VAPOR-GROWN CARBON FIBER AND PRODUCTION PROCESS THEREOF

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Abstract
The present invention provides a process for producing a vapor-grown carbon fiber by supplying a raw material at least containing a carbon source and a catalyst and/or catalyst precursor compound into a heating zone, wherein the raw material further containing an oxygen-containing carbon source compound which is selected from the group consisting of ketones and ethers. The process for producing a vapor-grown carbon fiber according to the present invention does not leave a residue in a reaction device because a raw material used contains a particular oxygen-containing carbon source compound and, thereby, can continuously produce a vapor-grown carbon fiber.
Fig. 1

CARBON COMPOUND

CARRIER GAS

(CATALYST)

(SUPPORTED CATALYST)
Fig. 2

- LIQUID RAW MATERIAL
- GAS RAW MATERIAL
- CARRIER GAS
- EXHAUST GAS
VAPOUR-GROWN CARBON FIBER AND PRODUCTION PROCESS THEREOF

TECHNICAL FIELD

[0001] The present invention relates to a process for efficiently producing a vapour-grown carbon fiber such as a carbon nanotube.

RELATED ART

[0002] A carbon fiber obtained by the vapour-grown process (vapour-grown carbon fiber) can have a large aspect ratio with relative ease. Accordingly, studies thereon have been aggressively carried out and there are a large number of reports on the production process. A carbon nanotube (that is, a carbon fiber having a fiber diameter on the nanometer order) has attracted particular attention in recent years, and can be synthesized by applying this vapour-growth process.

[0003] FIG. 1 is a schematic view showing one example of a reaction apparatus for continuously producing a carbon fiber by the vapour-growth process. In one example of the general production process, CO, methane, acetylene, ethylene, benzene, toluene or the like is used as the carbon source which is the raw material of the carbon fiber. A carbon source which is a gas at an ordinary temperature and pressure is supplied, in the gaseous state, by being mixed with a carrier gas. In the case of a liquid, the carbon source is vaporized in a vaporizer and mixed with a carrier gas and then supplied, or is sprayed in a liquid state into the heating zone. The carrier gas used is, for example, nitrogen gas, which is an inert gas, or hydrogen gas, which is reducing gas. In some cases, the carbon source is supplied into a depressurized apparatus.

[0004] As for a catalyst of a process for producing a vapour-grown carbon fiber, a supported catalyst in which a metal is supported on a support such as alumina, or an organic metal compound such as ferrocene, is used. In the case of using a supported catalyst, the supported catalyst is subjected to a necessary pretreatment by previously placing and heating it in a heating zone, and then a carbon source is supplied and reacted thereon (this is the example shown in FIG. 1). Alternatively, the reaction is performed by continuously or pulsedly supplying a supported catalyst which has been pre-treated, from outside of the system. It is also possible that an organic metal compound readily dissolvable in a carbon source, such as ferrocene, is employed as a catalyst precursor, and continuously or pulsedly fed to the heating zone together with a carbon source, and thereby a carbon fiber is produced by utilizing metal particles generated by thermal decomposition of the catalyst precursor as a catalyst.

[0005] The product obtained by a process for producing a vapour-grown carbon fiber performed in the apparatus shown in FIG. 1 is collected in the heating zone 2 heated by the heater 1 and the receiver 3 located at the end thereof, and then, after a predetermined time of reaction, is recovered.

[0006] The production process of a carbon fiber by a vapor-phase method is roughly classified into the following three types according to the method of supplying a catalyst or a precursor compound of the catalyst:

[0007] (1) a substrate or boat comprising an alumina or graphite supporting a catalyst or a precursor compound thereof is placed in a heating zone, and contacted with a gas of a carbon source supplied in a vapor phase;

[0008] (2) a particulate catalyst or a precursor compound thereof is dispersed in a liquid-state carbon source or the like, and continuously or pulsedly supplied to a heating zone from outside of the system, and thereby contacted with a carbon source at a high temperature; and

[0009] (3) a metalocene, a carbonyl compound, or like dissolvable in a liquid-state carbon source is used as a catalyst precursor compound, and a carbon source comprising this catalyst precursor compound dissolved therein is supplied to a heating zone, whereby a catalyst and the carbon source, which is a hydrocarbon or the like, are contacted at a high temperature.

[0010] As for the process of (2) and (3) above, Japanese Unexamined Patent Publication No. 6-146117 and No. 9-78360 describe, in the examples, a method comprising dissolving ferrocene in benzene as a carbon source and supplying the obtained solution to a heating zone. Japanese Unexamined Patent Publication No. 2004-539676 describes, in the examples, a method comprising dissolving ferrocene in benzene, toluene or p-xylene as a carbon source and supplying the obtained solution to a heating zone.

[0011] The purpose of the present invention is to provide a simple and effective process for producing a vapour-grown carbon fiber wherein the process does not leave a residue in a reaction apparatus, and thereby enables continuous production of a vapour-grown carbon fiber and, as a result, cost-effective production thereof.

DISCLOSURE OF THE INVENTION

[0012] As a result of intensive investigations to solve the above-described subjects, the present inventors have found that a process for producing a vapour-grown carbon fiber does not leave a residue in a reaction apparatus when a raw material used further contains a particular compound, and thereby achieve the present invention.

[0013] That is, the present invention relates to the following (1) to (24).

[0014] (1) A process for producing a vapour-grown carbon fiber by supplying a raw material at least containing a carbon source, and a catalyst and/or catalyst precursor compound into a heating zone,

[0015] wherein the raw material further contains an oxygen-containing carbon source compound selected from the group consisting of ketones and ethers.

[0016] (2) The process for producing a vapour-grown carbon fiber as described in (1) above, wherein the catalyst and/or catalyst precursor compound is in a solid or liquid state at an ordinary temperature and pressure, the oxygen-containing carbon source compound is in a liquid state at an ordinary temperature and pressure, and the catalyst and/or catalyst precursor compound is dissolved or suspended in the oxygen-containing carbon source compound to be supplied into the heating zone.

[0017] (3) The process for producing a vapour-grown carbon fiber as described in (2) above, wherein the oxygen-containing carbon source compound in which the catalyst and/or catalyst precursor compound has been dissolved or suspended is vaporized before being supplied into the heating zone.

[0018] (4) The process for producing a vapour-grown carbon fiber as described in any one of (1) to (3) above, wherein the oxygen-containing carbon source compound has a boiling point of 80°C. or more at an ordinary pressure.
(0019) (5) The process for producing a vapor-grown carbon fiber as described in (4) above, wherein the oxygen-containing carbon source compound has a boiling point of 115°C or more at an ordinary pressure.

(0020) (6) The process for producing a vapor-grown carbon fiber as described in (5) above, wherein the oxygen-containing carbon source compound has a boiling point of 150°C or more at an ordinary pressure.

(0021) (7) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (6) above, wherein the solubility of the catalyst and/or catalyst precursor compound at 25°C in the oxygen-containing carbon source compound is 1 g or more per 100 g of the oxygen-containing carbon source compound.

(0022) (8) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (7) above, wherein the ketones are acetone, 2-butanone, 2-pentanone, 3-pentanone, 3-methyl-2-butanone, 3,3-dimethyl-2-butanone, 3,3-dimethyl-2-pentanone, 3,3-dimethyl-2-pentanone, 2-methyl-3-pentanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone, 2-hexanone, 3-hexanone, cyclopentanone, hydroxyacetone, 2-heptanone, 3-heptanone, 4-heptanone, 2,4-dimethyl-3-pentanone, 4-methoxy-4-methyl-2-pentanone, 2-hydropyrone, 2,6-diheptanone, 3,3-methylenecyclohexanone, and isophorone.

