fischer-Tropsch synthesis cobalt catalyst was disclosed in CN 101698152A as follows:

[0054] An adequate amount of Al_2O_3 carrier was added to a muffle furnace, calcined at a temperature of 550°C for 4 hr, and 100 g of a resulting Al_2O_3 carrier was collected. To deionized water, 53.6 g of cobalt nitrate hexahydrate, 1.7 g of cerium nitrate hexahydrate, and 5.9 g of ruthenium nitrosyl nitrate were added and stirred for dissolving thereof, and a resulting solution was diluted to 110 mL to yield an aqueous solution. Thereafter, the aqueous solution was impregnated on the Al_2O_3 carrier of the calculated amount using a full pore impregnation method to yield an impregnated catalyst. The impregnated catalyst was vacuum dried in water bath at the temperature of 80°C , and then placed at the room temperature for aging for 24 hr. After that, an aged catalyst was transferred to the muffle furnace, dried for 6 hr after the temperature slowly

climbed to 120°C, and calcined for 8 hr after the temperature was increased to 500°C, whereby yielding the catalyst. Components of the catalyst were as follows: Co: Ce: Ru: Al₂O₃=10: 0.5:1.5: 88.

[0055] Activation of the catalyst was performed in a pressurized fixed bed reactor as follows: 100 g of the catalyst was placed in the reactor. Pure H₂ (the purity > 99.9 %) was used as a reducing gas and a volume velocity thereof was controlled at 1000 h⁻¹; a heating rate was controlled at 2°C/min, an activation temperature was controlled at 350°C, an activation pressure was controlled at 1.5 megapascal, and an activation time was 4 hr.

[0056] Catalytic reaction was performed in a slurry bed reactor as follows: 50 g of the activated catalyst was transferred to the slurry bed reactor in an anhydrous oxygen-free condition. Polyolefin was used as a reaction medium. A synthesis gas was introduced, in which, H₂ : CO = 1.5. A flow rate of the synthesis gas was controlled to allow the volume velocity to be 1000 h⁻¹, and the pressure in the reactor was controlled to be 3.0 megapascal. A heating program was set to increase the reaction temperature at a rate of 3°C /min to 150°C and then continue increasing the reaction temperature at a rate of 2°C /min until 220°C, where the reaction was performed. Selectivity (wt. %) of the product was as follows: C₁, 9.3; C₂₋₄, 9.1; C₅₋₁₁, 27.8; C₁₂₋₁₈, 21.2; C₁₈₊, 32.6. Conversion rate of CO reached 71.3.

[0057] It was known from Examples 1-3 that the catalyst prepared by the method according to embodiments of the invention had relatively high activity. In condition of 1000 h⁻¹ of the volume velocity, even the content of Co was only 10 wt. %, the conversion rate of CO reached 80 wt. % above, which means effects of the metal components of the Fischer-Tropsch synthesis cobalt catalyst were obvious. In the above Examples, methane had relatively low selectivity, and C₅₊ had good selectivity. Compared with Example 2 and Example 4, the catalyst prepared by the method of Example 2 had low production costs, selectivity of methane was relatively low, selectivity of C₅₊ was better, and particularly selectivity of C₁₂₊ was more advantageous.

Examples 5-12

[0058] According to embodiments of the invention, a plurality of the Fischer-Tropsch synthesis cobalt nano-catalysts based on porous material confinement were prepared, and catalytic performances thereof were shown in Table 1.

Table 1 Catalytic performance of cobalt nano-catalyst in Fischer-Tropsch synthesis

Ex am ple	Catalyst components	Calcining temperature	Particle diamet er of a core	Conversion rate of CO (%)	Selectivity of hydrocarbon				
					C ₁	C ₂₋₄	C ₅₋₁₁	C ₁₂₋₁₈	C ₁₈₊ ,
1	Co:La:Pt:SiO ₂ =15:10:0.5:74.5	450	12	81.5	6.1	7.3	32.2	29.5	24.9
2	Co:Ce:Ru:Al ₂ O ₃ =10:0.5:1.5:88	550	15	85.3	6.8	7.9	27.2	28.6	29.5
3	Co:Ce:Ru:SiO ₂ =10:0.5:1.5:88	450	17	71.3	5.6	7.1	23.9	29.8	33.6
5	Co:Ce:Ru:SiO ₂ =10:0.5:1.5:88	400	3	90.6	16.8	8.8	39.9	27.8	6.7
6	Co:La:Pt:Al ₂ O ₃ =15:10:0.5:74.5	550	8	87.4	7.3	5.6	31.6	28.2	27.3
7	Co:Zr:Re:Al ₂ O ₃ =25:2:0.3:72.7	500	16	61.3	6.3	8.7	25.6	28.9	30.5
8	Co:Zr:Re:SiO ₂ =25:2:0.3:72.7	400	2	92.6	16.8	10.9	38.2	28.5	5.6
9	Co:La:Ru:Al ₂ O ₃ =35:10:0.5:54.5	550	20	65.8	9.1	3.3	26.5	27.4	33.7
10	Co:La:Ru:SiO ₂ =35:10:0.5:54.5	400	1	93.7	17.6	11.1	40.1	27.3	3.9
11	Co:La:Rh:SiO ₂ =20:5:0.3:74.7	400	5	81.3	10.8	17.9	34.2	25.6	11.5
12	Co:La:Ru:Al ₂ O ₃ =20:5:0.3:74.7	550	10	51.3	8.9	7.6	33.2	28.6	21.7

