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(54) **Title:** PROCESS FOR PREPARING FISHER-TROPSCH CATALYST

(57) **Abstract:** The present invention relates to a process for preparing catalysts for Fisher-Tropsch synthesis, and more specifically, to a process for preparing a catalyst precursor for Fisher-Tropsch synthesis, which includes the steps of: a) preparing a solution of a polyether compound having two or more ether groups and a first transition metal compound; b) impregnating the solution into a carrier; c) drying the carrier impregnated with the solution; and d) calcining the dried carrier.

Description

Title of Invention: PROCESS FOR PREPARING FISHER-TROPSCH CATALYST

Technical Field

- [1] The present invention relates to a process for preparing Fisher-Tropsch catalysts used for preparing hydrocarbon compounds from syngas.

Background Art

- [2] Fisher-Tropsch synthesis (FTS) reaction is a reaction used for producing hydrocarbon compounds from a gas mixture (syngas) containing carbon monoxide and hydrogen generated by reforming natural gas, gasification of coal, or biomass, and it is schematically represented by reaction (1).
- [3] $n\text{CO} + 2n\text{H}_2 \rightarrow (\text{CH}_2)_n + n\text{H}_2\text{O}$ (1)
- [4] The water-gas shift (WGS) reaction (2), a competitive reaction that occurs with FTS reaction (1), produces carbon dioxide and hydrogen by the reaction between carbon monoxide and water produced from the reaction (1).
- [5] $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ (2)
- [6] Accordingly, the water produced from the reaction formula (1) changes the ratio of hydrogen and carbon monoxide during the entire Fisher-Tropsch synthesis.
- [7] In the Fisher-Tropsch process, catalysts having different ingredients and characteristics are used according to the syngas composition in terms of the hydrogen to carbon monoxide ratio and the desired products.
- [8] There have been reported numerous Fisher-Tropsch catalysts prepared by using at least one metal selected from Group 8B elements (cobalt, ruthenium, iron, or nickel) as the major ingredients of the catalysts, and at least one metal selected from Groups 1A, 3A, 4A, and 5A of the Periodic Table or at least one metal selected from Groups 1B, 2B, 3B, 4B, 5B, 6B, and 7B of the Periodic Table as additional promoters or structure stabilizing agents (U.S. Patent No. 7,067,562).
- [9] The carbon number distribution of the Fisher-Tropsch product may change depending on the major active ingredients of the catalyst used, but generally, in case a cobalt-based catalyst is used, reaction (1) predominates over water-gas shift reaction (2), and the hydrocarbon (HC) product generally follows the distribution pattern predicted by Anderson-Shulz-Flory (ASF) theory.
- [10] Further, when a cobalt- or ruthenium-based catalyst is used instead of an iron-based catalyst, the reaction may be conducted at a lower temperature. Accordingly, a cobalt-based catalyst which is much less expensive than a ruthenium-based catalyst is known to be more preferable for producing paraffin-based hydrocarbons such as liquid or

wax, especially when the feed syngas has a H₂/CO ratio of approximately 2. Thus, cobalt-based catalysts have been the subject of extensive studies in the past several decades. In this connection, several studies have reported improved catalytic activities, when certain organic additives were used during cobalt-based Fisher-Tropsch catalysts synthesis.

[11] For example, U.S. Patent No. 7,585,808 discloses a catalyst for Fisher-Tropsch reaction prepared by using ruthenium as a catalytic active metal and treating with tri-ethanolamine.

[12] U.S. Patent No. 5,928,983 discloses a cobalt-based Fisher-Tropsch catalyst prepared by adding an oxidative alcohol, oxidative aldehyde or oxidative ketone, particularly, glyoxal.

[13] U.S. Patent No. 5,968,991 discloses a process for activating a catalyst by impregnating a solution containing cobalt, a multifunctional carboxylic acid represented by HOOC-(CRR')_n-COOH and rhenium into a refractory inorganic carrier followed by drying.

Disclosure of Invention

Technical Problem

[14] The present invention provides a novel cobalt-based catalyst having an improved catalytic activity and stability, together with an improved selectivity for liquid and high melting point hydrocarbons, at the expense of a low methane selectivity over conventional cobalt-based Fisher-Tropsch catalysts.

