MULTICOMPONENT CATALYSTS FOR SYNTHESIS OF CARBON NANOTUBES BY CHEMICAL VAPOR DECOMPOSITION METHOD

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Abstract: Multicomponent catalysts for chemical vapor decomposition process of carbon nanotubes synthesis were developed. Efficient catalysts were synthesized on the basis of mixed metal oxide systems $(Fe,Co)/MgO–Al_2O_3$, $(Fe,Mo)/MgO–Al_2O_3$, $(Co,Mo)/MgO–Al_2O_3$, $(Fe,Co,Mo)/MgO–Al_2O_3$, $(Fe,Co,Mo)/Al_2O_3$. Effect of synergism of metals in multicomponent catalysts is discussed.

Introduction

Catalyst is a key for obtaining carbon nanotubes (**CNT**) of specified structure by chemical vapor decomposition (**CVD**) method. Particularly, following properties of carbon nanotubes are determined by or sensitive to the nature of catalyst used: structure and orientation of graphene layers; number of walls; external and internal diameter; length; structure ordering, content of disordered carbon; uniformity of diameter and thickness of wall along nanotube; mass yield; content of mineral admixtures in as-synthesized CNTs; structure of aggregates or bundles of the nanotubes grown.

Reviews on catalysts for CVD process are available [1, 2]. Usually, metal oxide catalysts are used for synthesis of CNTs by CVD technology. Briefly, following methods were most frequently used for synthesis of metal-oxide catalysts:

1) co-precipitation of metal hydroxides from aqueous solution; as a variant, precipitation of catalytically active metal hydroxides in presence of disperse supports (for instance, alumina);

2) impregnation of disperse supports (silica, alumina, magnesia, etc.) with solution of catalytically active metal nitrates in water or organic solvents, with subsequent drying and thermal decomposition;

3) ion exchange between solutions of salts of catalytically active metals and disperse supports like magnesia or magnesium carbonate;

4) different variants of sol-gel methods.

The methods listed above are commonly known and were used in numerous works, so we do not cite specific references here. Following methods are more specific.

5) Thermal decomposition of metal acetates soluted in high-boiling organic solvents (for instance mono-butyl ether of diethyleneglycol), which results in formation of nano-sized metal particles; as a variant, this process was conducted in presence of dispersed supports like alumina [3–10];

6) thermal decomposition (in furnace, flame, or plasma) of aerosols of sprayed or nebulized solutions containing metal compounds – alcoholates, carboxylates, nitrates, which thermally decompose with formation of fine particles of metal oxides [2, 11–14].

7) So called "wet combustion" method, which consists in thermal decomposition of homogeneous solutions or melts of metal compounds containing oxidative and reducing components, such as metal nitrates + organic compounds citric acid, tartaric acid, formic acid, urea, amino-acetic acid, ethylene glycol, polyethylene glycol, glycerol, sugar, etc. [1, 15–29]. This method or group of methods seems to be most convenient for laboratory use. Its advantages are simplicity and constancy of metal atoms ratio from starting components to the final multicomponent metal oxide.

Preferably the starting solution or melt should contain organic compounds able to form complexes with metal ions, and most preferable to form polymeric complexes. From this view using of polybasic organic acids like citric is most efficient because not only they themselves, but also products of their oxidation can form polymeric complexes with metal ions. Formation of polymeric complexes hampers separation of phases and crystal growth at least on first stages of thermal treatment and favor obtaining of fine multicomponent metal oxides with very small size of crystallites. This method was widely used for preparation of complex metal oxide catalysts from solutions or melts containing metal nitrates and organic compounds listed above.

The metals which are catalytically active in the process of CVD synthesis of CNTs are Fe, Co, Ni, Mo. Sometimes Mn, V, and W were used. Bimetallic catalysts (for instance Fe+Mo, Co+Mo, Fe+Co, Ni+Mo) have greatest catalytic activity. Metal-oxide catalysts were used most often. Mechanisms of CNTs growing on multicomponent catalysts are far from clarity in spite of numerous investigations in this area. The problem is sophisticates by transformation of structure of metal oxide catalysts upon reduction in CVD reactor and transformation of structure and particles size in the process of CNTs growing. As for reduction, contact of a metal-oxide catalysts with gas containing hydrogen or hydrocarbons at high temperature results in reduction of transition metal oxides to free metals. Then metal atoms or clusters can migrate on the surface of matrix to form larger clusters or crystallites. If content of reducible metal oxide in mixed metal oxide catalyst is large, the reduction can cause change of structure and fragmentation of matrix. Fragmentation of matrix can also occur in the process of CNTs growing. For instance, it was found that the CNTs growing process is accompanied by spontaneous fragmentation of catalyst particles [30]. Basing on analysis of the published data [1, 2, 31–40] following assumptions can be made for explanation of synergism of metals in multicomponent catalysts:

1) preparation of mixed metal oxides in the form of hetero-metalloxanes, solid solutions or crystals structures containing two or more metals (e.g., hetero-polymolybdates, ferrites, solid solutions like NiO–MgO) favors formation and stabilization of catalytically active metal particles (formed upon reduction) of smaller and uniform size;

2) clusters of molybdenum carbide (formed in the course of CVD process) retard sintering of particles of iron, cobalt, nickel or their mixtures. It should be mentioned that analogues effect was observed for solid acid catalysts (for instance WO_3/ZrO_2, MoO_3/ZrO_2, and similar); clusters of WO_3 or MoO_3, adsorbed on surface of ZrO_2 grains in co-precipitated mixed oxides retard sintering of ZrO_2 crystals upon calcining and this increases surface area and catalytic activity of the solid acids;

3) eutectic mixtures of metals with lower melting point temperature are formed and this accelerates diffusion of dissolved carbon in the process of CNTs growth.