(0023) (9) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (8) above, wherein the ethers are anisole, ethoxybenzene, 2-methoxytoluene, 3-methoxytoluene, 4-methoxytoluene, furan, tetrahydrofuran, 2,3-dihydrofuran, 2,5-dihydrofuran, 1,3-dioxolane, pyrane, tetrahydropryan, 1,3-dioxiane, 1,4-dioxane, diethyl ether, di-n-propyl ether, di-isopropyl ether, n-butyl methyl ether, s-butyl methyl ether, t-butyl methyl ether, n-butyl ethyl ether, t-butyl ethyl ether, di-n-butyl ether, di-isobutyl ether, ethylene glycol mono-methyl ether, ethylene glycol mono-ethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-isopropyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-s-butyl ether, ethylene glycol mono-i-butyl ether, ethylene glycol mono-t-butyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol di-n-propyl ether, ethylene glycol di-isopropyl ether, ethylene glycol di-n-butyl ether, ethylene glycol di-isobutyl ether, ethylene glycol di-t-butyl ether, propylene glycol, propylene glycol mono-methyl ether, propylene glycol mono-ethyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-isopropyl ether, propylene glycol mono-n-butyl ether, propylene glycol mono-s-butyl ether, propylene glycol mono-i-butyl ether, propylene glycol mono-t-butyl ether, propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol di-n-propyl ether, propylene glycol di-isopropyl ether, propylene glycol di-n-butyl ether, propylene glycol di-isobutyl ether, propylene glycol di-t-butyl ether, diethylene glycol, diethylene glycol mono-methyl ether, diethylene glycol mono-ethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-isopropyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-s-butyl ether, diethylene glycol mono-i-butyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol di-n-propyl ether, diethylene glycol di-isopropyl ether, diethylene glycol di-n-butyl ether, diethylene glycol di-isobutyl ether, diethylene glycol di-t-butyl ether, dipropylene glycol, dipropylene glycol mono-methyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-i-propyl ether, dipropylene glycol mono-n-butyl ether, dipropylene glycol mono-s-butyl ether, dipropylene glycol mono-i-butyl ether, dipropylene glycol di-n-propyl ether, dipropylene glycol di-isopropyl ether, dipropylene glycol di-n-butyl ether, dipropylene glycol di-isobutyl ether, dipropylene glycol di-t-butyl ether, tetraethylene glycol dimethyl ether, 3-methoxy-1-butanol, 3-methoxy-3-methyl-1-butanol, tetrahydrofurfuryl alcohol, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, and diethylene glycol monoethyl ether acetate.

(0024) (10) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (9) above, wherein the carbon source is at least one compound selected from the group consisting of carbon monoxide, carbon dioxide, methane, ethane, propane, butane, pentane, hexane, heptane, cyclohexane, ethylene, propylene, butene, butadiene, acetylene, benzene, toluene and xylene.

(0025) (11) The process for producing a vapor-grown carbon fiber as described in (10) above, wherein the carbon source is at least one compound selected from the group consisting of carbon monoxide, carbon dioxide, methane, ethane, propane, butane, pentane, hexane, heptane, cyclohexane, ethylene, propylene, butene, butadiene and acetylene.

(0026) (12) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (11) above, wherein the carbon source comprises at least methane.

(0027) (13) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (12) above, wherein the content of methane in the raw material is at or more than 15 mol% to less than 100 mol%, and the temperature in the high-temperature part of the heating zone is from 1,100 to 1,500°C.

(0028) (14) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (13) above, wherein the temperature at the raw material-introducing part of the heating zone is 700°C or less.

(0029) (15) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (14) above, wherein the supplied raw material resides in the law temperature part of the heating zone which is at a temperature of 600 to 1,000°C for 0.05 seconds or more before arriving at the high-temperature part of the heating zone.

(0030) (16) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (15) above, wherein the residence time at a temperature of 1,100°C or more in the heating zone is 0.001 second or more.

(0031) (17) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (16) above, wherein the total amount of carbon atoms contained in the carbon source other than methane is 60% or less of the amount of carbon atoms contained in methane.

(0032) (18) The process for producing a vapor-grown carbon fiber as described in (17) above, wherein the total amount of carbon atoms contained in the carbon source other than methane is 10% or less of the amount of carbon atoms contained in methane.
(19) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (18) above, wherein the ratio of the atomic number of a catalyst element and the number of carbon atoms in the raw material satisfies the following relationship:

\[
\frac{\text{Atomic number of a catalyst element}}{\text{Number of carbon atoms}} = 0.0000065 \text{ to } 0.0015.
\]

(20) The process for producing a vapor-grown carbon fiber as described in any one of (1) to (19) above, wherein the all or a part of the gas after reaction is circulated and reused.

(21) The process for producing a vapor-grown carbon fiber as described in (1) above, wherein a carbon fiber having an average fiber diameter of 10 nm or more is produced.

(22) A vapor-grown carbon fiber produced by the process for producing a vapor-grown carbon fiber as described in any one of (1) to (21) above.

(23) The vapor-grown carbon fiber as described in (22) above, having an average fiber length of 10 \( \mu \)m or more.

(24) The vapor-grown carbon fiber as described in (23) above, having the average fiber length of 13 \( \mu \)m or more.

(25) The process for producing a vapor-grown carbon fiber according to the present invention does not leave a residue in a reaction apparatus by the fact that a raw material used contains a particular oxygen-containing carbon source compound, and thereby can continuously produce a vapor-grown carbon fiber.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic view showing an example of the general horizontal reaction apparatus for producing a vapor-grown carbon fiber.

FIG. 2 is a schematic view showing an example of the vertical reaction apparatus for producing a vapor-grown carbon fiber.

BEST MODE FOR CARRYING OUT THE INVENTION

(26) The process for producing a vapor-grown carbon fiber according to the present invention is characterized in that a raw material further contains an oxygen-containing carbon source compound in addition to a carbon source, and a catalyst and/or catalyst precursor compound.

(27) The constituent elements of the present invention are described in detail below.

(Oxygen-Containing Carbon Source Compound)

(28) The oxygen-containing carbon source compound used in the process for producing a carbon fiber according to the present invention includes an oxygen-containing carbon source compound selected from the group consisting of ketones and ethers. Addition of such an oxygen-containing carbon containing compound into a raw material used for a process for producing a vapor-phase carbon fiber makes it possible to reduce or substantially eliminate a residue in a reaction apparatus. It is deemed that the residue is oxidized by oxygen atom of an oxygen-containing carbon source compound reacts with a carbon residue in a reaction apparatus to remove the carbon residue from the reaction apparatus. Incidentally, carbon atom of an oxygen-containing carbon source compound is counted as a carbon source described below.

(29) When a catalyst and/or catalyst precursor compound is in a solid or liquid state at an ordinary temperature and pressure, the catalyst and/or catalyst precursor compound is preferably dissolved or suspended in the oxygen-containing carbon source compound which is in a liquid state at an ordinary temperature and pressure, and then supplied into a heating zone. Since ethers and ketones, particularly ethers, used as an oxygen-containing carbon source compound in the process of the present invention are chemically stable, a catalyst and/or the catalyst precursor compound such as metalloocene, particularly ferrocene, can be dissolved or dispersed therein, and thereafter supplied.

(30) The oxygen-containing carbon source compound is preferably one having a higher boiling point at an ordinary pressure, and/or a large solubility of catalyst and/or catalyst precursor compound therein. For example, boiling point at an ordinary pressure of the oxygen-containing carbon source compound is preferably of 80° C. or more, more preferably 115° C. or more, and still more preferably 150° C. or more. The solubility of a catalyst and/or catalyst precursor compound at 25° C. in the oxygen-containing carbon source compound is preferably 1 g or more, more preferably 5 g or more, and still more preferably 10 g or more per 100 g of the oxygen-containing carbon source compound.

(31) In particular, the oxygen-containing carbon source compound preferably has a boiling point at an ordinary pressure of 115° C. or more, and a solubility of catalyst and/or catalyst precursor compound therein at 25° C. of 1 g or more per 100 g of the oxygen-containing carbon source compound. Further, the oxygen-containing carbon source compound preferably has a boiling point at an ordinary pressure of 150° C. or more, and a solubility of catalyst and/or catalyst precursor compound therein at 25° C. of 1 g or more per 100 g of the oxygen-containing carbon source compound.