Solution to Problem

[15] According to one aspect of the present invention, the present invention provides a process for preparing a catalyst precursor for Fisher-Tropsch synthesis comprising the steps of:

[16] a) preparing a solution of a polyether compound having two or more ether groups and a first transition metal compound;

[17] b) impregnating the solution into a carrier;

[18] c) drying the carrier impregnated with the solution; and

[19] d) calcining the dried carrier.

[20] Further, the present invention provides a process for synthesizing hydrocarbon comprising the steps of activating the catalyst precursor by means of treating the precursor with a gas stream containing hydrogen at an appropriate temperature, and bringing the activated catalyst into contact with a mixed gas containing hydrogen and carbon monoxide.

Advantageous Effects of Invention

[21] The catalyst according to the present invention may be used for Fisher-Tropsch

synthesis reaction, to improve the carbon monoxide conversion rate and lowering the selectivity to the undesired methane, to enhance the yield of high melting point hydrocarbons.

Best Mode for Carrying out the Invention

- [22] According to the present invention, a process for preparing a catalyst precursor for Fisher-Tropsch synthesis, which on activation, shows a high carbon monoxide (CO) conversion rate and a desirable product distribution characteristics.
- [23] Hereinafter, preferred embodiments of the present invention will be described in detail.
- [24] The process for preparing a catalyst precursor for Fisher-Tropsch (FT) synthesis according to the present invention comprises the steps of:
- [25] a) preparing a solution of a polyether compound having two or more ether groups and a first transition metal compound;
- [26] b) impregnating the solution into a carrier;
- [27] c) drying the carrier impregnated with the solution; and
- [28] d) calcining the dried carrier.
- [29] According to one embodiment of the present invention, the first transition metal compound may be cobalt.
- [30] According to another embodiment of the present invention, the present invention may further comprise the step of adding a second metal compound to the solution of the step a).
- [31] The second metal compound may be at least one metal selected from Groups 1A, 2A, 3A, 4A, 5A, 1B, 2B, 3B, 4B, 5B, 6B, 7B or 8B of the Periodic Table.
- [32] Particularly, the second metal compound may be a compound of aluminum, zinc, nickel, copper, tungsten, boron, chromium, platinum, magnesium or manganese.
- [33] The second metal compound may be selected from the group consisting of nitrates, carbonates, organic acid salts, oxides, hydroxides, halides, cyanides, and hydroxides thereof.
- [34] The polyether compound may be an aliphatic, aromatic or cyclic polyether compound.
- [35] The aliphatic polyether compound may be paraformaldehyde, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, or monoalkyl or dialkylether derivatives thereof.
- [36] According to one embodiment of the present invention, the cyclic polyether compound may be a crown ether.
- [37] The carrier used in the process for preparing a catalyst precursor according to the present invention may be silica, alumina, titania, $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ or a mixture thereof, or

active carbon or ZrO_2 .