CLAIMS

1. A Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement, **characterized in that**

the catalyst is prepared by a sol-gel method using an organogel as a template;

the catalyst uses a metal component as a core and a porous material as a shell;

the metal component comprises: a first metal component being Co, a second metal component being selected from Ce, La, and Zr, and a third metal component being selected from Pt, Ru, Rh, and Re;

a finished catalyst comprises: between 10 and 35 wt. % of a first metal component, between 0.5 and 10 wt. % of a second metal component, and between 0.02 and 2 wt. % of a third metal component, and a carrier;

the carrier is a porous material, a component thereof is a nano silica or alumina; the porous material is in the shape of a spheroid; the porous material has a pore size of between 1 and 20 nm and a specific area of between 300 and 500 m²/g; and

an active component has a particle size of between 0.5 and 20 nm.

2. The catalyst of claim 1, **characterized in that**

the catalyst comprises: between 15 and 30 wt. % of a first metal component, between 1 and 5 wt. % of a second metal component, and between 0.05 and 2 wt. % of a third metal component, and a carrier.

3. The catalyst of claim 1 or 2, **characterized in that**

the carrier is the porous material having the pore size of between 1 and 10 nm and the specific area of between 300 and 400 m²/g; and the active component has the particle size of between 0.5 and 5 nm.

4. The catalyst of claim 1 or 2, **characterized in that**

the carrier is the porous material having the pore size of between 10 and 15 nm and the specific area of between 400 and 500 m²/g; and the active component has the particle size of between 6 and 15 nm.

5. The catalyst of claim 1 or 2, **characterized in that**

the carrier is the porous material having the pore size of between 10 and 20 nm and the specific area of between 400 and 500 m²/g; and the active component has the particle size of between 16 and 20 nm

6. A method for preparing the Fischer-Tropsch synthesis cobalt nano-catalyst based on porous material confinement according to any one of claims 1-5, the method comprising:

- 1) selecting raw materials: collecting tetraethyl orthosilicate (TEOS) or aluminum nitrate, a water-soluble salt containing the first metal component Co, and a nitrate or a nitrosyl nitrate containing the second metal component, and a nitrate or a nitrosyl nitrate containing the third metal component according to the corresponding weight percents of each component; and providing a gel template agent;
- 2) dissolving the gel template agent in a polar solvent to yield a first solution, adding an aqueous solution containing the metal salts to the first solution at a constant temperature, adding adequate amount of ammonia to adjust the pH value to between 8

and 10, and stirring at the constant temperature of between 0.1 and 3 hr to yield a second solution;

- 3) adding TEOS or aluminum nitrate to the second solution and continuing stirring for between 3 and 24 hr at the constant temperature to yield a mixture;
- 4) spray drying the mixture at the temperature of between 90 and 150°C, whereby obtaining an organic-inorganic hybrid material in the form of powder; and
- 5) transferring the powder after the spray drying to a muffle furnace, calcining the powder at a temperature of between 300 and 753°C for between 3 and 12 hr, whereby yielding the finished catalyst.

7. The method of claim 6, **characterized in that** in step 4), the gel prepared by the sol-gel template method is spray dried at the temperature of between 110 and 150°C to yield the organic-inorganic hybrid material.
8. The method of claim 6 or 7, **characterized in that** in step 5), the powder after the spray drying is transferred to the muffle furnace and calcined at the temperature of between 350 and 753°C for between 5 and 10 hr for yielding the finished catalyst.
9. The method of claim 6 or 7, **characterized in that** the gel template agent is a linear amphiphilic polymer containing an amino group.
10. The method of claim 6 or 7, **characterized in that**

in preparation of the aqueous solution, water-soluble salt containing the first metal

component Co is cobalt nitrate, cobalt acetate, or cobalt carbonate;

the salt containing the second metal component is a nitrate thereof; and

the salt containing the third metal component is a nitrate thereof.