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- (56) Related Art
Flahaut, et al., CCVD synthesis of carbon nanotubes from (Mg, Co, Mo)O catalysts: influence of the proportions of cobalt and molybdenum, J. Mater. Chem. 2004; 14: 646-653
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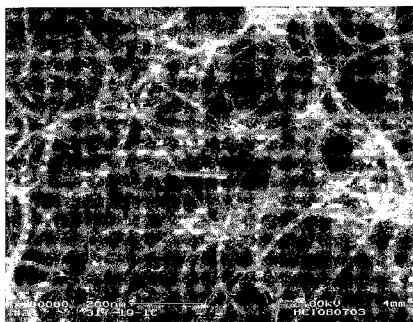
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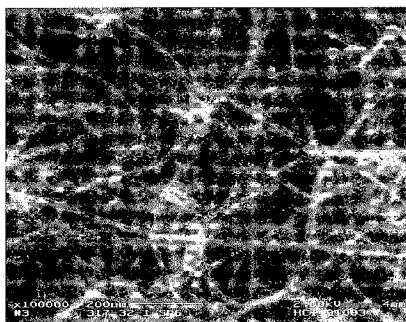
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(54) Title: SINGLE-WALLED CARBON NANOTUBE CATALYST



A



B

(57) Abstract: An activated catalyst capable of selectively growing single-walled carbon nanotubes when reacted with carbonaceous gas is provided. The activated catalyst is formed by reducing a catalyst that comprises a complex oxide. The complex oxide may be of formula $A_xB_zO_z$, wherein $x/y \leq 2$ and $z/y \leq 4$, A being a Group VIII element and B being an element such that an oxide of element B is not reducible in the presence of hydrogen at a temperature less than or equal to about 900°C. Methods of making, uses for and carbon fibril-containing product made with these activated catalysts are also provided.

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SINGLE-WALLED CARBON NANOTUBE CATALYST

CROSS REFERENCE INFORMATION

[0001] This application claims benefit to and priority of U.S. Provisional Application
5 No. 60/650,726, filed February 7, 2005, which is hereby incorporated by reference in its
entirety.

BACKGROUND OF THE INVENTION**Field of Invention**

10 [0002] The invention relates to materials and methods for commercially preparing single
walled carbon nanotubes. More specifically, this invention relates to material comprising
complex oxides, which, when further processed, are viable activated catalysts for carbon fibril-
containing products. These products exhibit both a Raman spectrum and characteristic
transmission electron micrographs known to indicate the presence of single walled carbon
15 nanotubes.

Description of the Related Art

[0003] This invention lies in the field of carbon nanotubes (also known as fibrils).
Carbon nanotubes are vermicular carbon deposits having diameters less than 1.0 μ , preferably
less than 0.5 μ , and even more preferably less than 0.2 μ . Carbon nanotubes can be either multi
20 walled (*i.e.*, have more than one graphene layer more or less parallel to the nanotube axis) or
single walled (*i.e.*, have only a single graphene layer parallel to the nanotube axis). Other types
of carbon nanotubes are also known, such as fishbone fibrils (*e.g.*, wherein the graphene layers
are arranged in a herringbone pattern, compared to the tube axis), etc. As produced, carbon
nanotubes may be in the form of discrete nanotubes, aggregates of nanotubes (*i.e.*, dense,
25 microscopic particulate structure comprising entangled carbon nanotubes) or a mixture of both.

[0004] Carbon nanotubes are distinguishable from commercially available continuous carbon fibers. For instance, diameter of continuous carbon fibers, which is always greater than 1.0 μ and typically 5 to 7 μ , is far larger than that of carbon nanotubes, which is usually less than 1.0 μ . Carbon nanotubes also have vastly superior strength and conductivity than carbon fibers.

[0005] Carbon nanotubes also differ physically and chemically from other forms of carbon such as standard graphite and carbon black. Standard graphite, because of its structure, can undergo oxidation to almost complete saturation. Moreover, carbon black is an amorphous carbon generally in the form of spheroidal particles having a graphene structure, such as carbon layers around a disordered nucleus. On the other hand, carbon nanotubes have one or more layers of ordered graphitic carbon atoms disposed substantially concentrically about the cylindrical axis of the nanotube. These differences, among others, make graphite and carbon black poor predictors of carbon nanotube chemistry.

[0006] It has been further accepted that multi walled and single walled carbon nanotubes are also different from each other. For example, multi walled carbon nanotubes have multiple layers of graphite along the nanotube axis while single walled carbon nanotubes only have a single graphitic layer on the nanotube axis.

[0007] The methods of producing multi walled carbon nanotubes also differ from the methods used to produce single walled carbon nanotubes. Specifically, different combinations of catalysts, catalyst supports, raw materials and reaction conditions are required to yield multi walled versus single walled carbon nanotubes. Certain combinations will also yield a mixture of multi walled and single walled carbon nanotubes.

[0008] As such, two characteristics are often examined in order to determine whether such process will be commercially feasible for the production of a desired carbon nanotube on an industrial scale. The first is catalyst selectivity (*e.g.*, will the catalyst yield primarily single wall carbon nanotubes or primarily multi-walled carbon nanotubes or other forms of carbon products?). A selectivity of at least 50% is preferred. The second is catalyst yield (*e.g.*, weight of carbon product generated per weight of catalyst used).

[0009] Single-wall nanotube catalyst selectivity can be measured through evaluation of Raman spectra signatures of fibril-containing products, which are informative for differentiating single (and perhaps, double)-walled nanotubes from multi-walled tubes. *E.g.*, "Diameter-

Selective Raman Scattering from Vibrational Modes in Carbon Nanotubes," Rao, A M et al, Science, vol. 257, p. 187 (1997); Dresselhaus, M.S., et al., "Single Nanotube Raman Spectroscopy," Accounts Of Chemical Research I, vol. 35, no. 12, pp. 1070-1078 (2002), both hereby incorporated by reference. For example, a sample having sufficiently small diameter nanotubes to be single-walled has a Raman spectrum exhibiting: "radial breathing mode" (RBM) peaks between 150 and 300 wave numbers, the area under the RBM peaks at least 0.1% of the area under a characteristic G band peak, and the intensity of the G band peak at least twice that of a characteristic D band peak (G/D of at least 2.0).

[0010] The following multi-walled tube (MWNT) process references are hereby incorporated by reference: Baker and Harris, Chemistry and Physics of Carbon, Walker and Throver ed., Vol. 14, 1978, p. 83; Rodriguez, N., J. Mater. Research, Vol. 8, p. 3233 (1993); Oberlin, A. and Endo, M., J. of Crystal Growth, Vol. 32 (1976), pp. 335-349; U.S. Patent No. 4,663,230 to Tennent et al.; U.S. Patent No. 5,171,560 to Tennent et al.; Iijima, Nature 354, 56, 1991; Weaver, Science 265, 1994; de Heer, Walt A., "Nanotubes and the Pursuit of Applications," MRS Bulletin, April, 2004, U.S. Patent No. 5,456,897 to Moy et al, U.S. Patent No. 6,143,689 to Moy et al, and U.S. Patent No. 5,569,635 to Moy et al.

[0011] Processes for making single-walled carbon nanotubes (SWNT) are also known. E.g., "Single-shell carbon nanotubes of 1-nm diameter", Iijima, S. and Ichihashi, T. Nature, vol.363, p. 603 (1993); "Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls," Bethune, D S, Kiang, C H, DeVries, M S, Gorman, G, Savoy, R and Beyers, R Nature, vol.363, p. 605 (1993); U.S. Pat. No. 5,424,054 to Bethune et al.; Guo, T., Nikoleev, P., Thess, A., Colbert, D. T., and Smalley, R. E., Chem. Phys. Letters 243: 1-12 (1995); Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y. H., Kim, S. G., Rinzler, A. G., Colbert, D. T., Scuseria, G. E., Tonarek, D., Fischer, J. E., and Smalley, R. E., Science, 273: 483-487 (1996); Dai, H., Rinzler, A. G., Nikolaev, P., Thess, A., Colbert, D. T., and Smalley, R. E., Chem. Phys. Letters 260: 471-475 (1996); U.S. Patent No. 6,761,870 (also WO 00/26138) to Smalley et al; "Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co-Mo catalysts," Chemical Physics Letters, 317 (2000) 497-503; U.S. Patent No. 6,333,016 to Resasco et al.; "Low-temperature synthesis of high-purity single walled carbon nanotubes from alcohol," Maruyama et al Chemical Physics Letters, 360, pp. 229-234 (July 10, 2002). These articles and patent documents are hereby

incorporated by reference. Currently known processes for forming single-walled tubes are unable to reach industrially acceptable levels of selectivity and yield under commercially viable reaction conditions.

[0012] Recent literature contains disclosures describing the benefits of using catalytic

precursors that comprise solid solutions of transition metal oxide(s) and non-reducible (at practical temperatures) oxides. These solid solutions of mixed oxides must be calcined at relatively high temperatures to avoid the presence of oxide phases. Bacsa, R.R. et al., Chem. Phys. Letters 323: 566-571 (2000) and J. Am. Ceram. Soc., 85: 2666-69 (2002), both

incorporated by reference, describe catalysts made by the selective reduction ($T > 800^{\circ}\text{C}$) in H_2/CH_4 of "solid solutions between one or more transition metal oxides and a non-reducible oxide such as Al_2O_3 , MgAl_2O_4 or MgO ." The solid solutions were made by combustion synthesis, employing combustion of both precursors and a fuel (typically urea). Both transmission electron micrographs and Raman spectra showed the presence of a mixture of single-walled/double walled tubes and a substantial amount of non-tubular amorphous products.