(32) The reason why the oxygen-containing carbon source compound preferably has a higher boiling point at an ordinary pressure, and/or a large solubility of catalyst and/or catalyst precursor compound therein is as follows:

(33) The minimum amount of a catalyst and/or catalyst precursor compound required for producing a vapor-phase carbon fiber is very small in comparison with the amount of carbon in a raw material. Many catalysts and/or catalyst precursor compounds are in a solid or liquid state at an ordinary temperature and pressure. However, it is very difficult to stably supply a small amount of a catalyst and/or catalyst precursor compound in a solid or liquid state to a heating zone.

(34) Therefore, when the oxygen-containing carbon source compound is in a liquid state at an ordinary temperature and pressure, it is possible to stably supply a catalyst and/or catalyst precursor compound to a heating zone by dissolving or dispersing it in the oxygen-containing carbon source compound. This is particularly preferable when the main carbon source is a gaseous compound such as methane, and when a carbon source has a small solubility of a catalyst and/or catalyst precursor compound therein.

(35) Also, when a catalyst and/or catalyst precursor compound is dissolved in an oxygen-containing carbon source compound, if the oxygen-containing carbon source compound has a lower boiling point (i.e. a higher vapor pressure), the oxygen-containing carbon source compound is vaporized before the catalyst and/or catalyst precursor compound is sufficiently vaporized, and thereby the catalyst and/or catalyst precursor compound is precipitated. This makes it impos-
sible to stably supply the catalyst and/or catalyst precursor compound to a heating zone. Therefore, an oxygen-contain-
ing carbon source compound preferably has a higher boiling point, when a catalyst and/or catalyst precursor compound is dissolved or dispersed in an oxygen-containing carbon source compound.

[0052] An oxygen-containing carbon source compound preferably has a large solubility of a catalyst and/or catalyst precursor compound therein in order to stably retain the cata-
lyst and/or catalyst precursor compound therein.

[0053] Ketones which can be used as an oxygen-containing carbon source compound includes acetone, 2-butane,
2-pentanone, 3-pentanone, 3-methyl-2-butanone, acetylaceton,
3-hydroxy-3-methyl-2-butanone, 3,3-dimethyl-2-butane,
2-methyl-3-pentanone, 2-methyl-2-pentanone, 4-methyl-2-pentanone, 2-hexanone, 3-hexanone, cyclo-
pentanone, hydroxycacetone, 2-heptanone, 3-heptanone, 2,4-heptanone, 2,4-dimethyl-3-pentanone, 4-methoxy-4-methyl-2-pentanone, 4-hydroxy-4-methyl-2-pentanone, cyclohexanone, 2,6-dimethyl-4-heptanone, 3-methylcyco-
hexanone, and isophorone.

[0054] Preferable ketones which can be used as an oxygen-con-
taining carbon source compound include ones having a boiling point of 80°C. or more at an ordinary pressure. The preferable ketones include 2-butane, 2-pentanone, 3-pen-
tanone, 3-methyl-2-butanone, 3,3-dimethyl-2-butane, 2-methyl-3-pentanone, acetylacetone, 3-hydroxy-3-methyl-
2-butanone, 4-methyl-2-pentanone, 2-hexanone, 3-hexanone, cyclo-
pentanone, hydroxycacetone, 3-heptanone, 2,4-heptanone, 2,4-dimethyl-3-pentanone, 3-methyl-2-pentan-
one, 2-heptanone, 4-methoxy-4-methyl-2-pentanone, 4-hydroxy-4-methyl-2-pentanone, cyclohexanone, 2,6-dim-
eethyl-4-heptanone, 3-methylcyclohexanone, and isophorone.

[0055] More Preferable ketones which can be used as an oxygen-con-
taining carbon source compound includes ones having a boiling point of 115°C. or more at an ordinary pressure. The preferable ketones include acetylacetone, 3-hy-
droxy-3-methyl-2-butanone, 4-methyl-2-pentanone, 2-hex-
anone, 3-hexanone, cyclopentanone, hydroxycacetone, 3-hep-
tanone, 2,4-heptanone, 2,4-dimethyl-3-pentanone, 3-methyl-2-
pentanone, 2-heptanone, 4-methoxy-4-methyl-2-pentanone, 4-hydroxy-4-methyl-2-pentanone, cyclohexanone, 2,6-di-
eethyl-4-heptanone, 3-methylcyclohexanone, and isophorone.

[0056] Particularly preferable ketones which can be used as an oxygen-con-
taining carbon source compound includes ones having a boiling point of 150°C. or more at an ordinary pressure. The particularly preferable ketones include 3-meth-
yl-2-pentanone, 2-heptanone, 4-methoxy-4-methyl-2-pen-
tanone, 4-hydroxy-4-methyl-2-pentanone, cyclohexanone, 2,6-di-
methyl-4-heptanone, 3-methylcylohexanone, and isophorone.

[0057] Ethers which can be used as an oxygen-con-
taining carbon source compound include anisole, ethoxybenzene,
2-methoxytoluene, 3-methoxytoluene, 4-methoxyto-
luene, furan, tetrahydrofuran, 2,3-dihydrofuran, 2,5-dihydrofur-
an, 1,3-dioxolane, pyrane, tetrahydropyran, 1,3-dioxane, 1,4-
dioxane, diethyl ether, di-n-propyl ether, di-isopropyl ether,
n-butyl methyl ether, s-butyl methyl ether, t-butyl methyl ether,
n-butyl ethyl ether, t-butyl ethyl ether, di-n-butyl ether,
di-s-butyl ether, ethyleneglycol mono-(methyl ether, ethyl-
englycol mono-propyl ether, ethyleneglycol mono-i-propyl ether, ethyleneglycol mono-t-butyl ether, ethyleneglycol mono-s-butyl ether, ethy-
leneglycol mono-i-butyl ether, ethyleneglycol mono-t-butyl ether, ethyleneglycol mono-2-ethylhexyl ether, ethyleneglycol dimethyl ether, ethyleneglycol diethyl ether, ethyleneglycol di-n-propyl ether, ethyleneglycol di-i-propyl ether, ethy-
leneglycol di-n-butyl ether, ethyleneglycol di-s-butyl ether, ethyleneglycol di-i-butyl ether, propylene glycol mono-methyl ether, propylene glycol mono-propyl ether, propylene glycol mono-n-butyl ether, propylene glycol mono-s-butyl ether, propylene glycol mono-i-butyl ether, propylene glycol mono-t-butyl ether, propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol di-n-propyl ether, propylene glycol di-i-propyl ether, propylene glycol di-n-butyl ether, pro-
pylene glycol di-s-butyl ether, propylene glycol di-i-butyl ether, diethyleneglycol diethyl ether, diethyleneglycol mono-methyl ether, diethyleneglycol mono-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-n-propyl ether, diethyleneglycol di-i-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-s-butyl ether, diethyleneglycol di-i-butyl ether, diethyleneglycol mono-methyl ether, diethyleneglycol mono-propyl ether, diethyleneglycol di-
ethyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-n-propyl ether, diethyleneglycol di-i-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-s-butyl ether, diethyleneglycol di-i-butyl ether, diethyleneglycol mono-methyl ether, diethyleneglycol mono-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-n-propyl ether, diethyleneglycol di-i-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-s-butyl ether, diethyleneglycol di-i-butyl ether, diethyleneglycol mono-methyl ether, diethyleneglycol mono-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-
ethyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-n-propyl ether, diethyleneglycol di-i-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-s-butyl ether, diethyleneglycol di-i-
butyl ether, diethyleneglycol mono-methyl ether, diethyleneglycol mono-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-
ethyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-n-propyl ether, diethyleneglycol di-i-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-s-butyl ether, diethyleneglycol di-i-butyl ether, diethyleneglycol mono-methyl ether, diethyleneglycol mono-propyl ether, diethyleneglycol di-
ethyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-n-propyl ether, diethyleneglycol di-i-propyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-s-butyl ether, diethyleneglycol di-i-butyl ether, diethyleneglyco-
...