4) molybdenum or tungsten oxide on alumina support (matrix) is classic solid acid system; Lewis acid centers (or Broensted acid centers formed upon reduction with hydrogen) activates hydrocarbon molecules; as well, reduced clusters of molybdenum or tungsten oxides in low metal valence state acts as dehydrogenation catalyst; when combined with nanoparticles of iron, cobalt or nickel, multifunctional catalytic systems are formed, similar to well-known bi-functional solid acid catalysts promoted with platinum or palladium.

Summarizing, synergism of transition metals in catalysts for CVD CNTs synthesis is well known, though its mechanism is open to question.

Much less information is available about synergism of components of matrix (support for catalytically active metals) in the catalysts for CNTs CVD [31, 41–43]. Most studies were performed using mono-phase metal oxides (e.g. SiO_2, MgO, or Al_2O_3) as a matrix. Composition of matrix has essential influence on catalyst activity and quality of the synthesized carbon nanotubes. In particular, the nature and ratio of components of the matrix determines the acid-base properties of the catalyst surface, which may significantly affect the growth process of CNTs [42, 44]. CNTs of high structural perfection were obtained at optimal surface acidity of catalyst, which was determined by ratio of matrix components. The system $MgO–Al_2O_3$ is strong solid base if magnesium oxide dominates, and solid acid, if aluminum oxide dominates.

Interaction of catalytically active metals with matrix also affects the tendency to aggregation of catalytically active particles, i.e., their size, and, in its turn, diameter of growing CNTs. It is known that the diameter of CNTs directly depends on size of particles of catalytically active metals [45–50].

Particularly, obtaining of catalytically active particles of a given size is important for synthesis of single-walled and double-walled carbon nanotubes, because if size of metallic clusters is too small nanotubes do not grow at all, and if the size is too great – very thick multi-walled nanotubes forms, often with great variation of parameters. In [42] double-walled carbon nanotubes were synthesized on the catalyst $Fe/MgO–Al_2O_3$. In this paper the size of catalyst particles was controlled by creating a micro-heterogeneous catalyst matrix. The basic idea was to use the phase separation of components of the matrix, which consists of phases which do not form solid solution in each other. This was achieved by introduction of aluminum oxide into the catalytic system Fe/MgO. At optimum ratio of Al/Mg micro-heterogeneous structure was formed consisting of $MgAl_2O_4$ and MgO phases. Due to mismatch of crystal lattices parameters of these phases they form micro-heterogeneous system in which size of crystallites is reduced compared to mono-phase system. Using of the catalyst with optimal Al/Mg ratio allowed obtaining double-walled carbon nanotubes with increased yield and high quality.

One can suppose that in multiphase micro-heterogeneous system clusters of catalytically active metals can be located at inter-grain borders and this can additionally improve properties of catalyst due to retarding diffusion of catalytically active metals on surface of matrix and sintering of metal clusters.

In this paper we have synthesized and studied some catalysts based on mixed $MgO–Al_2O_3$ matrix and different combinations of catalytically active metals.

Experimental

Catalysts containing mixed oxide $MgO–Al_2O_3$ as a matrix and oxides of catalytically active metals (Fe, Co, Mo) in different combinations were prepared by thermal decomposition of solutions, containing calculated amounts of metal nitrates, ammonium molybdate, and citric acid.

The catalysts synthesized were tested in industrial reactor of CNTs synthesis (NanoTechCenter Ltd., Tambov, Russia). Samples of catalysts were placed on Graflex sheets and series of samples was put on the reactor support. Technical grade propane-butane was used as a source of carbon. The process of CVD synthesis was conducted 40 min at 650 ºC. Multi-walled CNTs (**MWCNT**) were obtained in these conditions.

Few-walled nanotubes "Taunit-4" were obtained by CVD method using fixed bed laboratory reactor. Horizontal quartz tube reactor (inner diameter 37 mm, length 1150 mm, volume of hot zone nearly 0,5 L) was used in our experiments. Samples of catalysts were placed into reactor on semi-cylindrical Graflex (flexible graphite foil)

supports. The feed rates of gases were measured and regulated with "MassFlow" (Bronkhorst HIGH TECH) electronic device and are given below at normal conditions. Tubular ceramic furnace PT-1.2-70 was used for precision temperature control.

Mass yields of CNTs were calculated as ratio of mass of the crude product minus mass of starting catalyst divided by mass of catalyst.

Electron images of CNTs were recorded with using two-beam scanning electron microscopy (**SEM**) complex Neon 40, Carl Zeiss. It was found from SEM images that in all cases the products were nanotubes without visible admixture of other particles.

Results and discussion

It was shown that the MgO–Al_2O_3 mixed oxide (Mg:Al=3:1 at) prepared by citric acid-metal nitrate method in X-ray diffraction (XRD) exhibited very broad peaks corresponding to MgO [51]. The size of MgO crystallites estimated from width of the peaks by Debay–Sherrer formula was approximately 4 nm. Peaks corresponding to Al_2O_3 or $MgAl_2O_4$ were not observed. Probably the size of crystallites and/or concentration of these components were too small to be recorded in XRD. Thus, MgO–Al_2O_3 mixed oxide is micro-heterogeneous system with very small size of crystallites.

We have synthesized three series of catalysts with different combinations of catalytically active metals:

(Fe,Co)/MgO–Al_2O_3 with atomic ratio $Fe_1Co_{0.7}(Mg+Al)_{2.1}$;

(Fe,Mo)/MgO–Al_2O_3 with atomic ratio $Fe_1Mo_{0.1}(Mg+Al)_{2.1}$;

(Co,Mo)/MgO–Al_2O_3 with atomic ratio $Co_{1.4}Mo_{0.14}(Mg+Al)_{2.1}$.