Flahaut, et al., J. Materials Chemistry, 10: 249-252 (2000) describes the same catalyst synthesis as above except giving combustion synthesis temperature as "usually $>800^{\circ}\text{C}$ ".

[0013] Coquay, et al., J. Phys Chem B, 106: 13199 (2002) and Coquay, et al. J. Phys Chem B, 106: 13186 (2002) both identify that the use of oxide phase Co_3O_4 catalyzes a yield of thick nanofibers. This was a shortcoming of previous flame synthesis methods in making single-walled nanotube catalysts. Flame-synthesized $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ solid solutions are found to catalyze formation of single-walled nanotubes, while A_2BO_4 - like particles tend to yield only thick nanofibers. The electron micrographs of product made from flame-synthesized $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ solid solutions reveal that these catalysts only occasionally yield form SWNTs, rather than selectively, thus yielding a few SWNTS along with a broad spectrum of other carbonaceous products.

[0014] Wang and Ruckenstein, Carbon, 40: 1911-1917 (2002) discloses and characterizes a range of Co/Mg/O catalysts with differing stoichiometries and calcining temperatures used in their preparation. They report on the formation of filamentous carbon after methane decomposition at 900°C for the variously prepared catalysts. They found that the A_2BO_4 phase only forms at calcining $T < 700^{\circ}\text{C}$ and that only catalysts calcined at $T = 900^{\circ}\text{C}$.

However, XRD analysis revealed a solid solution of filamentous carbon, but not single-walled nanotubes.

The references cited above, while employing mixed metals as catalysts, all disclose and specifically conclude that solid solutions (in contrast with complex oxide phase material) are favored to generate either tubular or filamentous carbon products. There is a need for a method for producing single walled carbon nanotubes with industrially acceptable levels of activity, selectivity and yield under commercially viable reaction conditions. None of the prior art discloses such a methodology; discovery of an acceptable process remains elusive despite an ongoing worldwide search to develop it.

Summary of the Invention

According to a first aspect of the present invention, there is provided a method of making single walled carbon nanotubes comprising:

providing a composition comprising a complex oxide having a formula

$A_xB_yO_z$, wherein

$x/y \leq 2$ and $z/y \leq 4$,

A is a Group VIII element;

B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900°C;

reducing said composition to form an activated catalyst;

contacting a carbonaceous gas with said activated catalyst under suitable conditions for growing single walled carbon nanotubes, said suitable conditions including pressure greater than about 1 atmosphere and less than about 10 atmospheres and temperature greater than about 400°C and less than about 950°C; and

growing carbon nanotubes on said activated catalyst, said carbon nanotubes comprising single walled carbon nanotubes.

According to a second aspect of the present invention, there is provided a method of making single walled carbon nanotubes comprising:

contacting a carbonaceous gas with an activated catalyst in a reaction zone at suitable conditions for growing single walled carbon nanotubes,

said suitable conditions including a pressure greater than about 1 atmosphere and less than about 10 atmospheres and temperature greater than about 400°C and less than about 950°C,

said activated catalyst comprising a reduced form of a complex oxide, said complex oxide having a formula $A_xB_yO_z$, wherein

$x/y \leq 2$ and $z/y \leq 4$,

A is a Group VIII element;

B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900°C; and

growing carbon nanotubes on said activated catalyst, said carbon nanotubes comprising single walled carbon nanotubes.

According to a third aspect of the present invention, there is provided a method of making a catalyst for use in a process for the manufacture of single walled carbon nanotubes comprising the steps of:

reacting a source of A with a source of B at a temperature sufficiently low so as to form a complex oxide having a formula $A_xB_yO_z$, wherein

$x/y \leq 2$ and $z/y \leq 4$,

A is a Group VIII element, and

B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900°C, and

activating the complex oxide by reducing said complex oxide at a temperature less than about 950°C.

According to a fourth aspect of the present invention, there is provided a method of making a catalyst for use in a process for the manufacture of a single walled carbon nanotubes comprising the step of reducing a complex oxide of formula $A_xB_yO_z$ at a temperature less than 950°C, wherein

$x/y \leq 2$ and $z/y \leq 4$,

A is a Group VIII element, and

B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900°C.

According to a fifth aspect of the present invention, there is provided a catalyst manufactured by the method of the third aspect.

According to a sixth aspect of the present invention, there is provided a catalyst manufactured by the method of the fourth aspect.

[0016] An activated catalyst capable of growing single-walled carbon nanotubes when reacted with carbonaceous gas, and a method for making such an activated catalyst, is provided. The activated catalyst is formed by reacting a source of A with a source of B at a temperature sufficiently low so as to form a complex oxide having a formula $A_xB_yO_z$, wherein $x/y \leq 2$ and $z/y \leq 4$,

A is a Group VIII element, and B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900°C, and then activating the complex oxide by reducing said complex oxide at a temperature less than about 950°C.

- 5 [0017] Element A may comprise cobalt, iron, nickel, or a mixture thereof. Element B is selected from aluminum, lanthanum, magnesium, silicon, titanium, zinc, zirconium, yttrium, calcium, strontium and barium and may preferably be magnesium. The complex oxide may have a spinel crystallography, wherein the spinels comprise a group of oxides that have very similar structures. The general formula of the spinel group is AB_2O_4 . The element A represents a divalent metal ion
- 10 such as magnesium, ferrous iron, nickel, manganese and/or zinc. The element B represents trivalent metal ions such as aluminum, ferric ion, chromium and/or manganese. When A cobalt and B is magnesium, the complex oxide may comprise Co_2MgO_4 spinel and the calcining temperature (in air) may be less than about 800°C and greater than about 400°C. Reduction of the catalyst may occur under flowing hydrogen and the activated catalyst may be passivated as an additional
- 15 process step.

[0018] A further embodiment discloses a method of making single walled carbon nanotubes from the activated catalyst of the present invention.

[0019] In an exemplary embodiment, a method of making single walled carbon nanotubes is provided comprising providing a composition comprising a complex oxide having a formula $A_xB_yO_z$, wherein $x/y \leq 2$ and $z/y \leq 4$, A is a Group VIII element; B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900°C; reducing said composition to form an activated catalyst; contacting a carbonaceous gas with said activated catalyst under suitable conditions for growing single walled carbon nanotubes, said suitable conditions including pressure greater than about 1 atmosphere and less than about 10 atmospheres and temperature greater than about 400°C and less than about 950°C; and growing carbon nanotubes on said activated catalyst, said carbon nanotubes comprising single walled carbon nanotubes.

[0020] In another embodiment, a method of making single walled carbon nanotubes is provided which comprises contacting a carbonaceous gas with an activated catalyst in a reaction zone at suitable conditions for growing single walled carbon nanotubes, said suitable conditions including a pressure greater than about 1 atmosphere and less than about 10 atmospheres and temperature greater than about 400°C and less than about 950°C, said activated catalyst comprising a reduced form of a complex oxide, said complex oxide having a formula $A_xB_yO_z$, wherein $x/y \leq 2$ and $z/y \leq 4$, A is a Group VIII element; B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900 °C; and growing carbon nanotubes on said activated catalyst, said carbon nanotubes comprising single walled carbon nanotubes.

[0021] An additional embodiment provides for an activated catalyst capable of selectively growing a carbon fibril-containing product when reacted with carbonaceous gas. The activated catalyst is formed by reduction of a catalyst that comprises a complex oxide, wherein the product is characterized by a Raman spectrum exhibiting RBM peaks between 150 and 300 wave numbers, having the area under said RBM peaks being at least 0.1% of the area under a characteristic G band peak and having the intensity of the G band peak being at least twice that of a characteristic D band peak. Additional embodiments disclose methods of

making, use of, and the product formed by such use. Other improvements which the present invention provides over the prior art will be identified as a result of the following description which sets forth specific embodiments. The description is not in any way intended to limit the scope of the present invention, but rather only to provide examples. The scope of the present invention is pointed out in the appended claims.

Brief Description of the Drawings

[0022] FIG. 1 illustrates calcination of Co and Mg metal film coatings on a silicon wafer. The final composition of the coating is dependent upon the calcining temperature.

[0023] FIG. 2 illustrates Raman spectra of carbon fibril-containing products formed by catalytic decomposition of a carbonaceous gas on Co-Mg mixed oxide catalyst calcined in air at different temperatures. At above 400°C, the presence of single-walled nanotubes is evidenced by the appearance of radial-breathing mode (RBM) peak(s) in the 150-300 cm⁻¹ region.

[0024] FIG. 3 illustrates Raman spectra of carbon fibril-containing product formed by catalytic decomposition of a carbonaceous gas made on Co-Mg mixed oxide catalysts calcined in air at 800°C with and without further hydrogen treatment and passivation. Addition of a mild hydrogen treatment proved to enhance the selectivity of single-walled nanotubes as is shown by the greater intensity RBM peak.

[0025] FIG. 4 illustrates Raman spectrum of product made from a Fe-Mg complex oxide catalyst at 900°C in methane.

[0026] FIG. 5 illustrates scanning electron micrographs of carbon fibril-containing products made using Co-Mg complex oxide catalyst (A) and Fe-Mg complex oxide catalyst (B) at 900°C in methane. Both catalysts had been calcined in air at 675°C for one hour.

[0027] FIG. 6 illustrates a transmission electron micrograph of product made from an activated Co-Mg complex oxide catalyst at 900°C in methane.