[0059] More preferable ethers which can be used as an oxygen-containing carbon source compound include ones having a boiling point of 115°C or more at an ordinary pressure. The more preferable ethers includes di-n-butyl ether, di-s-butyl ether, ethyleneglycol mono-monomethyl ether, ethyleneglycol mono-n-propyl ether, ethyleneglycol mono-i-propyl ether, ethyleneglycol diethyl ether, propylene glycol mono-monomethyl ether, propylene glycol mono-n-propyl ether, ethyleneglycol mono-n-butyl ether, ethyleneglycol mono-i-butyl ether, ethyleneglycol mono-t-butyl ether, ethyleneglycol mono-s-butyl ether, propylene glycol mono-n-butyl ether, propylene glycol mono-i-butyl ether, propylene glycol mono-t-butyl ether, diethyleneglycol diethyl ether, diethyleneglycol mono-n-propyl ether, ethyleneglycol mono-n-propyl ether, diethyleneglycol mono-n-butyl ether, diethyleneglycol mono-i-butyl ether, diethyleneglycol mono-t-butyl ether, diethyleneglycol mono-s-butyl ether, diethyleneglycol diethyl ether, diethyleneglycol di-i-propyl ether, diethyleneglycol di-n-propyl ether, diethyleneglycol di-i-butyl ether, diethyleneglycol di-n-butyl ether, diethyleneglycol di-t-butyl ether, diethyleneglycol di-t-butyl ether, triethyleneglycol dimethyl ether, tetraethyleneglycol dimethyl ether, 3-methoxy-1-butanol, 3-methoxy-3-methyl-1-butanol, tetrahydrofurfuryl alcohol, ethyleneglycol mono-ethyl ether acetate, ethyleneglycol mono-n-butyl ether acetate, propylene glycol mono-n-butyl ether acetate, diethyleneglycol mono-n-butyl ether acetate.

[0060] Particularly preferable ethers which can be used as an oxygen-containing carbon source compound include ones having a boiling point of 150°C or more at an ordinary pressure. The preferable ethers include anisole, ethoxybenzene, 2-methoxytoluene, 3-methoxytoluene, 4-methoxytoluene, ethyleneglycol mono-n-butyl ether, ethyleneglycol mono-n-propyl ether, ethyleneglycol mono-i-propyl ether, ethyleneglycol mono-t-butyl ether, ethyleneglycol mono-s-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-n-butyl ether, diethyleneglycol mono-n-propyl ether, diethyleneglycol mono-n-butyl ether, diethyleneglycol mono-t-butyl ether, diethyleneglycol mono-s-butyl ether, tetrahydrofurfuryl alcohol, ethyleneglycol mono-ethyl ether acetate, ethyleneglycol mono-n-butyl ether acetate, propylene glycol mono-n-butyl ether acetate, ethyleneglycol mono-ethyl ether acetate, diethyleneglycol mono-ethyl ether acetate, and diethyleneglycol mono-n-propyl ether acetate.

[0061] An oxygen-containing carbon source compound used for the present invention can be used in an amount such that the molar ratio of oxygen atom in the oxygen-containing carbon source compound to carbon atom in the carbon source becomes 100 to 100,000 ppm, particularly 1,000 to 3,000 ppm.

(Carbon Source)

[0062] As a carbon source, any compound can be used as long as it has carbon atom. The useful carbon compound includes inorganic gases such as carbon monoxide, carbon dioxide; alkalines such as methane, ethane, propane, butane, pentane, hexane, heptane, octane; alkene such as ethylene, propylene, butene, butadiene; alkenes such as acetylene; monocylic aromatic hydrocarbons such as benzene, toluene, xylene, styrene; Poly cyclic compounds having condensed rings such as indene, naphthalene, anthracene, phenanthrene; cyclic paraffins such as cyclopropane, cyclopentane, cyclohexane; cyclic olefins such as cyclopentene, cyclohexene, cyclopentadiene, bicyclopentadiene; alicyclic hydrocarbon compounds having condensed rings such as steroid; These
compounds also can be used as an oxygen-containing carbon source if they satisfy the requirements as an oxygen-containing carbon source.

[0063] Also, compounds containing oxygen, nitrogen, sulfur, phosphorus, halogen, and like can be used as a carbon source. The mixtures of the carbon sources naturally can be used. Particularly, a carbon source containing sulfur also can be used as a sulfur source described below.

[0064] When a catalyst and/or catalyst precursor compound used is dissolved or dispersed in an oxygen-containing carbon source compound, a carbon source which is preferable in view of carbon fiber productivity and cost includes carbon monoxide, carbon dioxide, methane, ethane, propane, butane, pentane, hexane, heptane, cyclohexane, ethylene, propylene, butene, butadiene, acetylene, benzene, toluene, xylene, and mixtures thereof. A particularly preferable carbon source includes methane.

[0065] Further, in this case, a compound in a gaseous state at an ordinary temperature can easily be used as a carbon source compound. The compound in a gaseous state at an ordinary temperature includes carbon monoxide, carbon dioxide, methane, ethane, propane, butane, pentane, heptane, cyclohexane, ethylene, propylene, butene, butadiene, acetylene, particularly methane, and mixtures thereof.

[0066] It is particularly effective to dissolve or disperse a catalyst and/or catalyst precursor compound in an oxygen-containing carbon source compound according to the present invention, when all or part of a carbon source, and optionally the other contents such as carrier gas, is in a gaseous state at an ordinary temperature and pressure, and/or when all or part of a carbon source, and optionally the other contents such as carrier gas, is in a liquid state at an ordinary temperature and pressure, but has no or substantially no solubility of a catalyst and/or catalyst precursor compound therein at 25°C.

[0067] When methane is used as a carbon source, the methane concentration in the supplied raw material is preferably at or more than 15 mol% to less than 100 mol%, more preferably from 30 to 95 mol%, still more preferably from 45 to 90 mol%. If the methane concentration in the raw material is excessively low, the productivity of a carbon fiber decreases, whereas if the methane concentration is excessively high, a non-fibrous product may possibly be produced. The “raw material supplied” means a composition containing a carbon source, an oxygen-containing carbon source compound, a catalyst and/or catalyst precursor, a carrier gas, etc., i.e. a composition containing all components supplied to a heating zone.

[0068] When methane is used as a carbon source, the carbon source other than methane, which is used along with methane, is preferably not used in an excessively large amount. This is because if used in a large amount, the carbon source inhibits the properties of methane. The carbon source other than methane is used in such an amount that the total amount of carbon atom contained in such a carbon source is preferably 60% or less, more preferably 40% or less, still more preferably 20% or less, further still more preferably 10% or less, and most preferably 5% or less, based on the total amount of carbon atom contained in methane. If the carbon source other than methane is used in an excess amount, the amount of a non-fibrous solid matter produced abruptly increases. Regarding this concentration, however, carbon monoxide and carbon dioxide are not considered as a carbon source since these behave differently from the other carbon source.

(Catalyst)

[0069] The catalyst used for the present invention is not particularly limited as long as it is a substance capable of accelerating the growth of a carbon fiber. The catalyst is, for example, at least one metal (particularly, a fine particle thereof) selected from the group consisting of Groups 3 to 12 of the 18 Groups-Type Periodic Table of Elements recommended by IUPAC in 1990, preferably at least one metal selected from the group consisting of Groups 3, 5, 6, 8, 9 and 10, more preferably iron, nickel, cobalt, rhodium, palladium, platinum or a rare earth element.

(Catalyst Precursor Compound)

[0070] The “catalyst precursor compound” means a compound which is thermally decomposed upon heating and, in some cases, further reduced to provide the catalyst. The catalyst precursor compound includes an organic metal compound, a metal salt, etc. For example, metalloocene as a catalyst precursor compound is thermally decomposed upon heating to provide fine metal particles which work as a catalyst. Especially, ferrocene is thermally decomposed upon heating to provide fine iron particles. Accordingly, as for the catalyst precursor compound, a compound of providing the above-described metal can be suitably used. More specifically, the catalyst precursor compound is, for example, a metal compound containing at least one element selected from the group consisting of Groups 3 to 12, preferably a compound containing at least one element selected from the group consisting of Groups 3, 5, 6, 8, 9 and 10, and most preferably a compound containing iron, nickel, cobalt, ruthenium, rhodium, palladium, platinum or a rare earth element.