- [38] In the present invention, the polyether compound may be used in an amount in the range of 0.01 to 2 moles per 1 mole of the first transition metal.
- [39] In one embodiment of the present invention, the inventive process may further comprise the step of calcining the carrier at 400 to 1000°C before impregnating the catalytic solution into the carrier.
- [40] The step of impregnating the solution into the carrier may be conducted by wet impregnation, dry impregnation, vacuum impregnation, or spray drying or extrusion drying a slurry-type mixture, but not limited thereto.
- [41] According to one embodiment of the present invention, the first transition metal compound may be supported on the carrier to the metal amount of 5 to 60 wt% after reducing the catalyst precursor.
- [42] In the present invention, the drying of the step c) may be conducted under ambient pressure at room temperature to 150°C for 12 to 24 hours, and the calcining of the step d) may be conducted by heating from 150°C to 300~ 500°C for 1 to 50 hours. The calcining may be conducted in an inert atmosphere.
- [43] Further, the present invention provides a process for synthesizing hydrocarbons comprising the steps of activating the catalyst precursor by means of treating the precursor with a gas stream containing hydrogen at a suitable temperature ranging from 150°C to 500°C and bringing the activated catalyst into contact with a mixed gas containing hydrogen and carbon monoxide.
- [44] The transition metal which is capable of hydrogenating carbon monoxide may be, for example, cobalt, nickel, iron, copper, chromium, manganese, zirconium, molybdenum, tungsten, rhenium, osmium, iridium, palladium, silver, ruthenium, rhodium, and platinum. Particularly, cobalt, iron and ruthenium are preferred to synthesize high molecular weight hydrocarbons.
- [45] The transition metal may be used as at least one metal compound selected from the group consisting of metal salts such as nitrates, carbonates, organic acid salts, oxides, hydroxides, halides, cyanides, and the like, among which, nitrates and acetates are particularly preferred. The metal compound may be used alone or as a mixture of two or more.
- [46] Further, in order to improve catalyst activity, a second metal selected from Groups 1A, 2A, 3A, 4A, 5A, 1B, 2B, 3B, 4B, 5B, 6B, 7B or 8B of the Periodic Table may be further added. According to one preferred embodiment of the present invention, the second metal compound may be aluminum, zinc, nickel, copper, tungsten, boron, chromium, platinum, magnesium, or manganese.
- [47] The polyether compound used in the present invention may be an aliphatic, unsaturated hydrocarbon, aromatic or cyclic polyether.

- [48] The aliphatic polyether compound may be selected from paraformaldehyde, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, or monoalkyl or dialkylether derivatives thereof.
- [49] More preferably, the polyether compound may be a compound having carbon number of 3 to 15.
- [50] Further preferably, the cyclic polyether compound is a crown ether.
- [51] The transition metal compound and the polyether compound may be dissolved to prepare a solution (an impregnating solution). As the solvent, water, alcohols, ethers, ketones, and aromatics may be used, and particularly preferable are water, alcohols or a mixture of water and an alcohol.
- [52] For applying the polyether compound to the metal compound, it is preferred that a mixing ratio of the polyether compound may be 0.01 to 2 moles, particularly, 0.1 mole or more per 1 mole of the metal element contained in the metal compound, but the molar ratio may be controlled according to molecular weight of the polyether.
- [53] It is assumed that the metal ion of the metal compound in the solution forms a coordinated complex to form a well-dispersed solution of the complex.
- [54] The carrier to be impregnated with the solution thus obtained may be silica, alumina, titania, $\text{SiO}_2\text{-Al}_2\text{O}_3$, active carbon, ZrO_2 or a mixture thereof, or other porous materials, and most preferably, it is silica or alumina.
- [55] The surface area, pore volume and mean pore diameter of the carrier may not be particularly limited, but the carrier having the surface area of 10 m^2/g or more, the pore volume of 0.5 mL/g or more, and the mean pore diameter of 10 nm or more may be suitable for preparing a catalyst for conducting hydrogenation of carbon monoxide.
- [56] Prior to impregnating the solution, the carrier may be calcined at 300 to 600°C in the air or inert atmosphere so as to remove internal impurities from its pores.
- [57] As a method for impregnating the complex solution into a carrier, wet impregnation, dry impregnation, and vacuum impregnation may be used. At this time, the amount of the solution may be adjusted to the volume equivalent to the inherent pore volume of the porous body, to perform incipient-wetness impregnation.
- [58] Further, for the catalyst precursor prepared by the process according to embodiments of the present invention, the preferred amount of the first transition metal supported on the carrier may be decided depending on the desired specifications. For example, in the case of cobalt, the amount of cobalt supported on the carrier after activating the precursor by reduction is in the range of 5 to 60 wt%. When the supported amount of cobalt is less than the lower limit of the range, the activity of the activated catalyst for converting a mixed gas of hydrogen and carbon monoxide may become low. On the other hand, when the supported amount is more than the upper limit, the specific activity of the cobalt atoms becomes low due to poor dispersion thereof on the carrier.

