Until now, using this method a sulphur compound has always been required to control the size of the iron catalyst particles. Sulphur is known to form stable bonds with iron, thereby demobilizing the catalyst on the surface and preserving the particle in its current size and guaranteeing a narrow size distribution of the iron nanoparticles. Iron atoms become available from their ferrocene precursor from about 400 °C and start to collide in the reactor tube. During the time until carbon becomes available for reaction, the growth of iron particles by coalescence of the atoms is uncontrolled and produces a variety of sizes in iron clusters. Due to its high stability, CH_4 (methane) has a comparatively high pyrolization temperature and thus carbon only becomes available for reaction with the transition metal at around 1200 °C. In order to keep these clusters small and in a narrow size range, sulphur compounds such as thiophene, carbon disulphide and others have been applied. These less stable hetero-compounds were chosen to release sulphur at temperatures similar to ferrocene pyrolization. Due to their high vapour pressure these sulphur compounds however are difficult to dose. Too much sulphur present for the reaction entirely encapsulates iron and thus hinders its catalytic activity completely. As a result, an excessive amount of very short, unaligned tubes are formed around the catalyst particles, commonly referred to as “impurities”. Moreover, sulphur compounds suitable for the continuous CNT production process generally show a high toxicity for humans, particularly the hazard of reproductive damage. Therefore, developing a process without any sulphur utilization is highly desirable.

Summary of the Invention

Embodiments of the present invention seek to provide a solution to the above problem by providing a method of catalyst control not requiring sulphur, for example.

The present invention is a floating catalyst chemical vapour deposition method as defined in Claim 1 of the appended claims, for producing nanotubes. Also provided is a floating catalyst chemical vapour deposition system as defined in Claim 14. Optional features are set out in the dependent claims.

Thus, according to a first aspect of the present invention there is provided a floating catalyst chemical vapour deposition method for producing nanotubes, the method including: supplying a nanotube-material precursor and a catalyst precursor,

heating said precursors and injecting said precursors into a heated reaction chamber containing a process gas (such as hydrogen, helium or argon, for example); pyrolysing the catalyst precursor within the reaction chamber to produce catalyst particles; and pyrolysing the nanotube-material precursor within the reaction chamber in the presence of the catalyst particles in order to produce nanotubes.

By controlling the operational parameters of the reaction chamber and/or of the precursor supplies, and thereby controlling the size of the catalyst particles at the point of pyrolysis of the nanotube-material precursor, this obviates the need for heteroatomic additives (e.g. sulphur-, nitrogen- or oxygen-containing compounds) to be provided to the catalyst, and preferably no heteroatomic additives are provided. This in turn mitigates any toxicity issues associated with the nanotube production process. The likelihood of impurities being present in the nanotube product is also reduced, thereby giving a cleaner material. It also removes any need for doping.

Further advantages are that the catalyst preparation process is simplified, undesirable reactions between the catalyst and the heteroatomic additives (e.g. iron atoms combining with nitrogen or sulphur atoms to produce Fe_xN or FeS) are avoided, and there is no need to remove reaction products of this kind (e.g. Fe_xN or FeS) during the course of the nanotube production process. This in turn makes the overall production process more efficient and better suited to continuous, scalable, one-step operation.

The expression “the reaction chamber containing a process gas” should be interpreted broadly, to encompass a dedicated process gas that is used to prefill the reaction chamber, and also the use of a carrier gas (used to transport one or both of the precursors to the reaction chamber) as the process gas.

is not as high as the pyrolisation temperature itself. In practice, the injection temperature is determined experimentally and depends on the precursor material in question. For example, in the case of ferrocene the ideal injection temperature is typically in the range of 300-320 °C, whereas pyrolisation of ferrocene occurs at 400 °C.

Preferably the nanotube-material atoms contact the catalyst particles such that the nanotube-material atoms act as an arresting agent that limits the growth of the catalyst particles.

The nanotube-material precursor may be injected using a carrier gas (such as hydrogen, helium or argon, for example). Likewise, the catalyst precursor may be injected using a carrier gas (such as hydrogen, helium or argon, for example). The carrier gas may be the same as the process gas.