[0071] It is also possible to add a metal compound containing at least one element, selected from the group consisting of Groups 1 to 17 as a modification component (so-called cocatalyst), to the main component to modify the catalytic performance of the main component metal.

(Support)

[0072] The catalyst and/or catalyst precursor compound may also be used, if desired, by loading it on a support. The support is preferably a compound stable in the heating zone, and examples of such a compound include alumina, silica, zeolite, magnesia, titania, zirconia, graphite, activated carbon and carbon fiber. However, this support must be introduced together with a carbon source, etc. into a heated furnace without previously charging it into a reaction furnace.

(Amounts of Catalyst, Etc.)

[0073] The amount of the catalyst or catalyst precursor compound to be used is, in terms of the ratio of the atomic number of an a catalyst element (for example, Fe) to the number of carbon atoms in the carbon source, preferably 0.000005 to 0.0015, more preferably from 0.00001 to 0.001, still more preferably from 0.00002 to 0.0005, and most preferably from 0.00004 to 0.0004. If this ratio is less than 0.000005, the amount of catalyst is too small and the number of fibers may decrease or the fiber diameter may increase, whereas if the ratio exceeds 0.0015, not only the profitability is low but also coarsened catalyst particles, not functioning as
a catalyst, may be mixed in the fiber. As for the total number of carbon atoms of the carbon source in the raw material, when the catalyst precursor compound contains a carbon, the carbon atoms thereof are also included. That is, the total number of carbon atoms is a total amount of all carbon atoms excluding carbons contained in the carbon monoxide and carbon dioxide in the supplied raw material.

(Method of Supplying Raw Material)

[0074] The method of supplying the raw material is not particularly limited. A carbon source, an oxygen-containing carbon source compound containing a catalyst and/or catalyst precursor compound dissolved or suspended therein may be vaporized and supplied in the gaseous state, or a part or all thereof may be supplied in a liquid state. In order to efficiently produce a carbon fiber, these raw materials are preferably vaporized before the production of carbon fiber starts, and then supplied. More preferably the solution or suspension containing the catalyst and/or catalyst precursor is vaporized and thoroughly mixed with the carbon source, and then supplied.

(Carrier Gas)

[0075] In the production of the vapor-grown carbon fiber of the present invention, it is recommended to use a carrier gas in addition to the above-described composition. As for the carrier gas, hydrogen, nitrogen, helium, argon, krypton or a mixed gas thereof may be used, but a gas containing an oxygen molecule (that is, oxygen in the molecular state (Oₙ)) such as air, is not suited. The catalyst precursor compound for use in the present invention is sometimes in the oxidized state and in such a case, a hydrogen-containing gas is preferably used as the carrier gas. Accordingly, the carrier gas is preferably a gas containing hydrogen at a concentration of 1 vol % or more, preferably 30 vol % or more, and most preferably 85 vol % or more, and this is, for example, a gas of 100 vol % hydrogen or a gas of hydrogen diluted with nitrogen. The hydrogen gas concentration used here is based only on the carrier gas, but the amounts of a carbon source, the gasified catalyst and/or catalyst precursor compound and the like are not considered.

(Sulfur Compound)

[0076] In the production of the vapor-grown carbon fiber of the present invention, a sulfur compound considered to be effective in controlling the carbon fiber diameter may be used in combination. The sulfur compound which can be used in the present invention includes sulfur; thiophene; hydrogen sulfide; carbon disulfide; mercaptans such as methyl mercaptan, tert-butyl mercaptan; sulfides such as dimethyl sulfide; and disulfides such as dimethyl disulfide. The preferred sulfur compound includes thiophene, carbon disulfide, dimethyl sulfide and dimethyl disulfide, and more preferred sulfur compound includes dimethyl sulfide and dimethyl disulfide.

[0077] These sulfur compounds may be supplied in the gaseous state or by dissolving it in a solvent. The total molar number of sulfur supplied is suitably 100 times or less, preferably 10 times or less, more preferably 2 times or less, of the molar number of a catalyst element. If the amount of sulfur supplied is excessively large, this is not only unprofitable but also it also inhibits the growth of a carbon fiber, and is not preferred.

(Synthesis of Carbon Fiber)

[0078] The synthesis of a vapor-grown carbon fiber is achieved by supplying the raw materials described above and, if desired, a carrier gas to a heating zone, and contacting these under heating. The reactor (heating zone) is not particularly limited as long as predetermined residence time and heating temperature are obtained, but a vertical or horizontal tubular furnace is preferred in view of the supply of raw material and the control of residence time.

[0079] If the temperature in the heating zone is too low, a solid product as well as a carbon fiber is not produced at all or is produced in an extremely small amount, whereas if the temperature is excessively high, a carbon fiber does not grow or only a thick fiber is obtained. Therefore, particularly when methane is used as a carbon source, the temperature in the high-temperature part of the heating zone is preferably from 1,100 to 1,500° C., more preferably from 1,150 to 1,350° C.

[0080] When methane is used as a carbon source, the main component of the carbon source in the gas after the reaction is methane which can be a carbon source. Accordingly, all or a part of the gas after reaction can be circulated and reused by supplying it to the heating zone as-is or after adding carbon source, carrier gas, etc. thereto.

[0081] FIG. 2 shows one example of the reaction apparatus. In this case, a quartz-made reaction tube 1 used as a heating zone is equipped with a heater 2 and, at the top, is connected to a supply line of mixing and supplying raw material components of a carrier gas, a carbon source such as methane and a liquid raw material component containing a catalyst and/or catalyst precursor compound. In this supply line, a vaporizer 4 is disposed. At the bottom of the reaction tube 1, a receiver 3 for collecting the produced carbon fibers is provided. By using such an apparatus, the heater 2 is set to a predetermined temperature of 1,100° C. or more, and raw materials are introduced from the introduction line 4 and reacted.

[0082] When methane is used as a carbon source, the fundamental mechanism of the present invention is mainly such that a carbon fiber produced upon contact of methane with a catalyst at a low temperature of 1,000° C. or less is effectively grown in the diameter direction at a high temperature of 1,000° C. or more by using a carbon source, for example, methane, an aliphatic hydrocarbon such as ethylene and propylene and/or an aromatic hydrocarbon such as benzene, which all are a decomposition product of methane.

[0083] If raw materials are directly supplied to a high-temperature zone, a carbon source is rapidly decomposed and forms a non-fiber solid matter before forming a carbon fiber. In order to avoid this problem, the temperature at the raw material-introducing part from which a raw material is induced into the reaction tube, that is, the heating zone, must be kept lower than the temperature in the high-temperature part of the heating zone. The temperature of the raw material-introducing part is preferably 700° C. or less, more preferably 600° C. or less, and still more preferably 400° C. or less. The residence at 1,000° C. or less must be kept to a certain period of time by introducing the raw material into the low-temperature region. In particular, the residence time at 600 to 1,000° C. is important, and the raw material is preferably caused to stay in this temperature range for 0.05 seconds or more, preferably 0.5 seconds or more, still more preferably from 1.0 to 30 seconds.

[0084] The actual gas temperature in the region is hard to measure. Therefore, the temperature used here is a value obtained, for example, by inserting a platinum-platinum, 13% rhodium alloy thermocouple capable of measuring even a temperature of 1,000° C. or more into the heating zone. To be precise, this measured value is affected by radiation and does
not necessarily agree with the gas temperature but can be satisfactorily used as an index for specifying the preferred condition of the present invention.

The residence time in the temperature range of 600 to 1,000°C is a time of passage of the raw material gas through a region where the temperature measured as above on the inlet side of the reaction apparatus elevates from 600°C to 1,000°C. The residence time is calculated on the assumption that the raw material gas creates a plug flow in this region and the temperature of the raw material gas is elevated to the temperature measured as above. In the case where the temperature at the upstream end of heating zone or the temperature of ejection part of a nozzle or the like inserted into the heating zone as a feed line having an inner diameter smaller than, for example, 1/8 as compared with the heating zone, exceeds 600°C, the residence time is a residence time in the region from the upstream end of heating zone or the ejection part of a nozzle or the like to a part where the temperature is elevated to 1,000°C. In this case, the residence time is calculated on the assumption that the raw material creates a plug flow in this region and the temperature of the raw material gas is elevated to the temperature measured as above.