- [59] Finally, in order to achieve the desired loading of the first transition metal as mentioned above, the impregnating and drying processes may be repeated as many times as necessary.
- [60] The silica impregnated with the solution may be molded into the shape of a cylinder-type, three leaves-type, four leaves-type, sphere-type or others.
- [61] The drying may be conducted by a normal pressure drying method, a vacuum drying method and the like. For example, the normal pressure drying method may be conducted under ambient pressure at room temperature to 150°C for 12 to 24 hours.
- [62] According to preferred embodiments of the present invention, the drying may be conducted by gradually increasing temperature and keeping at a desired temperature for a measured time. Starting at an initial drying temperature of T1, the second step drying temperature (T2) may be set at T1+10 to 50°C, the third step drying temperature T3, T2+10 to 50°C, and the drying time of the second step and the third step may be 1 to 24 hours. Generally, it may be conducted under ambient normal pressure at room temperature to 150°C for 12 to 24 hours.
- [63] Then, calcining may be conducted in the air or inert atmosphere, at a temperature of 300 to 500°C for 1 to 50 hours, most preferably for about 2 to 5 hours. According to the method as mentioned above, a catalyst, wherein cobalt oxides able to hydrogenize carbon dioxide are highly dispersed on the carrier, is prepared. The obtained catalyst precursor may be activated according to a preset reducing process to be used for Fisher-Tropsch synthesis reaction.
- [64] The activation may be conducted by charging the catalyst precursor into a reactor and passing a reducing gas stream containing hydrogen therethrough while slowly heating the reactor up to 200 to 500°C, and then keeping at a preset operating temperature for about 4 to 12 hours.
- [65] A hydrocarbon product containing gasoline and diesel fuel fractions among others is produced bringing a mixed gas containing hydrogen and carbon monoxide at a temperature of 150 to 350°C and a pressure of 0.1 to 5 MPa into contact with the activated catalyst prepared by the process according to embodiments of the present invention.
- [66] For example, the catalyst precursor is charged in a tube reactor and activated, and a syngas feed is passed therethrough at a temperature of 150 to 350°C under a pressure of 0.1 to 5 MPa.
- [67] After activating, it is also possible to use a slurry reactor containing a powder-type catalyst dispersed in an organic solvent having a high melting point, to achieve the desired FT synthesis under similar conditions, as is widely known in the art.
- [68] The catalyst prepared by the embodiments of the present invention may be used in the form of a powder (for example, mean diameter: 50 to 150 micron) or granules such as a pellet.

[69] The H₂/CO ratio of the syngas feed may range from 1 to 4, depending on the method of syngas generation, but it is preferably approximately 2 when a cobalt-based catalyst is used for the production of high molecular weight hydrocarbons.

Mode for the Invention

[70] Hereinafter, the present invention is explained by the following Examples and Test Examples which are intended to further illustrate the present invention, and the scope of the present invention is not limited thereby in any way.

[71] **Carrier**

[72] (1) Silica carrier

[73] As a silica carrier for supporting a transition metal, Aerolyst 3041 (SiO₂, excluded type, 0.40 to 0.46 kg/L, 99+%) of Evonik Industries was used. The silica was heated at a rate of 5°C/min to 450°C and kept at the temperature for 10 hours, and then crushed to the size of 100 to 300 mesh. BET and other analyses showed that the silica had a specific surface area of about 150 m²/g, a void volume of about 0.80 cm³/g, and an average pore size of about 20 nm.

[74] (2) Alumina carrier

[75] As an alumina carrier for supporting a transition metal, gamma-alumina (γ-Al₂O₃, 1/4" x 1/4" white pellets, 15 mg/m³, 99+%) of STREAM was used. The alumina was heated at a rate of 5°C/min to 1000°C and kept at the temperature for 5 hours, and then crushed to the size of 100 to 300 mesh. BET and other analyses showed that the alumina had a specific surface area of about 100 m²/g, a void volume of about 0.30 cm³/g, and an average pore size of about 15 nm.

[76] (3) Titania carrier

[77] As a titania carrier for supporting a transition metal, Aerolyst 7708 (TiO₂, anatase:rutile ≅ 7:3) of Evonik Industries was used. The titania was heated at a rate of 5°C/min to 560°C and kept at the temperature for 5 to 8 hours, and then crushed to the size of 100 to 300 mesh. BET and other analyses showed that the titania had a specific surface area of about 25 m²/g, a void volume of about 0.15 cm³/g, and an average pore size of about 25 nm was prepared.