The nanotube-material precursor may be injected into the reaction chamber using a first injection pipe, and the catalyst precursor may be injected into the reaction chamber using a second injection pipe. The term “injection pipe” as used herein should be interpreted broadly, to encompass pipes which are tapered or terminate in some kind of nozzle, as well as pipes of a constant cross-section.

The process gas may be injected using a third injection pipe.

In some cases, at least two of the nanotube-material precursor, the catalyst precursor and the process gas may be injected into the reaction chamber via a common injection pipe. This may involve pre-mixing the at least two gases before supplying them to the common injection pipe.

For a given catalyst, controlling the operational parameters of the reaction chamber and/or precursor supplies comprises controlling one or more of: the injection temperature of the catalyst precursor; the flow rate of the carrier gas of the catalyst precursor (which in turn can affect the concentration of the catalyst precursor); the injection temperature of the nanotube-material precursor; the flow

rate of the carrier gas of the nanotube-material precursor (which in turn can affect the concentration of the nanotube-material precursor); and the reaction temperature.

According to the present invention, the catalyst precursor is injected by an injection pipe having an adjustable length within the reaction chamber, and controlling the injection temperature of the catalyst precursor comprises adjusting the extent to which its injection pipe extends into the reaction chamber; and/or the nanotube-material precursor is injected by an injection pipe having an adjustable length within the reaction chamber, and controlling the injection temperature of the nanotube-material precursor comprises adjusting the extent to which its injection pipe extends into the reaction chamber.

In addition, controlling the injection temperature of the catalyst precursor may further comprise controlling the temperature of its injection pipe (e.g. by heating, cooling or otherwise regulating the temperature of the injection pipe).

Likewise, controlling the injection temperature of the nanotube-material precursor may further comprise controlling the temperature of its injection pipe (e.g. by heating, cooling or otherwise regulating the temperature of the injection pipe).

Alternatively, or in addition, controlling the injection temperature of the catalyst precursor and/or the nanotube-material precursor may further comprise controlling the heating of the catalyst precursor and/or the nanotube-material precursor before they are injected.

Through the above techniques which affect the injection temperature of the catalyst precursor, this enables the point of injection of the catalyst precursor to be optimised. This is important, since injection at too low a temperature can result in the formation of a great variety of catalyst particle diameters, whereas injection at too high a temperature can result in the catalyst precursor pyrolising within the (comparatively) narrow space of the injector pipe. The resulting higher collision

Preferably the walls of the injector subsystem are formed from metal, and particularly preferably from a single piece of metal.

The present disclosure also provides an injector subsystem for attachment to a reaction chamber, the injector subsystem comprising: a first portion having a first set of injection pipes for receiving species for delivery into the reaction chamber; and an interface portion that is removably attachable between the first portion and the reaction chamber in use, the interface portion comprising at least one injection pipe arranged to receive the species provided by the first set of injection pipes and to inject said species into the reaction chamber in use; the injector subsystem being operable in use such that, with the interface portion removed, said first set of injection pipes are operable to individually inject their respective species into the reaction chamber, and with the interface portion attached, a pre-mixing chamber is defined by the interface portion in combination with the first portion, for pre-mixing the species provided by the first set of injection pipes prior to the species entering the at least one injection pipe of the interface portion.

Preferably the extent to which each of the first set of injection pipes protrudes within the first portion is adjustable. Likewise, preferably the extent to which the at least one injection pipe of the interface portion extends into the reaction chamber is adjustable.

In one example of the injector subsystem, when the interface portion is attached, the side walls of the pre-mixing chamber are provided by the first portion. Alternatively, when the interface portion is attached, the side walls of the pre-mixing chamber may be provided by the interface portion. In a further alternative, when the interface portion is attached, the side walls of the pre-mixing chamber may be provided partly by the first portion and partly by the interface portion.