[0028] FIG. 7 illustrates spectra of reduction of Co nitrate (Sample A) and Co acetate (Sample B) with 5% H₂/Ar as reducing carrier gas

[0029] FIG. 8 illustrates the spectrum of reduction of 9% Fe/Al₂O₃ with 5% H₂/Ar reducing carrier gas. The first reduction (I) at 400° C indicated the transition from Fe₂O₃ to Fe₃O₄, followed by Fe₃O₄ to FeAl₂O₄ at 530° C (II) and finally to metallic Fe at 740° C (III).

[0030] FIG. 9 illustrates Raman spectrum of a high quality single-wall nanotubes-containing product formed by catalytic decomposition of a carbonaceous gas on 9% Fe/Al₂O₃ calcined at 800° C. The presence of high quality single wall carbon nanotubes is evidenced by the presence of strong RBM and G-bands with minimum D-band signal.

Detailed Description of Specific Embodiments

[0031] For the purposes of this disclosure, a catalyst is a material or composition which may be further processed to become capable of forming carbon nanotubes (note that vapor grown carbon fibers, fibrils, graphitic fibrils, linear fullerenes, and buckytubes are herein to be considered equivalent terminology to nanotubes) by catalytic decomposition of a carbonaceous gas. A carbonaceous gas is defined as a gas consisting of, containing, relating to or yielding carbon.

[0032] More specifically, prior to (or simultaneously with) exposure of the material to the carbonaceous gas, the catalyst is "activated" so that nanotube formation will be thermodynamically and kinetically favorable. Catalysts for the formation of carbon nanotubes are typically "activated" by a reduction process which alters or reduces that material's valence state. As such, an "activated" catalyst is a reduced form of a catalyst or a catalyst that has been further processed to alter or reduce its valence state.

[0033] In the literature, as well as on the production floor, it is commonly believed that microregions and even nanoregions (clusters of atomic dimensions) of Group VIII elements (typically, iron, cobalt, nickel) provide excellent nucleation sites from which nanotubes will readily grow. These regions may be metallic in nature from the outset or may be formed by the selective reduction of Group VIII-containing compounds (the Group VIII element as a cation), as described below in the embodiments. The compounds disclosed herein are oxides.

[0034] Further, the compounds of interest are complex oxides, which are defined herein as oxides of at least two elements (for these purposes, at least one of the elements being of Group VIII) that form a crystallographic lattice within which the Group VIII atoms formulaically reside at specific periodic sites. Complex oxides are distinct from simple oxides which are defined here as compounds comprising a single element and oxygen. While mixtures of simple oxides retain the crystal structures of each of the simple oxides when mixed, the complex oxides often possess different lattice structures and crystal symmetry than those of the

simple oxides. Complex oxides are also distinct from solid solutions, the latter defined herein as structures into which the cations are randomly distributed with no long range periodic ordering. In other words, the atoms in a solid solution composition may substitute freely into the various “sites” of the structure. There are several well-known complex oxide crystallographic structures including, for example, spinel and K_2NiF_4 -type (A_2BO_4), rock salt (A_2BO_3), and Perovskite (ABO_3).

[0035] Although the remaining discussion centers about the structural class comprising the magnesium cobalt system forming spinel structures, the disclosure, embodiments and appended claims contained herein are not limited to spinel structure complex oxides. In the spinel structure, the oxygens are arranged in a cubic close packed, face-centered structure. There are two types of interstitial sites between the oxygen anions in this structure, named for the crystallographic symmetries which these sites possess. In prototypical magnesium aluminate spinel as defined herein (Al_2MgO_4 - aluminum being A, magnesium being B in the general spinel group composition A_2BO_4), the magnesium ion has a complex valence state of +2 and the aluminum ion has a complex valence state of +3. Within the spinel structure, all of the magnesium ions reside at tetrahedral interstitial sites, while all of the aluminum atoms reside on the distinct octahedral interstitial sites. Simple oxides magnesite, MgO , and alumina, Al_2O_3 have very different crystal structures (cubic and hexagonal, respectively) from the aluminate spinel. The simple oxides are defined herein having a magnesium simple oxide valence state of +2 and an aluminum simple oxide valence state of +3. Thus, the magnesium simple oxide valence state is the same as the magnesium complex oxide valence state.

[0036] Furthermore, one skilled in the art will understand that the actual calcining temperature and condition (atmosphere, etc.) to form complex oxide such as spinel, rock salt, or Perovskite will depend on the chemical interactions between elements A and B. A lower formation temperature will tend to result from stronger interactions between the elements.

[0037] The cobalt-magnesium oxide system has been of interest to nanotube manufacturers for some time. This is due to the fact that nanotubes may be relatively easily separated from residual supporting Co-Mg material after the catalytic decomposition is completed. Examples 1 and 2 describe preparations of cobalt-magnesium catalysts and Example 3 reports x-ray diffraction data obtained from Example 1 specimens calcined at various temperatures. The calcining temperature effectively determines what phases will predominate

in the prepared catalyst sample. For example, a solid solution begins to form when calcining is performed in air at a temperature above about 800°C, while an inverse spinel of formula Co_2MgO_4 is formed at temperatures between 400°C and 800°C, most dominantly in the samples with Co/Mg ratio of about 2.

5 [0038] The interaction between Co and Si can be influenced greatly by various Co precursors, and preparation procedures, and in some cases, it leads to the formation of complex Co silicate which is much more stable under reducing environment as compared to other Co oxides. For example, in Journal of Catalysis, vol.162, 220-229, 1996, van Steen discovered that during the impregnation step, the precursor of surface cobalt silicate was formed by a reaction
10 between surface silanol groups and aqueous cobalt complexes. A solution of Co acetate with mild pH will favor this interaction and lead to more silicate formation. Moreover, It was found by Girardon and co-workers, Journal of Catalysis, vol.230, 339, 2005, that after impregnation and drying cobalt exists in octahedrally coordinated complexes in catalysts prepared from cobalt nitrate or cobalt acetate. Decomposition of the octahedral complexes results in the appearance of
15 Co_3O_4 crystallites and cobalt silicate species. Cobalt repartition between crystalline Co_3O_4 and the cobalt silicate phase in the oxidized samples depends on the exothermicity of salt decomposition in air and the temperature of the oxidative pretreatment. Co_3O_4 crystallite is the dominant phase in the samples prepared via endothermic decomposition of supported cobalt nitrate. The high exothermicity of cobalt acetate decomposition leads primarily to amorphous,
20 barely reducible complex cobalt silicate (Co_2SiO_4 -like). It is also believed that stable Co oxides such as complex Co-Si oxides will stabilize Co under mild or even severe reducing environment, thus prevent sintering of metallic Co and preserve their fine particles suitable for the growth of single-wall carbon nanotubes. For the case of Co_3O_4 supported on SiO_2 , due to lack of strong interaction between Co and Si oxides, Co_3O_4 tends to reduce under very mild
25 condition, thus, upon contacting hydrogen and carbon containing gases, reduced Co particles can undergo fast sintering to form bigger particles unsuitable for the growth of single-wall nanotubes.

[0039] In addition to Co-Mg and Co-Si or similar system such as Fe-Mg, Fe-Si, Fe-Al system can also undergo a complex oxide formation after a series calcination and reduction, a
30 procedure often encountered in catalytic growth of carbon nanotubes. Tang, et. al, in Journal of Catalysis, vol.106, 440, 1987, has reported the observation of change in the chemical state as

well as crystallography of Fe species in a Fe-Al oxide system during calcination and reduction. After deposition onto an alumina support, the Fe species will be in the form of Fe_2O_3 on the surface of Al_2O_3 . Temperature programmed reduction indicated the Fe species can undergo multi-step changes in chemical state before being completely reduced into metallic iron at above 850°C. The initial reduction will reduce Fe_2O_3 to Fe_3O_4 , followed by reduction to Fe(III)-Fe(II) oxides and transition into FeAl_2O_4 . Thus due to the strong interaction between Fe and Al, especially the formation of a complex oxide, FeAl_2O_4 , the resultant metallic Fe particles can be very fine and stable even at very high temperatures, e.g. >850°C, a condition usually ripe for nanotube growth when a carbon containing reactant is introduced.

EXAMPLES

Example 1

[0040] 4 grams of magnesia (Martin Marietta MagChem 50) were slurried with deionized water at 80°C for 3 hours and then allowed to cool. 29 grams of cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alpha Chemical) dissolved in deionized water was slowly added to the $\text{Mg}(\text{OH})_2/\text{MgO}$ slurry while the mixture was constantly stirred. 6N ammonia was used to adjust the slurry pH to be maintained at about 8-9. The resulting slurry was pink and was filtered and washed twice with 1N ammonium acetate by re-slurrying and refiltering. The filter cake was dried at 100°C for 24 hours and then calcined at various temperatures from 200°C to 900°C for 4 hours. The nominal composition of the calcined catalyst is 57 wt% Co and 11.8% Mg (molar ratio of Co/Mg ~ 2). Additional samples were prepared using the same procedure to achieve molar ratio of Co/Mg ~1, 0.5, 0.1 and 0.01 respectively.

Example 2

[0041] 4 grams of magnesia were placed in a flask maintained at 80°C with constant stirring using a magnetic bar. 29 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alpha Chemical) were dissolved in 200 mL methanol and slowly added into the flask. After all solution was added, the slurry was kept at 80°C with constant stirring in order to remove all solvent. The resulting powder was further dried at 110°C for 24 hours and then calcined at various temperatures from 200°C to 900°C for 4 hours. The nominal composition of the calcined catalyst is 57 wt% Co and 11.8%

Mg (molar ratio of Co/Mg $\sim$ 2). Additional samples were prepared using the same procedure to achieve molar ratio of Co/Mg $\sim$ 1, 0.5, 0.1 and 0.01 respectively.