[78]

[79] <Example 1>

[80] Equimolar amounts of tetraethylene glycol and Co(NO₃)₂·H₂O were added to distilled water to obtain an impregnation solution having a volume to perform incipient wetness impregnation of 8.8 g of the silica carrier. The resulting mixture was dried at 110°C for 24 hours, heated to 130°C at a rate of 1°C/min, kept at 130°C for 3 hours, and then heated to 150°C at a rate of 0.5°C/min to be kept at that temperature for 3 hours. Then, the dried mixture was heated to 350°C at a rate of 0.5 to 1°C/min and kept at 350°C for

3 hours, to obtain a Co/SiO₂ catalyst precursor which on activation contained a cobalt loading of 12 wt%.

[81] <Example 2>

[82] The procedure of Example 1 was repeated except for using tetraethylene glycol dimethylether instead of tetraethylene glycol to prepare a catalyst precursor.

[83] <Example 3>

[84] The procedure of Example 1 was repeated except for using poly(ethylene glycol)dimethylether (number average molecular weight 250 g/mol) and ethanol solvent instead of tetraethylene glycol to prepare a catalyst precursor.

[85] <Example 4>

[86] The procedure of Example 1 was repeated except for using 18-crown-6 instead of tetraethylene glycol to prepare a catalyst precursor.

[87] <Example 5>

[88] The procedure of Example 1 was repeated except for using 12-crown-4 instead of tetraethylene glycol to prepare a catalyst precursor.

[89] <Example 6>

[90] The procedure of Example 3 using poly(ethylene glycol) dimethylether was repeated except for further adding aluminum (Al) as the second metal to prepare a catalyst precursor.

[91] <Example 7>

[92] The procedure of Example 3 using poly(ethylene glycol) dimethylether was repeated except for further adding zinc (Zn) as the second metal to prepare a catalyst precursor.

[93] <Example 8>

[94] The procedure of Example 3 using poly(ethylene glycol) dimethylether was repeated except for further adding nickel (Ni) as the second metal to prepare a catalyst precursor.

[95] <Example 9>

[96] The procedure of Example 5 using 12-crown-4 was repeated except for further adding copper (Cu) as the second metal to prepare a catalyst precursor.

[97] <Example 10>

[98] The procedure of Example 5 using 12-crown-4 was repeated except for further adding boron (B) as the second metal to prepare a catalyst precursor.

[99] <Example 11 to Example 16>

[100] The procedure of Example 6 was repeated except for changing the kinds of the organic agent and the second metal as listed in Table 1 to prepare a catalyst precursor.

[101] <Comparative Example 1>

[102] The procedure of Example 1 was repeated except for not adding the polyether compound at all to prepare a 12 wt% Co/SiO₂ catalyst precursor.

[103] <Comparative Example 2>

[104] The procedure of Example 1 was repeated except for using diethylene glycol instead of tetraethylene glycol to prepare a catalyst precursor.

[105]

[106] **Fisher - Tropsch Reaction Test**

[107] 1g of each catalyst precursor prepared in Examples and Comparative Examples was mixed with 3 g of a diluent (a quartz powder having the same particle size distribution), charged into a high-pressure fixed reactor, and then activated at 723K in a hydrogen gas stream. Then, a mixed gas containing hydrogen and carbon monoxide was introduced therethrough, and then the FT reaction was conducted under the following conditions to prepare a hydrogenized product:

[108] Reaction temperature: 200°C;

[109] Pressure: 20 bar;

[110] H₂/CO=2 (containing 4% nitrogen as GC internal standard material); and

[111] SV=4000 hr⁻¹ [standard cc syngas/hr·g catalyst (measured at the standard condition of 25°C and 1 atm).

[112] After 15 hours, when the activity of each catalyst was stabilized, in line GC analysis was conducted for examining activity (mol/g-Co/hr) and selectivity (%). The results are shown in Table 1.