Preferably the injector subsystem comprises one or more temperature sensors and one or more heating elements for controlling the temperature of the species

CLAIMS

1. A floating catalyst chemical vapour deposition method for producing nanotubes, the method including:

heating a nanotube material precursor and a catalyst precursor and injecting said precursors into a heated reaction chamber containing a process gas;

pyrolysing the catalyst precursor within the reaction chamber to produce catalyst particles; and

pyrolysing the nanotube-material precursor within the reaction chamber in the presence of the catalyst particles in order to produce nanotubes;

wherein the method further comprises controlling one or more operational parameters of the reaction chamber and/or of the precursor supplies selected from (a) the injection temperature of the catalyst precursor, (b) the injection temperature of the nanotube-material precursor, (c) the flow rate of a carrier gas of the catalyst precursor, (d) the flow rate of a carrier gas of the nanotube-material precursor, and (e) the reaction temperature;

wherein the catalyst precursor is injected by an injection pipe having an adjustable length within the reaction chamber, and controlling the injection temperature of the catalyst precursor comprises adjusting the extent to which its injection pipe extends into the reaction chamber;

and/or the nanotube-material precursor is injected by an injection pipe having an adjustable length within the reaction chamber, and controlling the injection temperature of the nanotube-material precursor comprises adjusting the extent to which its injection pipe extends into the reaction chamber.

2. A method as claimed in claim 1, wherein the nanotubes are carbon nanotubes, the nanotube-material is carbon, and the nanotube-material precursor is a carbon precursor such as ethanol, hexane, methane or toluene;

or wherein the nanotubes are boron nitride nanotubes, the nanotube-material is boron nitride, and the nanotube-material precursor is a boron nitride precursor such as borazine.

3. A method as claimed in claim 1 or claim 2, wherein the catalyst precursor comprises a transition metal derivative such as cobaltocene, ferrocene, nickelocene or iron pentacarbonyl, or a non-metallic precursor such as zirconium oxide powder or silica powder.

4. A method as claimed in any preceding claim, wherein no heteroatomic additives are provided to the catalyst.

5. A method as claimed in any preceding claim, wherein the catalyst precursor is heated to its sublimation temperature and the nanotube-material precursor is heated to its vaporisation temperature;

and/or wherein the catalyst precursor is injected close to its pyrolisation temperature and the nanotube-material precursor is injected close to its pyrolisation temperature.

6. A method as claimed in any preceding claim, wherein the nanotube-material precursor is injected using a carrier gas;

and/or wherein the catalyst precursor is injected using a carrier gas.

7. A method as claimed in any preceding claim, wherein the nanotube-material precursor is injected into the reaction chamber using a first injection pipe and the catalyst precursor is injected into the reaction chamber using a second injection pipe;

optionally wherein the process gas is injected using a third injection pipe.

8. A method as claimed in any of claims 1 to 6, wherein at least two of the nanotube-material precursor, the catalyst precursor and the process gas are injected into the reaction chamber via a common injection pipe;

optionally wherein the method further comprises pre-mixing the at least two of the nanotube-material precursor, the catalyst precursor and the process gas before supplying them to the common injection pipe.

9. A method as claimed in any preceding claim, wherein controlling the injection temperature of the catalyst precursor further comprises controlling the temperature of its injection pipe, and/or wherein controlling the injection temperature of the nanotube-material precursor further comprises controlling the temperature of its injection pipe;

and/or wherein controlling the injection temperature of the catalyst precursor and/or the nanotube-material precursor further comprises controlling the heating of the catalyst precursor and/or the nanotube-material precursor before they are injected.

10. A method as claimed in any preceding claim,

wherein controlling the operational parameters of the reaction chamber and/or precursor supplies comprises:

selecting, from the pre-stored operational parameters, the operational parameters corresponding to a desired nanotube diameter;

configuring the reaction chamber and/or precursor supplies according to the selected operational parameters; and then

carrying out the chemical vapour deposition process to produce nanotubes having the desired diameter.