Example 3

[0042] The phase analysis of samples made in Examples 1 and 2 is carried out using X-ray diffraction technique on a Rigaku 300 X-ray diffractometer equipped with Cu target for X-ray generation and Ni monochromator to remove dispersive X-rays. The samples made from example 1 and calcined under various conditions were pressed into sample holders and XRD spectra are collected. Table 1 summarizes the data obtained. The data correlates well with data previously obtained by Wang and Ruckenstein, Carbon, 40: 1911-1917 (2002), a reference cited earlier.

Table 1 XRD phase analysis of Co/Mg catalyst prepared at different calcining T

Calcining T	Crystalline Phase
200°C	Co ₂ O ₃ , MgO
400°C	Co ₃ O ₄ , Co ₂ MgO ₄ , MgO
600°C	Co ₃ O ₄ (trace) Co ₂ MgO ₄ , MgO
800°C	Co ₂ MgO ₄ , MgO, (Co,Mg)O solid solution(?)
900°C	(Co,Mg)O solid solution, MgO

[0043] It is instructive to study Table 1 to understand the relevant phase equilibria in the Co/Mg/O system. Simple oxides, Co₂O₃ (cobalt with a simple oxide valence state of +3) and MgO are stable up to a calcining temperature somewhat exceeding 200°C. While in this discussion all calcining is performed in air, all the embodiments disclosed are not limited to the use of an air atmosphere, as would be clear to one of ordinary skill in the art.

Crystallographically, this is analogous to the magnesium aluminate spinel example described above (MgO and Al₂O₃ being stable there.) Magnesium oxide remains stable for much higher temperature excursions. Above about 400°C (the exact temperature appears dependent on the method of processing, *e.g.* mechanical mixing requiring a higher temperature than impregnation of a nitrate over MgO) cobaltous oxide (formula Co₃O₄) becomes the stable simple oxide.

Some of the cobalt cations acquire a simple oxide valence state of +2; leading to an inverse spinel crystallography, in which some of the cobalt ions will fill octahedral sites and some will fill tetrahedral sites. With increasing calcining temperature, more and more MgO will decompose with magnesium anions diffusing into the cobaltosic oxide structure occupying octahedral sites. Because the +2 ions occupy the octahedral sites, this structure is referred to as an inverse spinel. As equilibrium is approached at increasing calcining temperatures, formation of complex Co_2MgO_4 proceeds to completion. Once the inverse spinel structure is filled, Co_2MgO_4 would have half of the cobalt ions occupying octahedral sites and half in tetrahedral sites. At even higher calcining temperatures $>800^\circ\text{C}$, the complex oxide becomes unstable and formation of a solid solution is favored. Note that some magnesia remains in samples calcined at all of the temperatures in this study.

[0044] FIG. 1 illustrates how a Group VIII-containing precursor 2 (in FIG. 1(a)) may be placed upon a silicon (or other suitable material) wafer 1. The Group VIII element, for this embodiment and illustration is cobalt. Atop precursor 2 is placed a second precursor 3 as a source of element B. The assembly 4 is then exposed to temperatures ranging from about 200°C to about 900°C to react to make a Co-Mg catalyst 5. Example 4 provides additional detail on a generic way to prepare catalyst in this manner.

Example 4

[0045] Cobalt and Mg wire (Purity $>99.9999\%$) was placed in a metal evaporator, and both metal were evaporated sequentially on a tungsten filament, the temperature being controlled by current. A quartz positioner was used to measure and monitor the resulting film thickness. In a common run, 5 nm of Co and 10 nm of Mg were deposited on a Si substrate, where Co/Mg molar ratio is approximately 1/1 (Figure 1). The coated Si wafers were then placed in an oven and calcined in air at 200°C , 400°C , 600°C and 800°C separately.

[0046] Examples 5 and 6 are illustrative of a catalytic decomposition procedure performed on samples made in Examples 1 or 2 (Example 5) or in Example 4 (Example 6.) Inert gas is maintained until a reaction temperature of 900°C is achieved. The carbonaceous gas introduced in these examples was methane; however many other known reactive gases may work as well and use of such gases is well known in this art.

Example 5

[0047] A 0.05 gram sample made from example 1 or 2 which has been calcined in air at 400°C for 1 hour was placed on a frit in a 1-inch vertical quartz reactor under argon flow of 200 mL/min. The temperature was then raised to 900°C by a Lindberg tube furnace, and inlet gas was switched to methane at 500 mL/min. The reaction was allowed to proceed for 30 minutes before it was turned off. After the reaction, the powder sample was collected and subject to analysis using Laser Raman spectrometer and transmission electron microscope.

Example 6

[0048] A 0.5"x 0.5" sample cut from example 4 was placed on a frit in a 1-inch quartz reactor under argon flow of 200 mL/min. The temperature was then quickly raised to 900°C, and inlet gas was switched to methane at 500 mL/min. The reaction was allowed to proceed for 30 minutes before turned off. After the reaction, the wafer sample was subject to analysis using Laser Raman spectrometer.

[0049] FIG. 2 illustrates Raman spectra of carbon fibril-containing products formed in Examples 5 and 6 and discussion is included below as Example 7.

Example 7

[0050] A Raman spectrometer equipped with continuous He-Ne laser with wavelength of 632.8 nm was used to collect Raman excitation. A Raman peak at $\sim 1580\text{ cm}^{-1}$ is present in all types of graphite samples such as highly oriented pyrolytic graphite (HOPG), pyrolytic graphite and charcoal. This peak is commonly referred to as the 'G-band'. The peak at 1355 cm^{-1} occurs when the material contains defects in the graphene planes or from the edges of the graphite crystal. This band is commonly referred to as the 'D-band' and the position of this band has been shown to depend strongly on the laser excitation wavelength. "Radial breathing modes (RBM)" (typically below 300 cm^{-1}) were observed with single-walled nanotubes, where all the carbon atoms undergo an equal radial displacement. A small change in laser excitation frequency produces a resonant Raman effect. Therefore, in most cases it is possible to distinguish multi-walled carbon nanotubes (MWNT) from single-walled carbon nanotubes (SWNT) from Raman spectroscopy from the presence or absence of RBM and the split in the G

band. Raman spectra of products made on silicon wafer unambiguously indicated the characteristic frequencies of SWNTs when the catalyst was calcined at 400°C or higher. As is illustrated in Table 2, this is consistence with the presence of complex oxide, Co_2MgO_4 (Table 2). The weak D-band demonstrates that the as-synthesized samples contain a very small amount of amorphous carbonaceous materials. In other words, it is likely that high-purity SWNTs were synthesized.

[0051] Summarizing, carbon fibril-containing product having sufficiently small diameter nanotubes to be single-walled (or possibly double-walled) has a Raman spectrum exhibiting: "radial breathing mode" (RBM) peaks between 150 and 300 wave numbers, the area under the RBM peaks being at least 0.1% of the area under a characteristic G band peak, the intensity of the G band peak being at least twice that of a characteristic D band peak (G/D of at least 2.0).

[0052] The Raman spectrum, described in Example 7 and shown in FIG. 2, reveals 4 to 5 components at 138, 192, 216, 256, and 283 cm^{-1} respectively. The expression: $\omega_{\text{RBM}} = (223.75 / d) \text{ cm}^{-1}$, where ω_{RBM} is radial breathing mode (RBM) frequency in cm^{-1} and d is the diameter of SWNT in nm, can be used to calculate the SWNT diameters. According to this formula, the peaks at 138, 192, 216, 256, and 283 cm^{-1} correspond to the SWNTs with diameter of 1.62, 1.17, 1.04, 0.87 and 0.79 nm respectively. Nanotubes with diameter of 1.17nm (peak at 192 cm^{-1} 6) appear to dominate based upon relative peak height.

Table 2 Correlation between complex oxide phase in a catalyst
with SWNT growth after activation and decomposition

Calcination Condition
Crystalline Phase
Containing Co_2MgO_4
Crystalline Phase
containing (Co,Mg)O solid solution
Grow Single-walled
Nanotubes
200°C
No
No
No
400°C
Yes, trace
No
Yes, low selectivity
600°C
Yes, some
No
Yes, medium selectivity
800°C
Yes, majority
Not clear
Yes, high selectivity

[0053] FIG. 3 illustrates a Raman spectrum of a carbon fibril-containing product formed in Example 6 plus the additional processing steps of reduction and passivation of the catalyst prior to catalytic decomposition; discussion is included below as Example 8.

Example 8

5 [0054] A sample from Example 4, calcined at 800°C in air for one hour, was then placed in a 1-inch quartz reactor under hydrogen flow of 100 mL/min and slowly heated up to 250°C for 30 minutes. The reduced sample was then passivated using 2% O₂/Ar. The treated sample was then placed in a reactor following the procedure described in Example 6 to grow single-walled nanotubes.

10 [0055] Peak height 6', when compared with peak height 6, shows significantly enhanced single-wall feature for those grown from this treated sample. Meanwhile, the D-band region was found to become smaller and sharper. This is another indication of substantial improvement of the selectivity of growing single-walled carbon nanotubes.

[0056] Examples 9-13 describe embodiments for which Group VIII element A is iron
15 rather than cobalt.

Example 9

[0057] Same procedures as described in Example 1 and 2 were applied and
20 Co(NO₃)₂·6H₂O was replaced with 40.4 grams of Fe₂(NO₃)₃·9H₂O.

Example 10

[0058] Same procedure as described in Example 4 was applied and Co wire was replaced with iron wire (purity>99.9999%)

Example 11

25 [0059] Same procedure as described in Example 5 was applied to make single-walled nanotubes with catalyst from Example 9.