Mg to Al atomic ratio was changed from 100% Mg to 100% Al within each series. For each catalyst mass yield of CNTs was determined and recalculated to grams of carbon (CNTs) per 1 gram of starting catalyst. According to SEM images, the carbon products obtained were nanotubes with diameter near 10…20 nm; surface area of samples was in the range of nearly 200…300 m^2/g. Typical SEM images are shown in Fig. 1–3.
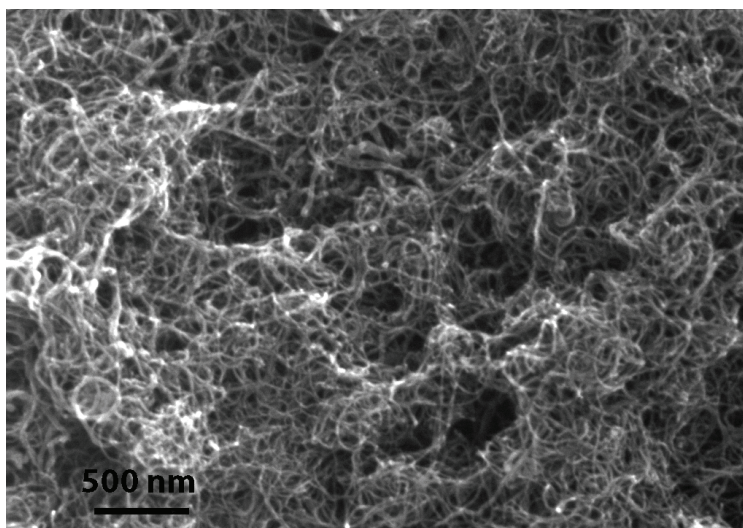

Fig. 1. Scanning electron microscopy image of CNTs obtained from propane-butane on (Fe,Co)/MgO–Al_2O_3 catalyst (40 min, 650 ^{o}C)
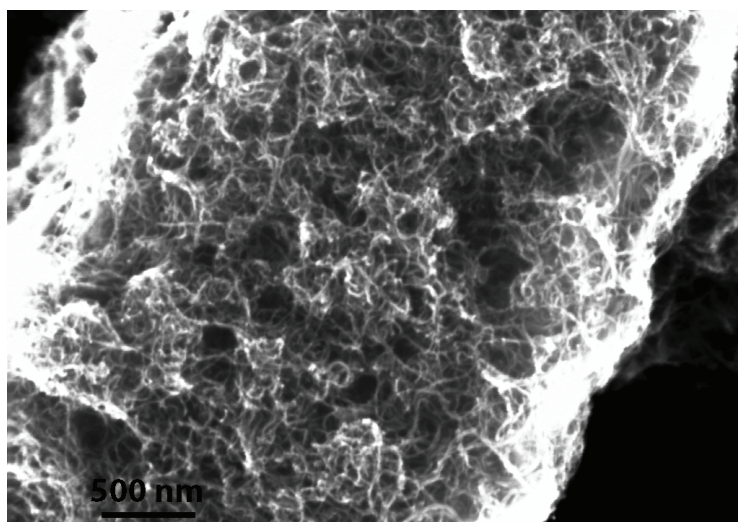
Fig. 2. Scanning electron microscopy image of CNTs obtained from propane-butane on (Fe,Mo)/MgO–Al$_2$O$_3$ catalyst (40 min, 650 ^{o}C)
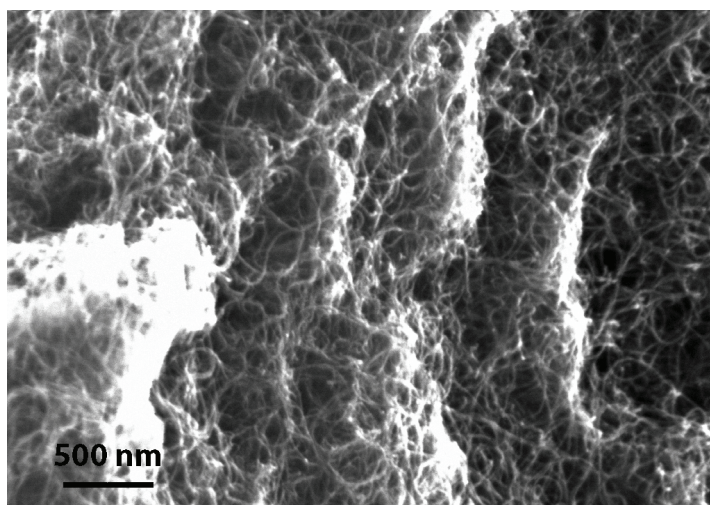

Fig. 3. Scanning electron microscopy image of CNTs obtained from propane-butane on (Co,Mo)/MgO–Al$_2$O$_3$ catalyst (40 min, 650 ^{o}C)

In Fig. 4–6 there are shown dependences of CNTs mass yield on atomic ratio of Mg/(Mg+Al) for different combinations of catalytically active metals (Fe+Co, Fe+Mo, Co+Mo).

As it follows from Fig. 4–6, for all combination of catalytically active metals maximum of CNTs yield is observed near Mg/(Mg+Al) = 0.75 (Mg:Al = 3:1). It is interesting, that just this ratio of magnesium to aluminum is characteristic for the natural layered mineral hydrotalcite, Mg$_6$Al$_2$(OH)$_{16}$CO$_3$4H$_2$O, pyrolysis of which gives mixed Mg–Al oxide. It is interesting to note that metal oxide catalysts based on double layer hydroxides or hydroxy-carbonates like hydrotalcite (containing catalytically active metals) were successfully used in CVD process of CNTs synthesis [15–20, 41, 52–57].