11. A method as claimed in any of claims 1 to 9, wherein controlling the operational parameters of the reaction chamber and/or precursor supplies comprises producing one or more samples of nanotubes, removing the sample(s) from the reaction chamber, determining the size of catalyst particles present in the sample(s), comparing the determined catalyst particle size with a predetermined target particle size, and adjusting the operational parameters of the reaction chamber and/or precursor supplies in dependence on the result of the comparison.

12. A method as claimed in any of claims 1 to 9, wherein controlling the operational parameters of the reaction chamber and/or precursor supplies comprises operating a particle counter in the reaction chamber, processing the particle count results to determine the size of catalyst particles present in the reaction chamber, comparing the determined particle sizes with a predetermined

target particle size value, and adjusting the operational parameters of the reaction chamber and/or precursor supplies in dependence on the result of the comparison.

13. A method as claimed in any preceding claim, further comprising extracting the nanotubes using a continuous extraction process.

14. A floating catalyst chemical vapour deposition system for producing nanotubes, the system including:

a heatable reaction chamber;

means for heating a nanotube-material precursor and a catalyst precursor, and means for injecting said precursors into the reaction chamber ;

means for pyrolysing the catalyst precursor within the reaction chamber to produce catalyst particles, and means for pyrolysing the nanotube-material precursor within the reaction chamber in the presence of the catalyst particles in order to produce nanotubes; and

means for controlling one or more operational parameters of the reaction chamber and/or of the precursor supplies selected from (a) the injection temperature of the catalyst precursor, (b) the injection temperature of the nanotube-material precursor, (c) the flow rate of a carrier gas of the catalyst precursor, (d) the flow rate of a carrier gas of the nanotube-material precursor, and (e) the reaction temperature;

wherein the means for injecting the catalyst precursor comprises an injection pipe having an adjustable length within the reaction chamber, and the means for controlling the injection temperature of the catalyst precursor comprise means for adjusting the extent to which its injection pipe extends into the reaction chamber;

and/or the means for injecting the nanotube-material precursor comprises an injection pipe having an adjustable length within the reaction chamber, and the means for controlling the injection temperature of the nanotube-material precursor comprises means for adjusting the extent to which its injection pipe extends into the reaction chamber.

15. A system as claimed in claim 14, wherein said means for injecting comprise a first injection pipe for injecting the nanotube-material precursor into the reaction chamber, and a second injection pipe for injecting the catalyst precursor into the reaction chamber;

optionally wherein the system further comprises a third injection pipe for injecting a process gas into the reaction chamber.

16. A system as claimed in claim 14, wherein said means for injecting comprise a common injection pipe via which at least two of the nanotube-material precursor, the catalyst precursor and a process gas are arranged to be injected into the reaction chamber;

optionally wherein the system further comprises means for pre-mixing the at least two of the nanotube-material precursor, the catalyst precursor and the process gas before supplying them to the common injection pipe.

17. A system as claimed in claim 14, further comprising an injector subsystem comprising:

a first portion having a first set of injection pipes for receiving species for delivery into the reaction chamber; and

an interface portion that is removably attachable between the first portion and the reaction chamber, the interface portion comprising at least one injection pipe arranged to receive the species provided by the first set of injection pipes and to inject said species into the reaction chamber;

the injector subsystem being operable such that, with the interface portion removed, said first set of injection pipes are operable to individually inject their respective species into the reaction chamber, and with the interface portion attached, a pre-mixing chamber is defined by the interface portion in combination with the first portion, for pre-mixing the species provided by the first set of injection pipes prior to the species entering the at least one injection pipe of the interface portion.

18. A system as claimed in claim 17 wherein, when the interface portion is attached, the side walls of the pre-mixing chamber are provided by the first portion;

or wherein, when the interface portion is attached, the side walls of the pre-mixing chamber are provided by the interface portion;

or wherein, when the interface portion is attached, the side walls of the pre-mixing chamber are provided partly by the first portion and partly by the interface portion.

19. A system as claimed in claim 17 or claim 18, wherein the injector subsystem comprises one or more temperature sensors and one or more heating elements for controlling the temperature of the species being injected.

20. A system as claimed in any of claims 14 to 19, further comprising means for extracting the nanotubes using a continuous extraction process.