Example 12

30 [0060] Same procedure as described in Example 6 was applied to make single-walled nanotubes with catalyst from Example 10.

Example 13

[0061] In FIG. 4, the Raman spectra of products made from Fe-Mg catalyst system (Example 12) showed similar results to those from the Co-Mg system (Example 6) except that the Raman peak height corresponding to single-walled nanotubes having a diameter of 1.17 nm (peak 6'') is less than was previously shown for a Co-Mg activated catalyst in FIG. 2.

[0062] FIG. 5 illustrates scanning electron micrographs of carbon fibril-containing product produced by catalytic decomposition of methane on activated catalysts from the Co-Mg system (FIG. 5A) and the Fe-Mg system (FIG. 5B) and is discussed as Example 14 below.

Example 14

[0063] FIG. 5A and B show low-magnification SEM images of the as-synthesized carbon fibril-containing product produced by catalytic reaction of CH₄ over Co-Mg and Fe-Mg complex oxide catalyst at 900°C. They indicate a large amount of tangled carbon filaments with lengths of several tens of microns.

[0064] A high resolution transmission electron micrograph (HRTEM) of SWNTs formed using a catalyst comprising Co-Mg complex oxide phase is shown in FIG. 6 and described in the embodiment of Example 15.

Example 15

[0065] FIG. 6 shows a typical HRTEM image of the as synthesized carbon fibril-containing product from Example 5. Examination of such HRTEM images indicates that the produced carbon filaments are mainly SWNT materials consisting of both bundles of SWNTs and small quantities of isolated, discrete SWNTs.

[0066] Examples 16 and 17 describe results obtained from samples having lower Co/Mg ratios than that for stoichiometric spinel, namely 0.1 and 1, respectively.

Example 16

[0067] 0.05 gram of sample made from Example 2 with Co/Mg ratio of 0.1 was placed in a 1-inch vertical quartz reactor. The sample was first calcined in air at 400°C for 1 hour, and

then the temperature of the reactor was rapidly raised to 850°C under argon flow of 200 mL/min. Once the temperature reaches 850°C, the inlet gas was switched to CO (99.95%) at 300 mL/min and the reaction was allowed to proceed for 15 minutes before being turned off. After the reaction, the product was weighed. Carbon yield was measured to be 0.5. Selectivity of single-walled carbon nanotubes growth was estimated to be better than 70% (as determined from Raman spectrum and HRTEM analysis.)

Example 17

[0068] 0.05 gram of sample made from Example 2 with Co/Mg ratio of 1 was placed in a 1-inch vertical quartz reactor. The sample was first calcined in air at 400°C for 1 hour, and then the reactor was purged with argon at 200 mL/min and the temperature was decreased down to 250°C. A 5% H₂/Ar was then introduced to the reactor at 100 mL/min. After two hours of hydrogen reduction, the inlet gas was then switched back to argon and the temperature was rapidly raised to 850°C. Once the temperature reached 850°C, CO (99.95%) was introduced to the reactor at 300 mL/min and the reaction was allowed to proceed for 15 minutes before being turned off. After the reaction, the product was weighed. Carbon yield was measured to be 1. Selectivity of single-walled carbon nanotubes growth was estimated to be better than 90% (as determined from Raman spectrum and HRTEM analysis.)

[0069] Example 18 illustrates the sensitivity of the processing steps involved.

Example 18

[0070] A 0.5"x 0.5" sample cut from Example 4 is placed on a frit in a 1-inch quartz reactor under argon flow of 200 mL/min. The temperature is then quickly raised to 700°C, and inlet gas is switched to Ethylene/H₂/Ar (0.5/2/97.5) at 500 mL/min. The reaction is allowed to proceed for 15 minutes before turned off. After the reaction, both Raman and SEM analysis show that the product consists of a mixture of single-walled and multi-walled carbon nanotubes.

Example 19

[0071] Co nitrate and Co acetate was applied as catalyst precursors to form silica-supported Co oxides. Ethanol solution of Co acetate and nitrate with equivalent of 3% metal

basis on SiO₂ were impregnated on a fumed silica and followed by calcination in air at 400°C. Two distinct products resulted from this process, black powder from nitrate (Sample A) and pink powder from acetate (Sample B). XRD diffractions indicate the black powder contained Co₃O₄ while pink powder contains CoSiO₃, a trioctahedral layered silicate or stevensite.

5

Example 20

[0072] Temperature programmed reduction (TPR) was carried out on a Quanta Chrome Autosorb 1C with 5% H₂/Ar as reducing carrier gas. The spectra were shown in FIG 7. Clearly, different Co precursors have yielded distinct reduction profile. When the nitrate was applied, the resulted Co species was in the Co₃O₄ form and can be reduced under mild conditions, while acetate precursor would produce a much stable Co species on the surface of silica, namely, Co silicate, the complete reduction of Co species required a much higher temperature than Co₃O₄.

10

Example 21

[0073] Pre-calcined Co/SiO₂ catalyst from Example 19 was placed in a 1-inch tube reactor and the temperature were quickly raised to 850°C under Ar. Immediately after the temperature reached 850°C, the carrier gas was switched to methane and the reaction was allowed to proceed for 30 minutes. Raman analysis was applied to characterize the product from the reaction, and two dramatic different carbon product have resulted from the two catalysts. The product made from methane when catalyzed by Co₃O₄/SiO₂ appeared to be amorphous in nature, no Raman signature of single-wall nanotubes was found. On the other hand, a clear single-wall feature was presented in the product made from Co silicate catalyst.

20

Example 22

[0074] Al(NO₃)₃·9H₂O and Fe(NO₃)₃·9H₂O salts with equivalent of 3%, 6% and 9% of Fe on metal basis versus Al₂O₃ were dissolved in 25 mL deionized water. Then this nitrate mixture was added concurrently with 20% (NH₄)₂CO₃ solution to a round-bottom three neck flask containing 200 ml DI water under strong agitation. The pH of the resultant slurry was kept at ~6 by controlling the addition rate of carbonate. After adding all nitrate solutions, the slurry was stirred for another 15 minutes, followed by filtration and drying at 80°C. After calcined in argon at 500°C, the samples were set aside for reaction tests.

30

Example 23

[0075] Reduction of Fe-Al oxide was studied by using temperature programmed reduction with 5% H₂/Ar as reducing carrier gas. The spectrum of 9% Fe/Al₂O₃ was shown in FIG 8. As seen in the spectrum, three major reduction steps were revealed. The first reduction (I) at 400°C indicated the transition from Fe₂O₃ to Fe₃O₄, followed by Fe₃O₄ to FeAl₂O₄ at 530°C (II) and finally to metallic Fe at 740°C (III).

Example 24

[0076] The calcined 9% Fe/Al₂O₃ was placed in a 1-inch tube reactor. After completely purged with Ar, the reactor was heated to 500°C under 5% H₂/Ar flow. When the temperature reached 500°C, the carrier gas was then switched back to Ar and the reactor was quickly heated to 800°C. At 800°C, the carrier gas was switched to CO and the reaction was allowed to carry for 30 minutes. The black product was analyzed by Raman spectroscopy. As seen in Figure 9, the product contains high quality single-wall nanotubes with strong RBM and G-bands and minimum D-band signal.

[0077] Selective reduction of the complex oxide materials disclosed herein requires that during activation only the Group VIII element be reducible under decomposition conditions. Therefore, element B should be limited to those elements capable of forming simple oxides of element B in which valence state for B in the simple oxide is equivalent to the valence state for B in the complex oxide, and which are not reducible in the presence of hydrogen gas at a temperature less than or equal to about 900 °C. Such elements B include aluminum, lanthanum, magnesium, titanium, zinc, zirconium, yttrium, calcium, strontium and barium. Further, although selective reduction of the complex oxide is herein defined in terms of the reducibility of element B in hydrogen at a specific temperature, it is to be understood that actual catalytic decomposition may, in other embodiments, occur in an atmosphere composed of a wide variety of carbonaceous gases other than methane or other hydrocarbons.

[0078] Those catalytic areas formed via selective reduction may be "fully" reduced to the Group VIII element itself or may be areas quite rich in that element to the exclusion of other materials. The morphology, size and spacing of such regions within an activated catalyst are probably critically important to the resultant selectivity and to the yield of fibril-containing

products. Without being limited to a particular theory, it is reasonable to postulate that the morphology, size and spacing of the elemental-rich regions derived from selective reduction will vary, for a given recipe of further processing, on whether the Group VIII element is previously located in specific crystallographic states at specific structure sites or is randomly distributed throughout the catalyst in a "solid solution." Further, because the prior art discusses apparent detrimental effects of the coarsening (size increase) of areas reduced from, for example, simple oxide cobaltous oxide (formula Co_3O_4), the presence of the complex oxide in the catalyst to promote SWNT formation is required.

[0079] Not wishing to be bound by a particular theory, it is believed that without an appropriate chemical and, perhaps, physical interaction between the complex oxide catalyst (A-rich) and its support (B-rich), the micro or nanoregions of Group VIII (A-rich) activated catalyst will tend to agglomerate to form bigger regions (sintering) upon heating to a temperature that is equal to or greater than half of its melting temperature ($^{\circ}\text{K}$). A strong interaction with the support will tend to stabilize these small catalytic regions even at such temperatures. By forming a complex oxide system, not only is there a strong interaction between A and B, but further, as discussed above, each metal site is separated in an orderly manner which may further improve the resistance to sintering. Thus, a selective (or controlled) reduction will result in the formation of small metal particles from component A, separated and stabilized by the much less reducible metal oxide of B.