Exploring ideas considered above, we have developed several efficient catalysts for synthesis of different carbon nanotubes. Below we regard several examples.
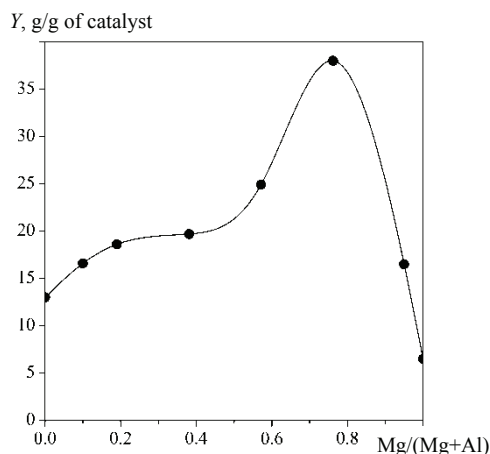
Fig. 4. Mass yield of CNTs (Y, g/g of catalyst) obtained from propane-butane on (Fe,Co)/MgO–Al$_2$O$_3$ catalyst dependently on Mg/(Mg+Al) atomic ratio (40 min, 650 $^{\circ}$C)
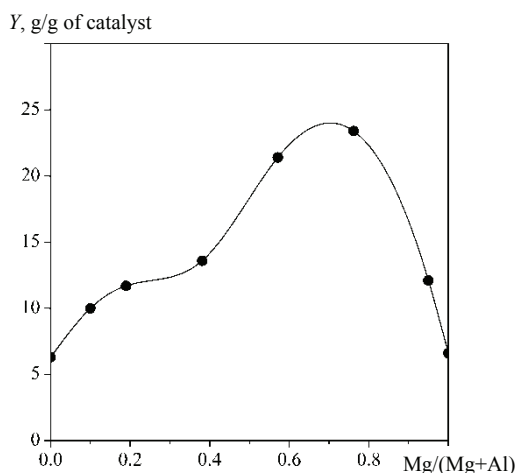

Fig. 5. Mass yield of CNTs (Y, g/g of catalyst) obtained from propane-butane on (Fe,Mo)/MgO–Al$_2$O$_3$ catalyst dependently on Mg/(Mg+Al) atomic ratio (40 min, 650 $^{\circ}$C)

Scanning electron microscopy images in Fig. 7 and 8 illustrate difference in CNTs diameter obtained from propane-butane on Ni-containing catalyst. Change of Ni/MgO catalyst for Ni/MgO–Al$_2$O$_3$ allows obtaining much more thin nanotubes. Presumably, this effect is achieved due to micro-heterogeneity of the MgO–Al$_2$O$_3$ matrix, which retards sintering of catalytically active nickel particles.

Combination of Fe, Co, and Mo as catalytically active metals and micro-heterogeneous MgO–Al$_2$O$_3$ matrix allows obtaining of thin CNTs with number of carbon layers 2–4, diameter 4…8 nm and surface area 600…700 m^2/g. These are CNTs "Taunit-4", by our trademark. Mass yield of these nanotubes amounts 1.5…2.5 g/g of catalyst, which is relatively high compared to typical mass yields of double-walled nanotubes (**DWCNTs**) 50–150 % from mass of catalyst reported in literature. CVD process was conducted at 800 $^{\circ}$C, propylene or acetone were used as carbon sources with the same success. Nanotubes in this systems grow in bundles (Fig. 9).
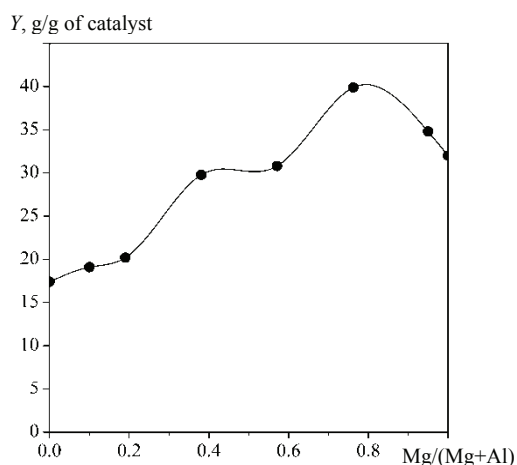
**Fig. 6. Mass yield of CNTs (Y, g/g of catalyst) obtained from propane-butane
on (Co, Mo)/MgO–Al$_2$O$_3$ catalyst dependently on Mg/(Mg+Al) atomic ratio** (40 min, 650 ºC)
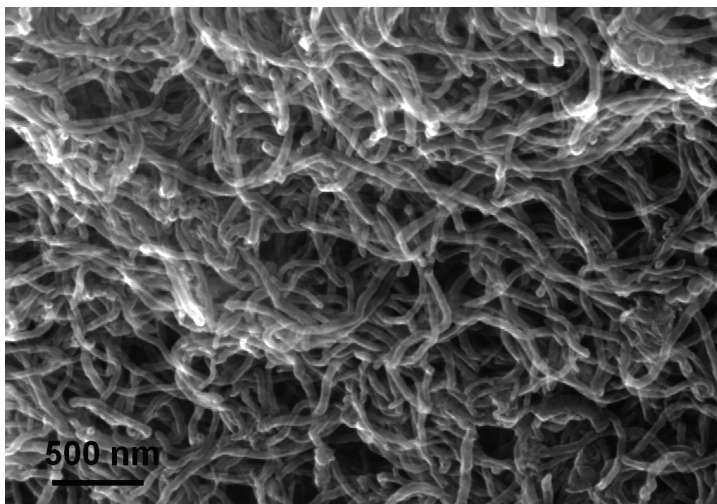

**Fig. 7. CNTs "Taunit" (industrial product, NanoTechCenter Ltd., Tambov, Russia)
obtained on Ni/MgO catalyst from propane-butane** (CNTs diameter 20…70 nm)

Fig. 10 illustrates mechanism of bundles formation – they grow perpendicularly to surface of flakes of catalyst. The sample shown in Fig. 10 was obtained with other catalyst, and the nanotubes were MWCNTs. Due to their large diameter individual nanotubes are clearle seen in this case. In SEM image Fig. 9 only bundles of nanotubes are visible, but sometimes thin belts on bundles can be recognized which are remainders of catalyst flakes.