The residence time at a temperature of 1,100°C or more can be determined in the same manner as the residence time in the temperature range of 600 to 1,000°C. This residence time is, for example, 0.001 second or more, preferably 0.01 second or more, more preferably from 0.1 to 30 seconds. However, the residence time at a temperature of 1,100°C or more can be arbitrarily determined depending on the desired fiber thickness, raw material concentration, temperature in the high-temperature part, or the like.

(Shape of Carbon Fiber, Etc.)

As described above, when methane is used as a carbon source, the carbon fiber obtained by the process of the present invention becomes a thick fiber by using a high temperature of 1,100°C or more. Accordingly, the production process of the present invention is particularly suited for the production of a relatively thick fiber rather than the production of a carbon fiber having a very small outer diameter, such as single wall or dual wall carbon fiber. More specifically, the production process of the present invention is optimal as a production process of a carbon fiber having an average outer diameter of 10 nm or more, preferably 50 nm or more, and most preferably 100 nm or more. The outer diameter of a carbon fiber as used herein can be determined, for example, by measuring the outer diameter of the images of about 100 fibers in a photograph from an SEM.

Furthermore, the present invention is characterized in that, despite its being a production process with high productivity, a carbon fiber having a long fiber length can be produced. That is, the production process of the present invention is optimal as a production process of a carbon fiber having an average fiber length of 10 μm or more, preferably 13 μm or more, and most preferably 15 μm or more. The length of a carbon fiber as used herein can be determined, for example, by measuring the length of the images of about 100 fibers in a photograph from an SEM, similarly to the case of the outer diameter.

According to the present invention, the effectiveness of a catalyst or a catalyst precursor can be remarkably enhanced. That is, a carbon fiber can be efficiently obtained even with a small amount of a catalyst. In a carbon fiber produced by a normal process, a catalyst (e.g., iron) of about 50,000 mass ppm generally remains. Therefore, the carbon fiber produced is subjected to firing (at around 1,500°C) or graphitization treatment (at 2,000 to 3,000°C) in an inert gas so as to enhance the physical properties. A part of iron or the like as the catalyst is vaporized or transpired by this treatment, and the catalyst residual amount decreases in the carbon fiber after graphitization treatment. On the other hand, according to the production process of the present invention, the catalyst content in the carbon fiber can be extremely decreased even in the state not subjected to a treatment such as firing and graphitization. For example, a carbon fiber having a catalyst content of 5,000 ppm or less or, under preferred conditions, a catalyst content of 500 ppm or less can be obtained in the state not subjected to a treatment such as firing and graphitization, and therefore depending on usage, the graphitization treatment is not necessary.

In the process of the present invention, the average outer diameter of the fiber obtained tends to change by varying the ratio of the catalyst and/or catalyst precursor compound to a carbon source such as methane. That is, with the fiber diameter becoming small when the ratio of the catalyst and/or catalyst precursor compound is increased, and becomes large when the ratio is decreased. This reveals that the average outer diameter of the carbon fiber obtained can be controlled merely by changing the composition of a raw material carbon source and a catalyst without changing the reaction apparatus or detailed conditions. For example, a carbon fiber having a fiber outer diameter of 80 to 150 nm can be very easily produced.

EXAMPLES

The present invention is described in greater detail below by referring to Examples, but the present invention is not limited thereto.

The reagents and the like used in Examples and Comparative Examples below are as follows:

<Reagents>

1. Carbon Source
- Methane: Takachiho Trading Co., Ltd.
- Benzene: Wako Pure Chemical Industries, Ltd.
- Tetrachloroethylene: Wako Pure Chemical Industries, Ltd.
- Toluene: Wako Pure Chemical Industries, Ltd.
- p-xylene: Wako Pure Chemical Industries, Ltd.
- Cyclohexane: Wako Pure Chemical Industries, Ltd.
- Diethylene glycol dimethyl ether: Tokyo Chemical Industry Co., Ltd.

2. Catalyst Precursor Compound
- Ferrocene: Nippon Zeon Co., Ltd.
- Cyclopentadienylmanganese: Wako Pure Chemical Industries, Ltd.
- N,N-Dimethylformamide: Tokyo Chemical Industry Co., Ltd.
- Toluene: Wako Pure Chemical Industries, Ltd.
- Tetrachloroethylene: Wako Pure Chemical Industries, Ltd.
- Benzene: Wako Pure Chemical Industries, Ltd.
- Ethanol: Wako Pure Chemical Industries, Ltd.
- Diethylene glycol dimethyl ether: Tokyo Chemical Industry Co., Ltd.

3. Solvent for dissolving and supplying catalyst precursor compound (Compound which is in a liquid state at an ordinary temperature and pressure)

- Benzene: Wako Pure Chemical Industries, Ltd.
- Tetrachloroethylene: Wako Pure Chemical Industries, Ltd.
- Toluene: Wako Pure Chemical Industries, Ltd.
- p-xylene: Wako Pure Chemical Industries, Ltd.
- Cyclohexane: Wako Pure Chemical Industries, Ltd.
- Diethylene glycol dimethyl ether: Tokyo Chemical Industry Co., Ltd.
<Synthesis of Carbon Fiber>

Comparative Example 1

A vertical furnace equipped with a heating zone 1 of the quartz-mold reaction tube (inner diameter: 31 mm, outer diameter: 36 mm, length of heating zone: about 400 mm) shown in FIG. 2 was used. The temperature of the heating zone 1 was elevated to 1,200°C with an N₂ stream, the supply of N₂ was then stopped, and H₂ as a carrier gas was instead flown into the heating zone 1 at 1 NL/min. After the temperature was stabilized, ferrocene and dimethyl disulfide were dissolved into benzene (a compound which is in a liquid state at an ordinary temperature and pressure; boiling point at an ordinary pressure is 80° C.), and the resulting solution was introduced into a vaporizer 4 heated at 200° C. to introduce each component in the amount shown in Table 1, vaporized and then entrained in H₂. In this state, a solid product was not produced. Thereafter, the flow rate of H₂ was decreased to 0.5 NL/min and methane was mixed with hydrogen at a flow rate of 0.5 NL/min. In this way, all compounds were supplied in the gaseous state into the reaction tube. The unit “NL” as used herein indicates a volume (liter) in the standard state (0° C., 1 atm).

In order to determine the residence time, the temperature was elevated to 1,200° C. with a He stream at 1 NL/min, and when the temperature was stabilized, the inside temperature of the quartz tube was measured by using a platinum-platinum.13% rhodium alloy thermocouple. As a result, the temperature was 600° C. at 24 cm from the top of the quartz tube and 1,000° C. at 29 cm. The residence time theretwixt was determined and found to be 0.59 seconds. The temperature was higher than 1,100° C. at 33 cm from the top of the quartz tube and was lower than 1,100° C. at 60 cm. The residence time theretwixt was determined and found to be 2.25 seconds.

As a result of reaction, a grayish cobweb-like deposit was produced between the bottom of reaction tube and the collector 3. After the temperature was lowered, the deposit was recovered and the carbon recovery percentage was determined by dividing the amount of the recovered deposit by the amount of carbon initially contained in the carbon source used, and found to be 44%. The conditions and results of the test are shown in Table 1.

The concentration of methane is determined according to the following equations:

\[
\text{Concentration of Methane (mol %)} = \frac{\text{Amount of Methane Supplied (mmol/min)}}{\text{Amount of Raw materials Supplied (mmol/min)} \times 100}
\]

The ratio of a residue in the column (%) is determined according to the following equation:

\[
\text{Ratio of Residue in the Column (g)} = \frac{\text{Amount of Residue in Column (g)}}{\text{Amount of Material Collected Outside Column (g)}}
\]

With regard to the experimental conditions, ratios of a total amount of carbon atom in carbon sources supplied other than methane to a total amount of carbon atom in methane supplied (%) are calculated according to the following equation, and shown in Table 2:

\[
\text{Ratio of Total Amount of Carbon Atom in Carbon Sources Supplied Other Than Methane to Total Amount of Carbon Atom in Methane Supplied (\%)} = \frac{\text{Carbon Atom Amount in Carbon Sources other than Methane (mmol/min)}}{\text{Carbon Atom Amount in Methane (mmol/min) + Carbon Atom Amount in Sulfur Compound (mmol/min)) / Carbon Atom Amount in Methane (mmol/min) \times 100}}
\]

Also, the cobweb-like product was observed by a scanning electron microscope. Out of the product, the average outer diameter was examined on about 100 pieces, as a result, the product was found to be a fibrous material having an average outer diameter of 200 nm.