[0080] The terms and expressions which have been employed are used as terms of description and not of limitations, and there is no intention in the use of such terms or expressions of excluding any equivalents of the features shown and described as portions thereof, it being recognized that various modifications are possible within the scope of the embodiments of the invention, set forth in the following appended claims:

The claims defining the invention are as follows:

1. A method of making single walled carbon nanotubes comprising:
providing a composition comprising a complex oxide having a formula
 $A_xB_yO_z$, wherein
5 $x/y \leq 2$ and $z/y \leq 4$,
A is a Group VIII element;
B is an element different from A and is an element whose simple oxide, in which B is
at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas
at a temperature less than about 900°C;
10 reducing said composition to form an activated catalyst;
contacting a carbonaceous gas with said activated catalyst under suitable conditions for
growing single walled carbon nanotubes, said suitable conditions including pressure greater than
about 1 atmosphere and less than about 10 atmospheres and temperature greater than about
400°C and less than about 950°C; and
15 growing carbon nanotubes on said activated catalyst, said carbon nanotubes comprising
single walled carbon nanotubes.
2. The method of claim 1, wherein said A is cobalt, iron or nickel.
3. The method of claim 1 or 2, wherein said B is aluminum, lanthanum, magnesium,
silicon, titanium, zinc, zirconium, yttrium, calcium, strontium or barium.
- 20 4. The method of claim 1, 2 or 3, wherein said carbon nanotubes comprise at least 50%
single walled carbon nanotubes.
5. The method of any one of claims 1 to 4, wherein said B is magnesium.
6. The method of claim 5, wherein said A is cobalt.
7. The method of claim 6, wherein the complex oxide is Co_2MgO_4 .
- 25 8. The method of any one of claims 1 to 7, wherein said reducing step and said
contacting step occur contemporaneously.
9. A method of making single walled carbon nanotubes comprising:
contacting a carbonaceous gas with an activated catalyst in a reaction zone at suitable
conditions for growing single walled carbon nanotubes,
30 said suitable conditions including a pressure greater than about 1 atmosphere and less than
about 10 atmospheres and temperature greater than about 400°C and less than about 950°C,
said activated catalyst comprising a reduced form of a complex oxide, said complex oxide
having a formula $A_xB_yO_z$, wherein
 $x/y \leq 2$ and $z/y \leq 4$,
35 A is a Group VIII element;

B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900°C; and

growing carbon nanotubes on said activated catalyst, said carbon nanotubes comprising
5 single walled carbon nanotubes.

10. The method of claim 9, wherein said A is cobalt, iron or nickel.

11. The method of claim 9 or 10, wherein the B is aluminum, lanthanum, magnesium, silicon, titanium, zinc, zirconium, yttrium, calcium, strontium or barium.

12. The method of claim 9, 10 or 11, wherein said carbon nanotubes comprise at least
10 50% single walled carbon nanotubes.

13. The method of any one of claims 9 to 12, wherein said B is magnesium.

14. The method of claim 13, wherein said A is cobalt.

15. The method of claim 14, wherein the complex oxide is Co_2MgO_4 .

16. A method of making a catalyst for use in a process for the manufacture of single
15 walled carbon nanotubes comprising the steps of:

reacting a source of A with a source of B at a temperature sufficiently low so as to form a complex oxide having a formula $\text{A}_x\text{B}_y\text{O}_z$, wherein

$$x/y \leq 2 \text{ and } z/y \leq 4,$$

A is a Group VIII element, and

20 B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900°C, and

activating the complex oxide by reducing said complex oxide at a temperature less than about 950°C.

25 17. A method of making a catalyst for use in a process for the manufacture of a single walled carbon nanotubes comprising the step of reducing a complex oxide of formula $\text{A}_x\text{B}_y\text{O}_z$ at a temperature less than 950°C, wherein

$$x/y \leq 2 \text{ and } z/y \leq 4,$$

A is a Group VIII element, and

30 B is an element different from A and is an element whose simple oxide, in which B is at the same valence state as in the complex oxide, is not reducible in the presence of hydrogen gas at a temperature less than about 900°C.

18. A catalyst manufactured by the method of claim 16.

19. A catalyst manufactured by the method of claim 17.

20. A method of making single walled carbon nanotubes, substantially as hereinbefore described with reference to any one of the examples and/or any one of the accompanying drawings.

5 21. A method of making a catalyst for use in a process for the manufacture of single walled carbon nanotubes, substantially as hereinbefore described with reference to any one of the examples and/or any one of the accompanying drawings.

22. A catalyst manufactured by the method of claim 21.

10

Dated 24 November, 2010

Hyperion Catalysis International

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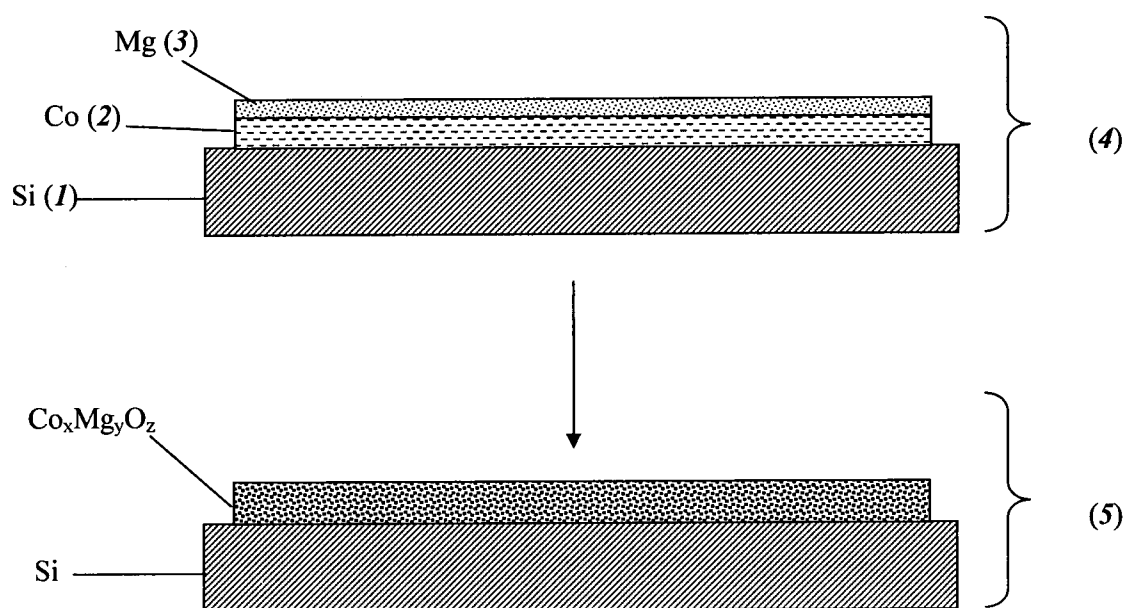