Formation of catalysts in form of flakes was often observed in our experiments when catalysts were obtained by "wet combustion" nitrate-citrate method. The reason of this is that very viscous melt is formed at the first stage of thermal treatment of concentrated solutions containing metal nitrates and citric acid. At further rapid heating the melt forms very fine foam consisting of thin-wall bubbles, which after grinding of the final metal-oxide catalyst give micro-flakes.

Interesting peculiarity of the "Taunit-4" CNTs is their ability to form dense, flexible, relatively strong films upon simple drying of moist layer of precipitate formed
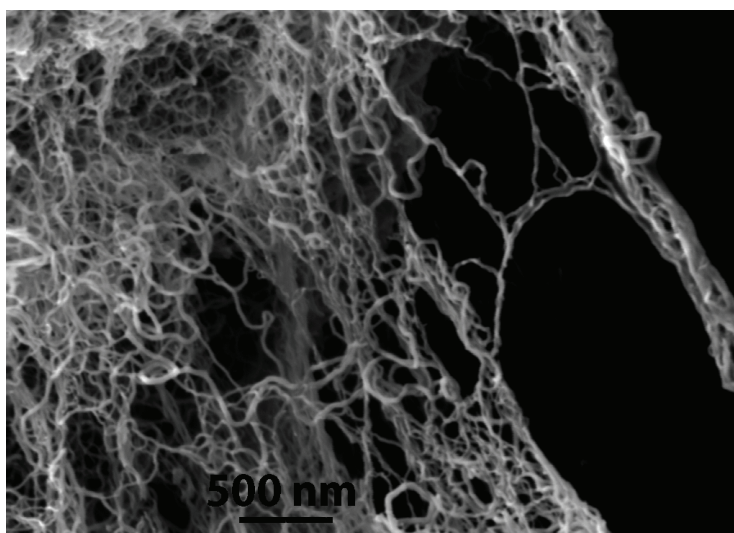
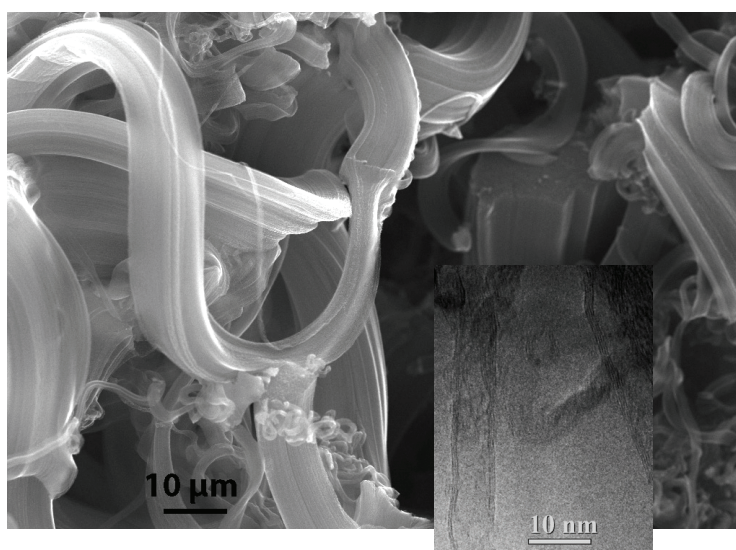**Fig. 8. Analogue of CNTs "Taunit" obtained on Ni/MgO–Al$_2$O$_3$ catalyst from propane-butane** (CNTs diameter 10…20 nm)

Fig. 9. Scanning electron microscopy and transmission electron microscopy (TEM) images of bundles of thin CNTs obtained on (Fe,Co,Mo)/MgO–Al$_2$O$_3$ catalyst (diameter of individual nanotubes 4…8 nm, length of bundles up to 100 mc and more)

on usual fibrous filter (polypropylene), without using micro-filters and surfactants. Dependently of conditions, apparent density of these sheets can be 0.1…0.4 g/cm^3, thickness 0.1…1 mm. Probably, the sheets are formed due to presence of very long (up to fractions of millimeter) strands of nanotubes bound together by strong capillar forces which tighten nanotubes strands upon drying. These materials can be interesting for creation of electrodes for fuel cells and other power sources, and for creation of nanocomposites with polymers.

Summarizing, multicomponent catalysts based on synergism of catalytically active metals and micro-heterogeneous matrix are very efficient for CVD synthesis of carbon
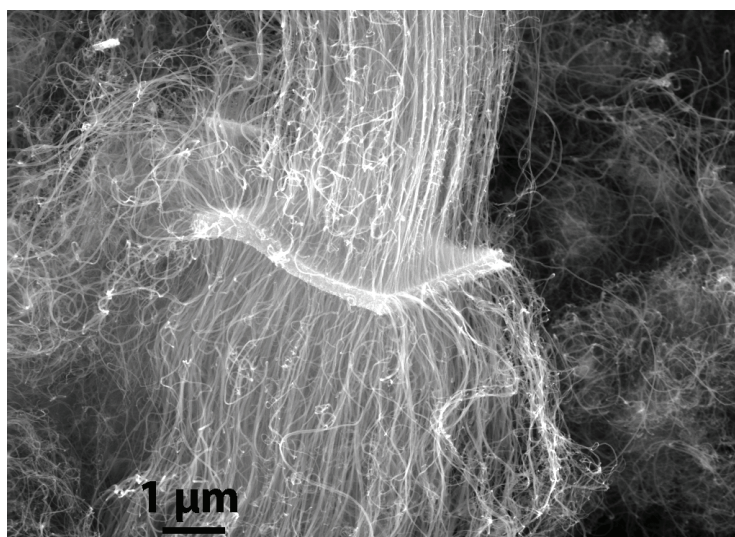
Fig. 10. Growing of CNTs bundles on flaky catalyst particles