[113] Activity: moles CO converted/g Co hr

[114] Selectivity: moles/100 mole CO converted

[115]

[116] Table 1

[Table 1]

Test results of 12 wt% Co/SiO₂ catalyst

Classification	Organic agent	Promoter	XCO[%]	Selectivity (%)				Activity mol/g Co hr
				CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	
Example 1	TEG	-	22.7	9.5	0.2	0.1	0.3	0.106
Example 2	TEGDME	-	22.6	8.4	0.2	0.1	0.3	0.103
Example 3	PEGDME	-	31.3	7.0	0.2	0.0	0.2	0.144
Example 4	18-crown-6	-	22.7	12.3	0.2	0.0	0.6	0.105
Example 5	12-crown-4	-	38.3	6.6	0.2	0.1	0.3	0.185
Example 6	PEGDME	Al	31.5	7.2	0.0	0.0	0.3	0.156
Example 7	PEGDME	Zn	23.7	6.4	0.1	0.1	0.2	0.117
Example 8	PEGDME	Ni	47.2	5.8	0.1	0.0	0.2	0.233
Example 9	12-crown-4	Cu	21.8	7.6	0.1	0.1	0.3	0.108
Example 10	12-crown-4	B	67.2	5.7	0.1	0.0	0.3	0.331
Example 11	12-crown-4	Cr	34.2	6.4	0.1	0.1	0.4	0.161
Example 12	PEGDME	Cr	33.6	6.2	0.07	0.07	0.36	0.156
Example 13	12-crown-4	Ni	23.8	8.5	0.24	0.07	0.34	0.108
Example 14	PEGDME	Mn	24.0	4.9	0.11	0.38	0.3	0.106
Example 15	12-crown-4	Pt	21.0	7.1	0.20	0.04	0.28	0.099
Example 16	PEGDME	Mg	20.3	5.9	0.11	0.21	0.41	0.095
Comparative Example 1	-	-	14.6	6.8	0.3	0.1	0.3	0.065
Comparative Example 2	DEG	-	19.4	10.1	0.1	0.2	0.9	0.088

[117]

[118] TEG: tetraethylene glycol

[119] TEGDME: tetraethylene glycol dimethylether

[120] PEGDME: polyethylene glycol dimethylether

[121] DEG: diethylene glycol

[122]

[123] <Example 17 to Example 21>

[124] The procedure of Example 6 was repeated except for using an alumina support instead of silica, and changing the kinds of the metal and the organic agent as listed in Table 2 to prepare a catalyst, and the Fisher-Tropsch reaction was conducted using the catalyst. The results are shown in Table 2.

[125]

[126] Table 2

[Table 2]

Test results of 12 wt% Co/Al₂O₃ catalyst

Classification	Organic agent	Promoter	XCO[%]	Selectivity(%)				Activity mol/g Co hr
				CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	
Example 17	12-crown-4	Zn	46.9	8.9	0.201	0.040	0.361	0.220
Example 18	12-crown-4	Cr	45.1	7.9	0.163	0.052	0.322	0.212
Example 19	12-crown-4	B	28.6	7.0	0.096	0.071	0.244	0.134
Example 20	12-crown-4	Al	27.9	7.4	0.144	0.075	0.275	0.131
Example 21	12-crown-4	-	27.1	6.6	0.099	0.077	0.218	0.127

[127]

[128] As can be seen the results of Tables 1 and 2, the catalyst of Comparative Examples not using the polyether compound showed conversion rate of less than 20%, but the catalyst according to the present invention showed higher conversion rate of over 20% to about 70%. Further, the catalyst of the present invention showed higher selectivity to carbon dioxide and three or four times higher activity.

[129] While the invention has been described with respect to the above specific em-

bodiments, it should be recognized that various modifications and changes may be made and also fall within the scope of the invention as defined by the claims that follow.

Industrial Applicability

[130] The catalyst according to the present invention may be used for Fisher-Tropsch synthesis reaction, to improve the carbon monoxide conversion rate and lowering the selectivity to the undesired methane, to enhance the yield of high melting point hydrocarbons.