Figure 1

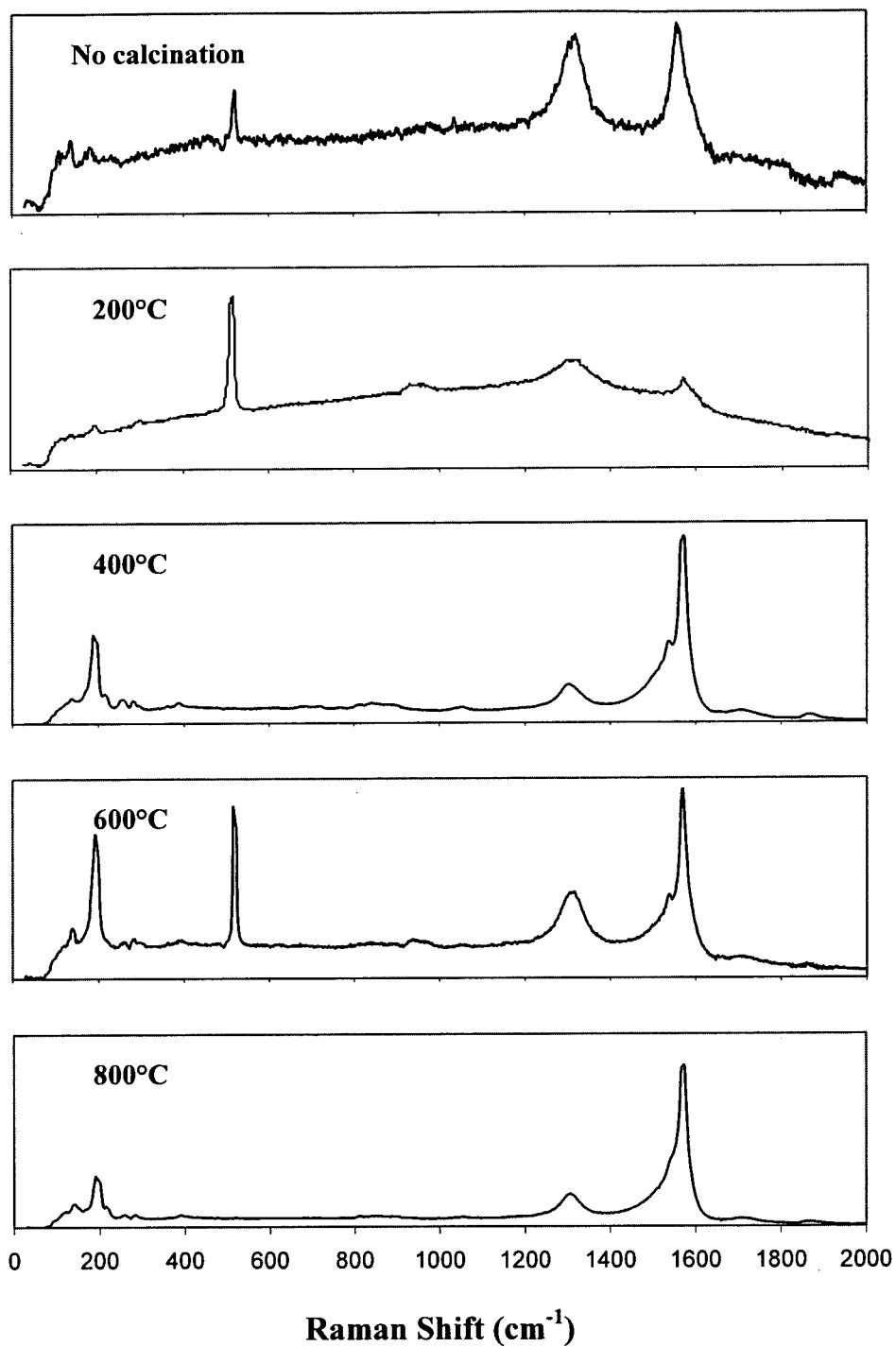


Figure 2

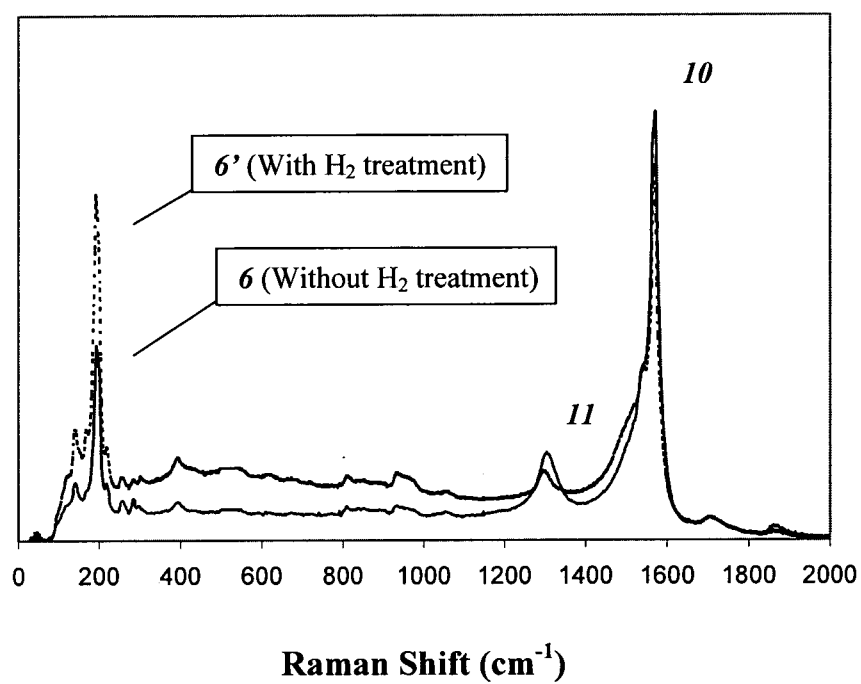


Figure 3

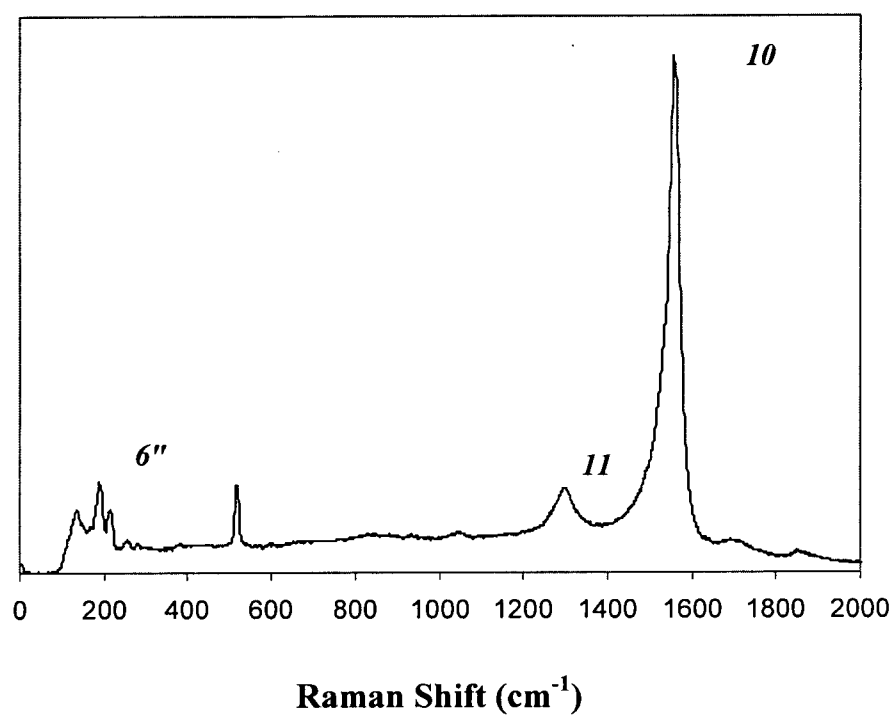
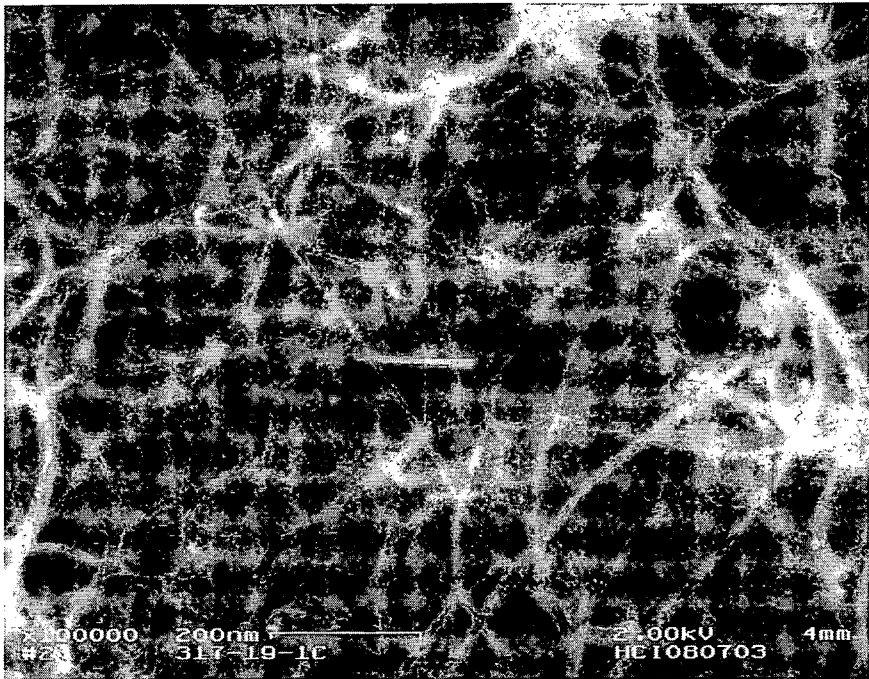