nanotubes. In principle, at least two approaches can be applied to synthesis of multicomponent micro-heterogeneous catalysts. The first was described above and consists in application of some method of synthesis of mixed metal-oxide nanoparticles. The second approach consists in synthesis of mixed metal hydroxides in form of double layered hydroxides [57–60]. Most known example of such structures is hydrotalcite [57] and its derivatives. These compounds (analogs of clays, but with positive charge of layers) are built from layers containing metal ions of different valency – 2, 3, rarely 4. Hydroxyls or anions of acids are disposed between positively charged metal hydroxide layers and compensate their charge. Compositions of these compounds can be varied in sufficiently wide range without separation of phases. Thermal treatment of double layered hydroxides results in mixed metal oxides in which components consist of grains (crystallites) with very small size. Taking into account that practically all metals catalytically active in CVD process of CNTs growing are 2- or 3-valent (Fe, Co, Ni, Mn), as well as metals of matrices (Al, Mg, Zn), this approach is very convenient for synthesis of multicomponent catalysts in which the components are uniformly mixed at atomic level before thermal treatment and are micro-heterogeneous after it. 5- and 6-valent metals like V, Mo, and W, addition of which promotes growth of CNTs, can be introduced into original layered structure in form of anions which substitute some part of hydroxyl groups or carbonate anions.

Both approaches are efficient for synthesis of the multicomponent catalysts under consideration.

Conclusion

Mixed oxides of magnesium and aluminum are efficient matrices for catalysts of CNTs CVD synthesis. Optimal atomic ratio of Mg to Al is nearly 3:1. Combination of Al and Mg oxides in matrix and transition metals as catalytically active components allows creation efficient catalysts for CVD process of CNTs synthesis.

References

1. Dupuis, A.-C. The Catalyst in the CCVD of Carbon Nanotubes – a Review / A.-C. Dupuis // Progress in Materials Science. – 2005. – Vol. 50. – P. 929–961.

2. Семенцов, Ю.И. Синтез, структура и физико-химические свойства угле-родных наноматериалов / Ю.И. Семенцов // Физикохимия наноматериалов и супрамолекулярных структур / Ю.И. Семенцов [и др.] ; под ред. А.П. Шпака, П.П. Горбика. – Киев, 2007. – Т. 2. – С. 116–158.

3. US Patent 8012447. Methods for Controlling the Quality of Metal Nanocatalyst for Growing High Yield Carbon Nanotubes / Harutyunyan A., Tokune T., Fernandez E.M. ; September 6, 2011.

4. US Patent 7981396. Methods for Production of Carbon Nanostructures / Harutyunyan A. ; July 19, 2011.

5. US Patent 7901654. Synthesis of Small Diameter Single–Walled Carbon Nanotubes / Harutyunyan A. ; March 8, 2011.

6. US Patent 7871591. Methods for Growing Long Carbon Single–Walled Nanotubes / Harutyunyan A., Mora E., Tokune T. ; January 18, 2011.

7. US Patent 7719265. Methods for Determining Particle Size of Metal Nanocatalyst for Growing Carbon Nanotubes / Harutyunyan A., Fernandez E.M., Tokune T. ; May 18, 2010.

8. US Patent 7485600. Catalyst for Synthesis of Carbon Single–Walled Nanotubes / Harutyunyan A., Tokune T., Fernandez E.M. ; February 3, 2009.

9. US Patent 7214361. Method for Synthesis of Carbon Nanotubes / Harutyunyan A., Grigorian L., Tokune T. ; May 8, 2007.

10. US Patent 7134618. Dry Powder Injector / Harutyunyan A., Isobe S. ; November 14, 2006.

11. US Patent 7220398. Mixed–Metal Oxide Particles by Liquid Feed Flame Spray Pyrolysis of Oxide Precursors in Oxygenated Solvents / Sutorik A., Laine R.M., Marchal J., Johns T., Hinklin T. ; May 22, 2007.

12. US Patent Application 20080075649. Methods and Apparatus for the Production of Ultrafine Particles / Hung C.-H., Vanier N.R. ; March 27, 2008.

13. US Patent Application 20090087372. Process for the Preparation of a Catalyst for the Production of Carbon Nanotubes / Buchholz S., Michele V., Mleczko L., Bellinghausen R., Wolf A. ; April 2, 2009.

14. US Patent 5958361. Ultrafine Metal Oxide Powders by Flame Spray Pyrolysis / Laine R.M., Bickmore C.R., Treadwell D.R., Waldner K.F. ; September 28, 1999.

15. Kinetic study of carbon nanotube synthesis over Mo/Co/MgO catalysts / L. Ni [et al.] // Carbon. – 2006. – Vol. 44. – P. 2265–2272.

16. Liu, Q. New Technique of Synthesizing Single–Walled Carbon Nanotubes from Ethanol Using Fluidized–Bed over Fe–Mo/MgO Catalyst / Q. Liu, Y. Fang // Spectrochimica Acta. Part A: Molecular and Biomolecular Spectroscopy. – 2006 – Vol. 64, No. 2. – P. 296–300.

17. Niu, Z. Effect of Temperature for Synthesizing Single–Walled Carbon Nanotubes by Catalytic Chemical Vapor Deposition over Mo-Co-MgO Catalyst / Z. Niu, Y. Fang // Materials Research Bulletin. – 2008. – Vol. 43. – P. 1393–1400.