Claims

- [Claim 1] A process for preparing a catalyst precursor for Fisher-Tropsch synthesis comprising the steps of:
- a) preparing a solution of a polyether compound having two or more ether groups and a first transition metal compound;
 - b) impregnating the solution into a carrier;
 - c) drying the carrier impregnated with the solution; and
 - d) calcining the dried carrier.
- [Claim 2] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 1, wherein the first transition metal compound is cobalt.
- [Claim 3] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 1, which further comprises the step of adding a second metal compound to the solution of the step a).
- [Claim 4] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 3, wherein the second metal compound is at least one metal selected from Groups 1A, 2A, 3A, 4A, 5A, 1B, 2B, 3B, 4B, 5B, 6B, 7B or 8B of the Periodic Table.
- [Claim 5] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 4, wherein the second metal compound is aluminum, zinc, nickel, copper, tungsten, boron, chromium, platinum, magnesium or manganese.
- [Claim 6] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 4, wherein the second metal compound is selected from the group consisting of nitrates, carbonates, organic acid salts, oxides, hydroxides, halides, and cyanides of the second metal.
- [Claim 7] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 1, wherein the polyether compound is an aliphatic, aromatic, or cyclic polyether.
- [Claim 8] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 7, wherein the aliphatic polyether is paraformaldehyde, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, or a monoalkyl or dialkylether derivative thereof.
- [Claim 9] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 7, wherein the cyclic polyether is a crown ether.
- [Claim 10] The process for preparing the catalyst precursor for Fisher-Tropsch

- synthesis according to claim 1, wherein the carrier is silica, alumina, titania, $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$, active carbon, ZrO_2 , or a mixture thereof.
- [Claim 11] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 1, wherein the polyether compound is used at a ratio of 0.01 to 2 moles per 1 mole of the first transition metal.
- [Claim 12] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 1, which further comprise the step of calcining the carrier at 400 to 1000°C before impregnating the solution into the carrier.
- [Claim 13] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 1, wherein the step of impregnating the solution into the carrier is conducted by wet impregnation, dry impregnation, vacuum impregnation, or spray drying or extrusion drying a slurry-type mixture.
- [Claim 14] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 2, wherein the amount of cobalt supported on the carrier is in the range of 5 to 60 wt% based on the reduced catalyst.
- [Claim 15] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 1, wherein the drying of the step c) is conducted under the ambient pressure at room temperature to 150°C for 12 to 24 hours.
- [Claim 16] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 1, wherein the calcining of the step d) is conducted at a temperature ranging from 150°C to 300~500°C for 1 to 50 hours.
- [Claim 17] The process for preparing the catalyst precursor for Fisher-Tropsch synthesis according to claim 16, wherein the calcining is conducted in an inert atmosphere.
- [Claim 18] A catalyst precursor prepared by a process of any one of claims 1 to 17.
- [Claim 19] A process for synthesizing hydrocarbon comprising the steps of activating the catalyst precursor of claim 18 by reducing the precursor in a gas stream containing hydrogen at a temperature ranging from 150°C to 500°C and bringing the activated catalyst into contact with a mixed gas containing hydrogen and carbon monoxide.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2013/006641**A. CLASSIFICATION OF SUBJECT MATTER****B01J 37/08(2006.01)i, B01J 23/75(2006.01)i, C10G 2/00(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
B01J 37/08; B01J 23/75; B01J 23/40; B01J 37/06; B01J 37/02; B01J 23/89; B01J 35/10; C10G 2/00Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: Fisher-Tropsch catalyst precursor, polyether compound, transition metal**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2003-512925 A (EXXON RESEARCH AND ENGINEERING COMPANY) 08 April 2003 See abstract; paragraph [0005-0014]	18-19
A		1-17
X	JP 2003-024786 A (NIPPON OIL CORP) 28 January 2003 See abstract; paragraph [0006-0017]	18-19
A		1-17
X	JP 2007-307436 A (IHI CORP) 29 November 2007 See abstract; paragraph [0020-0025]	18-19
A		1-17
X	KR 10-2011-0123051 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY et al.) 14 November 2011 See abstract, paragraph [0009-0018]	18
A		1-17, 19

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2013/006641

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JP 2003-024786 A	28/01/2003	None	
JP 2007-307436 A	29/11/2007	None	
KR 10-2011-0123051 A	14/11/2011	None	