Comparative Example 2

The reaction was performed according to the method of Comparative Example 1 except that toluene is used in the input amount shown in Table 1 in place of benzene as a compound which is in a liquid state at an ordinary temperature and pressure. The conditions and results of the test are shown in Tables 1 and 2. The carbon recovery percentage was 37% and the product was a fibrous material having an average outer diameter of 200 nm.

Comparative Example 3

The reaction was performed according to the method of Comparative Example 1 except that p-xylene is used in the input amount shown in Table 1 in place of benzene as a compound which is in a liquid state at an ordinary temperature and pressure. The conditions and results of the test are shown in Tables 1 and 2. The carbon recovery percentage
was 50% and the product was a fibrous material having an average outer diameter of 150 nm.

Example 1

[0104] The reaction was performed according to the method of Comparative Example 1 except that acetone is used in the input amount shown in Table 1 in place of benzene as a compound which is in a liquid state at an ordinary temperature and pressure. The conditions and results of the test are shown in Tables 1 and 2. The carbon recovery percentage was 31% and the product was a fibrous material having an average outer diameter of 200 nm.

Example 2

[0105] The reaction was performed according to the method of Comparative Example 1 except that tetrahydrofuran is used in the input amount shown in Table 1 in place of benzene as a compound which is in a liquid state at an ordinary temperature and pressure. The conditions and results of the test are shown in Tables 1 and 2. The carbon recovery percentage was 32% and the product was a mixture of similar amounts of a spherical shape material having an average diameter of 170 nm and a fibrous material having an average outer diameter of 200 nm.

Example 3

[0106] The reaction was performed according to the method of Comparative Example 1 except that tetrahydrofurane is used in the input amount shown in Table 1 in place of benzene as a compound which is in a liquid state at an ordinary temperature and pressure. The conditions and results of the test are shown in Tables 1 and 2. The carbon recovery percentage was 31% and the product was a fibrous material having an average outer diameter of 200 nm.

Example 4

[0107] The reaction was performed according to the method of Comparative Example 1 except that cyclohexanone is used in the input amount shown in Table 1 in place of benzene as a compound which is in a liquid state at an ordinary temperature and pressure. The conditions and results of the test are shown in Tables 1 and 2. The carbon recovery percentage was 32% and the product was a fibrous material having an average outer diameter of 170 nm.

Example 5

[0108] The reaction was performed according to the method of Comparative Example 1 except that diethylenglycol dimethyl ether is used in the input amount shown in Table 1 in place of benzene as a compound which is in a liquid state at an ordinary temperature and pressure. The conditions and results of the test are shown in Tables 1 and 2. The carbon recovery percentage was 32% and the product was a fibrous material having an average outer diameter of 200 nm.

---

**TABLE 1**

<table>
<thead>
<tr>
<th>Hydrocarbon Compound Introduced</th>
<th>Concentration of Methane (mol%)</th>
<th>Amount of Methane Introduced (mmol/min)</th>
<th>Boiling Point at Ordinary Pressure (°C.)</th>
<th>Amount Introduced (mmol/min)</th>
<th>Amount of Ferrocene Introduced (mmol/min)</th>
<th>Amount of Dimethyl disulfide Introduced (mmol/min)</th>
<th>Recovery Percentage Carbon Produced</th>
<th>Shape of Carbon Solid</th>
<th>Carbon Content</th>
<th>Amount of Residue in Column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Ex. 1</td>
<td>50</td>
<td>22</td>
<td>Benzene</td>
<td>80</td>
<td>0.012</td>
<td>0.0005</td>
<td>0.0002</td>
<td>44%</td>
<td>Fibrous material with fiber diameter of about 200 nm</td>
<td>38%</td>
</tr>
<tr>
<td>Comp. Ex. 2</td>
<td>50</td>
<td>22</td>
<td>Toluene</td>
<td>110</td>
<td>0.010</td>
<td>0.0005</td>
<td>0.0002</td>
<td>37%</td>
<td>Fibrous material with fiber diameter of about 200 nm</td>
<td>72%</td>
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<tr>
<td>Comp. Ex. 3</td>
<td>50</td>
<td>22</td>
<td>P-xylene</td>
<td>138</td>
<td>0.009</td>
<td>0.0005</td>
<td>0.0002</td>
<td>50%</td>
<td>Fibrous material with fiber diameter of about 150 nm</td>
<td>87%</td>
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<tr>
<td>Ex. 1</td>
<td>50</td>
<td>22</td>
<td>Acetone</td>
<td>56</td>
<td>0.015</td>
<td>0.0005</td>
<td>0.0002</td>
<td>28%</td>
<td>Mixture of Fibrous material and Spherical material (main)</td>
<td>0%</td>
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<tr>
<td>Ex. 2</td>
<td>50</td>
<td>22</td>
<td>Tetrahydrofuran</td>
<td>67</td>
<td>0.013</td>
<td>0.0005</td>
<td>0.0002</td>
<td>32%</td>
<td>Mixture of Fibrous material and Spherical material</td>
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<tr>
<td>Ex. 3</td>
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<td>22</td>
<td>Tetrahydropirin</td>
<td>88</td>
<td>0.011</td>
<td>0.0005</td>
<td>0.0002</td>
<td>31%</td>
<td>Fibrous material with fiber diameter of about 200 nm</td>
<td>0%</td>
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<td>Ex. 4</td>
<td>50</td>
<td>22</td>
<td>Cyclohexanone</td>
<td>155</td>
<td>0.010</td>
<td>0.0005</td>
<td>0.0002</td>
<td>32%</td>
<td>Fibrous material with fiber diameter of about 170 nm</td>
<td>0%</td>
</tr>
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</table>
TABLE 1-continued

<table>
<thead>
<tr>
<th>Hydrocarbon Compound Introduced</th>
<th>Concentration of Methane (mol %)</th>
<th>Amount of Methane introduced (mmol/min)</th>
<th>Boiling Point at Ordinary Pressure (°C)</th>
<th>Amount of Ferrocene introduced (mmol/min)</th>
<th>Amount of Dimethyl disulfide introduced (mmol/min)</th>
<th>Amount of Carbon Produced (mmol/min)</th>
<th>Carbon Recovery Percentage</th>
<th>Shape of Produced Carbon</th>
<th>Amount of Residue in Column</th>
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</thead>
<tbody>
<tr>
<td>Ex. 5</td>
<td>50</td>
<td>22</td>
<td>Diethylene glycol dimethyl ether</td>
<td>162</td>
<td>0.008</td>
<td>0.0005</td>
<td>32%</td>
<td>Fibrous material</td>
<td>0%</td>
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</table>

TABLE 2

<table>
<thead>
<tr>
<th>Condition of Test</th>
<th>Ratio of Total Amount of Carbon Atoms Contained in Carbon Source other than Methane to Total Amount of Carbon Atoms Contained in Methane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Ex. 1</td>
<td>0.35</td>
</tr>
<tr>
<td>Comp. Ex. 2</td>
<td>0.35</td>
</tr>
<tr>
<td>Comp. Ex. 3</td>
<td>0.35</td>
</tr>
<tr>
<td>Ex. 1</td>
<td>0.35</td>
</tr>
<tr>
<td>Ex. 2</td>
<td>0.35</td>
</tr>
<tr>
<td>Ex. 3</td>
<td>0.35</td>
</tr>
<tr>
<td>Ex. 4</td>
<td>0.35</td>
</tr>
<tr>
<td>Ex. 5</td>
<td>0.35</td>
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1. A process for producing a vapor-grown carbon fiber by supplying a raw material at least containing a carbon source and a catalyst and/or catalyst precursor compound into a heating zone, wherein the raw material further contains an oxygen-containing carbon source compound selected from the group consisting of ketones and ethers.

2. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the catalyst and/or catalyst precursor compound is in a solid or liquid state at an ordinary temperature and pressure, the oxygen-containing carbon source compound is in a liquid state at an ordinary temperature and pressure, and the catalyst and/or catalyst precursor compound is dissolved or suspended in the oxygen-containing carbon source compound to be supplied into the heating zone.

3. The process for producing a vapor-grown carbon fiber according to claim 2, wherein the oxygen-containing carbon source compound in which the catalyst and/or catalyst precursor compound has been dissolved or suspended is vaporized before being supplied into the heating zone.

4. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the oxygen-containing carbon source compound has a boiling point of 80° C. or more at an ordinary pressure.

5. The process for producing a vapor-grown carbon fiber according to claim 4, wherein the oxygen-containing carbon source compound has a boiling point of 115° C. or more at an ordinary pressure.

6. The process for producing a vapor-grown carbon fiber according to claim 5, wherein the oxygen-containing carbon source compound has a boiling point of 150° C. or more at an ordinary pressure.

7. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the solubility of the catalyst and/or catalyst precursor compound at 25° C. in the oxygen-containing carbon source compound is 1 g or more per 100 g of the oxygen-containing carbon source compound.

8. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the ketones are acetone, 2-butane, 2-pentanone, 3-pentanone, 3-methyl-2-butanoic, acetylacetone, 3-hydroxy-3-methyl-2-butanoic, 3,3-dimethyl-2-butanoic, 2-methyl-3-pentanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone, 2-hexanone, 3-hexanone, cyclopentanone, hydroxyacetone, 2-heptanone, 3-heptanone, 4-heptanone, 2,4-dimethyl-3-pentanone, 4-methoxy-4-methyl-2-pentanone, 4-hydroxy-4-methyl-2-pentanone, cyclohexanone, 2,6-dimethyl-4-heptanone, 3-methylcyclohexanone, and isophorone.

9. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the ethers are anisole, ethoxy benzene, 2-methoxytoluene, 3-methoxytoluene, 4-methoxytoluene, furan, tetrahydrofuran, 2,3-dihydrofuran, 2,5-dihydrofuran, 1,3-dioxolane, pyran, tetrahydroprynne, 1,3-dioxane, 1,4-dioxane, diethyl ether, di-n-propyl ether, di-i-propyl ether, n-butyl methyl ether, s-butyl methyl ether, t-butyl methyl ether, n-butyl ethyl ether, t-butyl ethyl ether, di-n-butyl ether, di-s-butyl ether, ethyleneglycol monomethyl ether, ethyleneglycol monomethyl ether, ethyleneglycol monoo-n-butyl ether, ethyleneglycol mono-i-butyl ether, ethyleneglycol mono-s-butyl ether, ethyleneglycol mono-i-butyl ether, ethyleneglycol mono-t-butyl ether, ethyleneglycol mono-2-ethylhexyl ether, ethyleneglycol dimethy ether, ethyleneglycol diethyl ether, ethyleneglycol di-n-propyl ether, ethyleneglycol di-i-propyl ether, ethyleneglycol di-n-butyl ether, ethyleneglycol di-s-butyl ether, ethyleneglycol di-i-butyl ether, ethyleneglycol di-t-butyl ether, propyleneglycol monomethyl ether, propyleneglycol mono-n-butyl ether, propyleneglycol mono-s-butyl ether, propyleneglycol mono-i-butyl ether, propyleneglycol mono-t-butyl ether, propyleneglycol di-n-butyl ether, propyleneglycol di-s-butyl ether, propyleneglycol di-i-butyl ether, propyleneglycol di-t-butyl ether, propyleneglycol di-s-butyl ether, propyleneglycol di-i-butyl ether, propyleneglycol di-t-butyl ether, propyleneglycol di-s-butyl ether, propyleneglyco
ether, propyleneglycol di-t-butyl ether, diethyleneglycol, diethyleneglycol monomethyl ether, diethyleneglycol monomethyl ether, diethyleneglycol mono-n-propyl ether, diethyleneglycol mono-i-propyl ether, diethyleneglycol mono-n-butyl ether, diethyleneglycol mono-s-butyl ether, diethyleneglycol mono-i-butyl ether, diethyleneglycol dimethyl ether, diethyleneglycol di-i-propyl ether, diethyleneglycol di-i-butyl ether, diethyleneglycol di-s-butyl ether, diethyleneglycol di-i-butyl ether, diethyleneglycol di-t-butyl ether, dipropyleneglycol, dipropyleneglycol monomethyl ether, dipropyleneglycol monomethyl ether, dipropyleneglycol mono-n-propyl ether, dipropyleneglycol mono-i-propyl ether, dipropyleneglycol mono-n-butyl ether, dipropyleneglycol mono-s-butyl ether, dipropyleneglycol mono-i-butyl ether, dipropyleneglycol di-n-propyl ether, dipropyleneglycol di-i-propyl ether, dipropyleneglycol di-n-butyl ether, dipropyleneglycol di-s-butyl ether, dipropyleneglycol di-i-butyl ether, dipropyleneglycol di-t-butyl ether, triethyleneglycol dimethyl ether, tetraethyleneglycol dimethyl ether, 3-methoxy-1-butanol, 3-methoxy-3-methyl-1-butanol, tetrahydrofurfuryl alcohol, ethyleneglycol monomethyl ether acetate, ethyleneglycol monomethyl ether acetate, propyleneglycol monomethyl ether acetate, propyleneglycol monoethyl ether acetate, diethyleneglycol monoethyl ether acetate, and diethyleneglycol monobutyl ether acetate.

10. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the carbon source is at least one compound selected from the group consisting of carbon monoxide, carbon dioxide, methane, ethane, propane, butane, pentane, hexane, heptane, cyclohexane, ethylene, propylene, butene, butadiene, acetylene, benzene, toluene and xylene.

11. The process for producing a vapor-grown carbon fiber according to claim 10, wherein the carbon source is at least one compound selected from the group consisting of carbon monoxide, carbon dioxide, methane, ethane, propane, butane, pentane, hexane, heptane, cyclohexane, ethylene, propylene, butene, butadiene and acetylene.

12. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the carbon source comprises at least methane.

13. The process for producing a vapor-grown carbon fiber according to claim 12, wherein the content of methane in the raw material is at or more than 15 mol % to less than 100 mol %, and the temperature in the high-temperature part of the heating zone is from 1,100 to 1,500° C.

14. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the temperature at the raw material-introducing part of the heating zone is 700° C. or less.

15. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the supplied raw material resides in the law temperature part of the heating zone which is at a temperature of 600 to 1,000° C. for 0.05 seconds or more before arriving at the high-temperature part of the heating zone.

16. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the residence time at a temperature of 1,100° C. or more in the heating zone is 0.001 second or more.

17. The process for producing a vapor-grown carbon fiber according to claim 12, wherein the total amount of carbon atoms contained in the carbon source other than methane is 60% or less of the amount of carbon atoms contained in methane.

18. The process for producing a vapor-grown carbon fiber according to claim 17, wherein the total amount of carbon atoms contained in the carbon source other than methane is 10% or less of the amount of carbon atoms contained in methane.

19. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the ratio of the atomic number of a catalyst element and the number of carbon atoms in the raw material satisfies the following relationship:

\[
\text{(Atomic number of a catalyst element)/(Number of carbon atoms)} = 0.0000005 \text{ to } 0.0015.
\]

20. The process for producing a vapor-grown carbon fiber according to claim 1, wherein the all or a part of the gas after reaction is circulated and reused.

21. The process for producing a vapor-grown carbon fiber according to claim 1, wherein a carbon fiber having an average fiber diameter of 10 nm or more is produced.

22. A vapor-grown carbon fiber produced by the process for producing a vapor-grown carbon fiber according to claim 1.

23. The vapor-grown carbon fiber according to claim 22, having an average fiber length of 10 μm or more.

24. The vapor-grown carbon fiber according to claim 23, having the average fiber length of 15 μm or more.

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