18. Niu, Z. Effects of Synthesis Time for Synthesizing Single–Walled Carbon Nanotubes over Mo–Fe–MgO Catalyst and Suggested Growth Mechanism / Z. Niu, Y. Fang // Journal of Crystal Growth. – 2006. – Vol. 297. – P. 228–233.

19. Mass Production of High-Quality Multi–Walled Carbon Nanotube Bundles on a Ni/Mo/MgO Catalyst / Y. Li [et al.] // Carbon. – 2005. – Vol. 43. – P. 295–301.

20. Flahaut, E. Catalytic CVD Synthesis of Double and Triple–Walled Carbon Nanotubes by the Control of the Catalyst Preparation / E. Flahaut, Ch. Laurent, A. Peigney // Carbon. – 2005. – Vol. 43. – P. 375–383.

21. Lamellar Fe/Al_2O_3 Catalyst for High-Yield Production of Multi–Walled Carbon Nanotubes Bundles / X.Q. Wang [et al.] // Materials Research Bulletin. – 2009. – Vol. 44. – P. 422–425.

22. US Patent 3330697. Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor / Pechini M.P. ; July 11, 1967.

23. Bulk Preparation and Characterization of Mesoporous Carbon Nanotubes by Catalytic Decomposition of Cyclohexane on Sol–Gel Prepared Ni–Mo–Mg Oxide Catalyst / L.J. Kennedy [et al.] // Materials Letters. – 2006. – Vol. 60. – P. 3735–3740.

24. US Patent 7138102. Method for Manufacturing Highly–Crystallized Double Oxide Powder / Akimoto Y., Nagashima K., Nageno Y., Ieda H., Tanaka N. ; November 21, 2006.

25. US Patent 6849115. Method of Manufacturing Aluminum–Substituted Hematite / Takada J., Fujii T., Nakanishi M. ; February 1, 2005.

26. US Patent 6482387. Processes for Preparing Mixed Metal Oxide Powders / Gulgun M., Kriven W., Nguyen M.H. ; November 19, 2002.

27. US Patent 5480862. Method for the Preparation of Precursors for Superconductors and Compounds thus Obtained / Miszenti G.S. ; January 2, 1996.

28. Пат. 2373995 Российская Федерация, МПК В 01 J 37/00, В 01 J 23/74, С 01 В 31/00, В 82 В 3/00, В 01 J 21/00. Метод получения высокодисперных нанесенных катализаторов и синтез углеродных нанотрубок / Кузнецов В.Л., Усольцева А.Н. ; заявитель и патентообладатель Ин-т катализа им. Г.К. Борескова Сиб. отд. Рос. Акад. наук. – № 2008143617/04 ; заявл. 01.11.2008 ; опубл. 27.11.2009, Бюл. № 33. – 18 с.

29. US Patent 7135161. Method of Producing Nanosized Oxide Powders / Holloway P.H., Abboudi M. ; November 14, 2006.

30. Agglomerated CNTs Synthesized in a Fluidized Bed Reactor: Agglomerate Structure and Formation Mechanism / Y. Hao [et al.] // Carbon. – 2003. – Vol. 41. – P. 2855–2863.

31. Layered Double Hydroxides as Catalysts for the Efficient Growth of High Quality Single–Walled Carbon Nanotubes in a Fluidized Bed Reactor / M.-Q. Zhao [et al.] // Carbon. – 2010. – Vol. 48. – P. 3260–3270.

32. Growth of Carbon Nanotubes on the Novel FeCo–Al$_2$O$_3$ Catalyst Prepared by Ultrasonic Coprecipitation / J. Wen [et al.] // Journal of Natural Gas Chemistry. – 2010. – Vol. 19. – P. 156–160.

33. El-Hendawy, A.-N.A. Impact of Mo and Ce on Growth of Single–Walled Carbon Nanotubes by Chemical Vapour Deposition Using MgO-Supported Fe Catalysts / A.-N.A. El-Hendawy, R.J. Andrews, A.J. Alexander // Applied Surface Science. – 2009. – Vol. 255. – P. 7446–7450.

34. The Role of Molybdenum in Fe–Mo–Al$_2$O$_3$ Catalyst for Synthesis of Multi–Walled Carbon Nanotubes from Butadiene-1,3 / V.V. Chesnokov [et al.] // Applied Catalysis A: General. – 2009. – Vol. 363. – P. 86–92.

35. Kinetic Study of Carbon Nanotube Synthesis over Mo/Co/MgO Catalysts / L. Ni [et al.] // Carbon. – 2006. – Vol. 44. – P. 2265–2272.

36. Synthesis of Carbon Nanotubes by Catalytic Conversion of Methane: Competition between Active Components of Catalyst / V.Z. Mordkovich [et al.] // Carbon. – 2007. – Vol. 45. – P. 62–69.

37. Chai, S.P. The Effect of Catalyst Calcination Temperature on the Diameter of Carbon Nanotubes Synthesized by the Decomposition of Methane / S.P. Chai, S.H.S. Zein, A.R. Mohamed // Carbon. – 2007. – Vol. 45. – P. 1535–1541.

38. A Simple Combinatorial Method to Discover Co–Mo Binary Catalysts that Grow Vertically Aligned Single–Walled Carbon Nanotubes / S. Noda [et al.] // Carbon. – 2006. – Vol. 44. – P. 1414–1419.

39. Mass Production of High-Quality Multi–Walled Carbon Nanotube Bundles on a Ni/Mo/MgO Catalyst / Y. Li [et al.] // Carbon. – 2005. – Vol.43. – P. 295–301.

40. CCVD Synthesis of Carbon Nanotubes with W/Co–MgO Catalysts / P. Landois [et al.] // Carbon. – 2009. – Vol. 47. – P. 789–794.