Figure 4

A



B

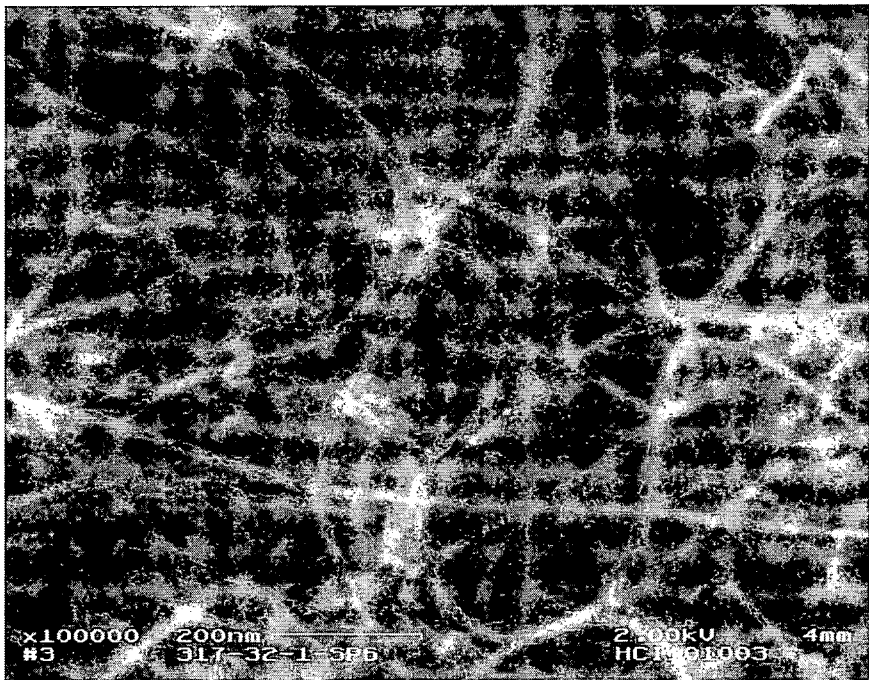


Figure 5

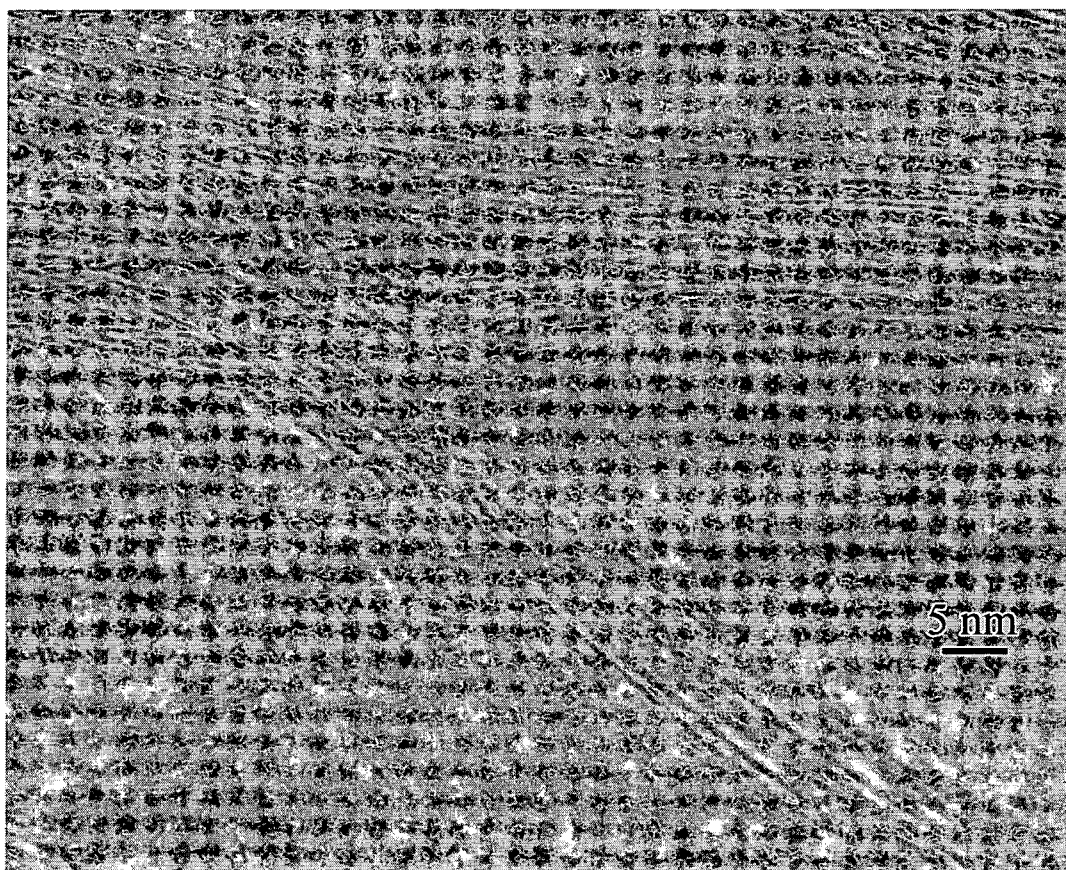


Figure 6

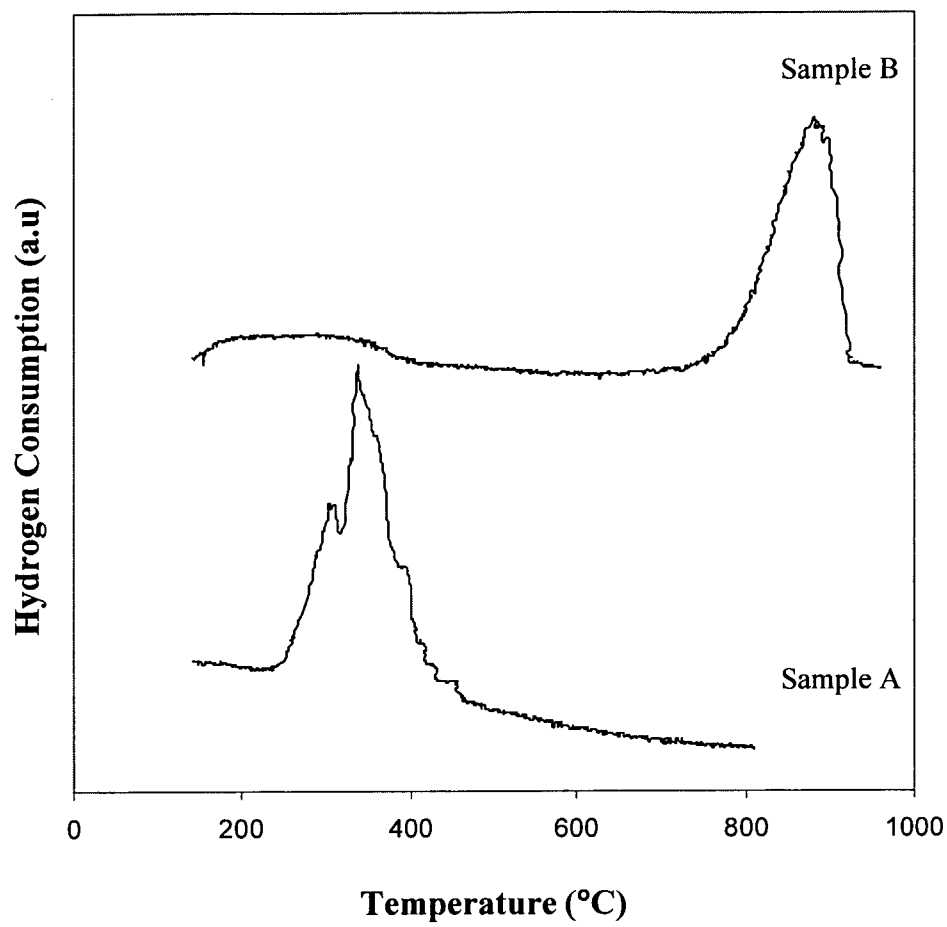


Figure 7

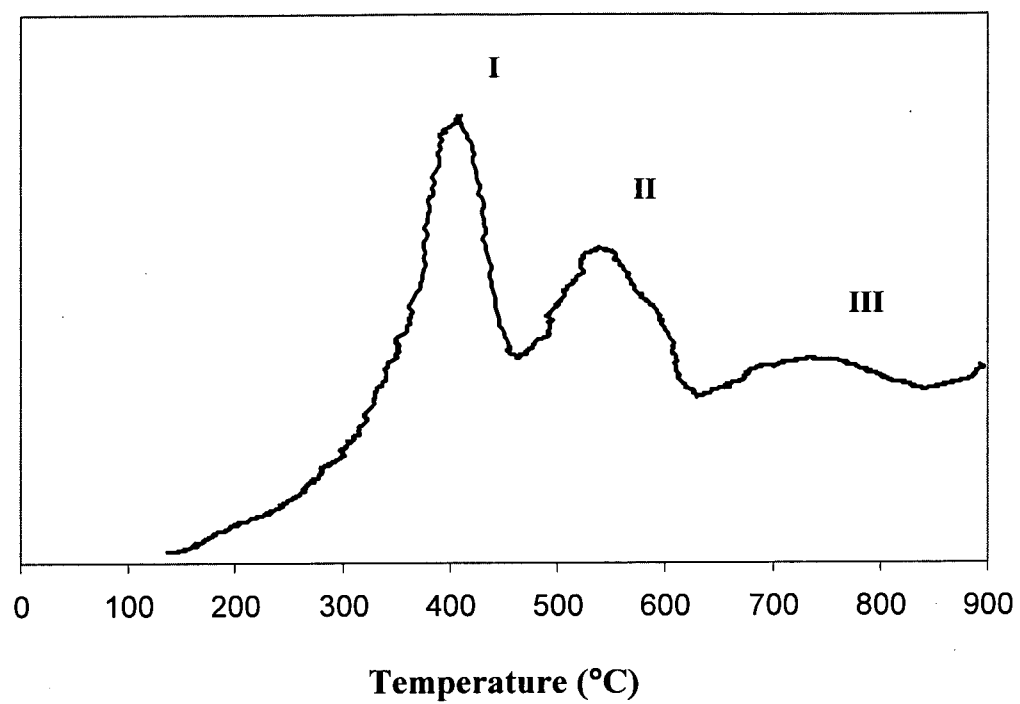


Figure 8

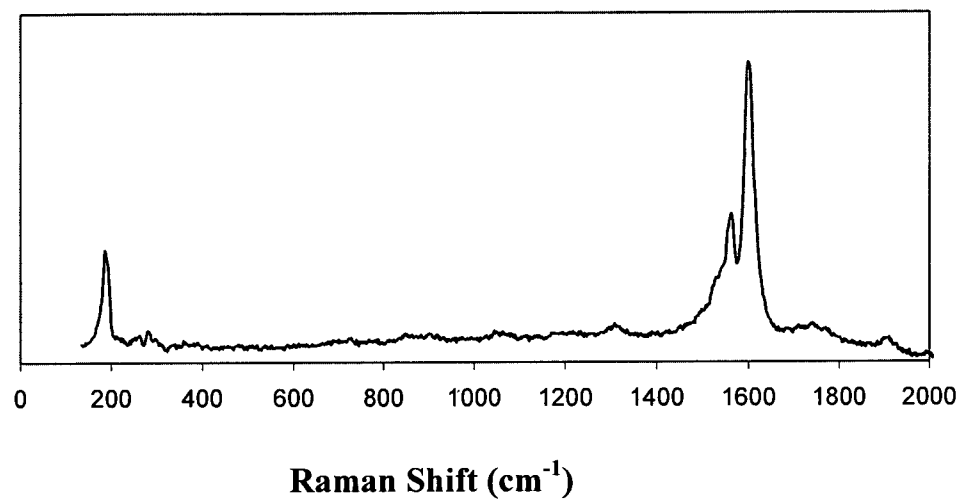


Figure 9