41. Zhang, L. Synthesis of Carbon Nanotubes/Metal Oxide Composites over Layered Double Hydroxides and Application in Electrooxidation of Ethanol / L. Zhang, F. Li // Applied Clay Science. – 2010. – Vol. 50. – P. 64–72.

42. The Effect of Phase Separation in Fe/Mg/Al/O Catalysts on the Synthesis of DWCNTs from Methane / Q. Zhang [et al.] // Carbon. – 2007. – Vol. 45. – P. 1645–1650.

43. Kinetics of Carbon Nanotubes Growth on a Ni–Mg–Al Catalyst by CCVD of Methane: Influence of Catalyst Deactivation / N. Latorre [et al.] // Catalysis Today. – 2010. – Vol. 154. – P. 217–223.

44. Growth Mechanism of Multi–Walled Carbon Nanotubes with or without Bundles by Catalytic Deposition of Methane on Mo/MgO / Y. Li [et al.] // Chemical Physics Letters. – 2004. – Vol. 386. – P. 105–110.

45. Alexiadis, V.I. Influence of Structural and Preparation Parameters of Fe_2O_3/Al_2O_3 Catalysts on Rate of Production and Quality of Carbon Nanotubes / V.I. Alexiadis, X.E. Verykios // Materials Chemistry and Physics. – 2009. – Vol. 117. – P. 528–535.

46. Combustion Synthesis of Carbon Nanotubes and Related Nanostructures / W. Merchan-Merchan [et al.] // Progress in Energy and Combustion Science. – 2010. – Vol. 36. – P. 696–727.

47. Correlation between Metal Catalyst Particle Size and Carbon Nanotube Growth / E.F. Kukovitsky [et al.] // Chemical Physics Letters. – 2002. – Vol. 355. – P. 497–503.

48. Growth Kinetics of MWCNTs Synthesized by a Continuous-Feed CVD Method / I. Kunadian [et al.] // Carbon. – 2009. – Vol. 47. – P. 384–395.

49. Deck, C.P. Growth Mechanism of Vapor Phase CVD-Grown Multi–Walled Carbon Nanotubes / C.P. Deck, K. Vecchio // Carbon. – 2005. – Vol. 43. – P. 2608–2617.

50. Correlation between Catalyst Particle and Single–Walled Carbon Nanotube Diameters / A.G. Nasibulin [et al.] // Carbon. – 2005. – Vol. 43. – P. 2251–2257.

51. Organic Precursor Synthesis of Al–Mg Mixed Oxides and Hydrotalcites / V.V. Brei [et al.] // Microporous and Mesoporous Materials. – 2008. – Vol. 113. – P. 411–417.

52. Мележик, А.В. Синтез тонких углеродных нанотрубок на соосажденных металлоксидных катализаторах / А.В. Мележик, Ю.И. Семенцов, В.В. Янченко // Журнал прикладной химии. – 2005. – Т. 78, вып. 6. – С.938–944.

53. Co-Based Catalysts from Co/Fe/Al Layered Double Hydroxides for Preparation of Carbon Nanotubes / X. Xiang [et al.] // Applied Clay Science. – 2009. – Vol. 42. – P. 405–409.

54. Catalytic Synthesis of Carbon Nanostructures Using Layered Double Hydroxides as Catalyst Precursors / Y. Zhao [et al.] // Carbon. – 2007. – Vol. 45. – P. 2159–2163.

55. Layered Double Hydroxides as Catalysts for the Efficient Growth of High Quality Single–Walled Carbon Nanotubes in a Fluidized Bed Reactor / M.-Q. Zhao [et al.] // Carbon. – 2010. – Vol. 48. – P. 3260–3270.

56. Production of Carbon Nanotubes from Methane: Use of Co-Zn-Al Catalysts Prepared by Microwave-Assisted Synthesis / P. Benito [et al.] // Chemical Engineering Journal. – 2009. – Vol. 149. – P. 455–462.

57. Mitchell, P.C.H. Propane Dehydrogenation over Molybdenum Hydrotalcite Catalysts / P.C.H. Mitchell, S.A. Wass // Applied Catalysis A: General. – 2002. – Vol. 225. – P. 153–165.

58. Arizaga, G.G.C. Layered Hydroxide Salts: Synthesis, Properties and Potential Applications / G.G.C. Arizaga, K.G. Satyanarayana, F. Wypych // Solid State Ionics. – 2007. – Vol. 178. – P. 1143–1162.

59. Catalytic Applications of Layered Double Hydroxides and Derivatives / Z.P. Xu [et al.] // Applied Clay Science. – 2011. – Vol. 53. – P. 139–150.

60. Goh, K.-H. Application of Layered Double Hydroxides for Removal of Oxyanions: A Review / K.-H. Goh, T.-T. Lim, Z. Dong // Water Research. – 2008. – Vol. 42. – P. 1343–1368.

Многокомпонентные катализаторы для синтеза углеродных нанотрубок методом химического осаждения из газовой фазы

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Ключевые слова и фразы: катализатор; многофазный; синергизм; углеродные нанотрубки; химическое осаждение из газовой фазы.

Аннотация: Разработаны многокомпонентные катализаторы для синтеза углеродных нанотрубок методом химического осаждения из газовой фазы. Эффективные катализаторы синтезированы на основе смешанных металлоксидных систем $(Fe,Co)/MgO–Al_2O_3$, $(Fe,Mo)/MgO–Al_2O_3$, $(Co,Mo)/MgO–Al_2O_3$, $(Fe,Co,Mo)/MgO–Al_2O_3$, $(Fe,Co,Mo)/Al_2O_3$. Обсужден эффект синергизма металлов в многокомпонентных катализаторах.

Vielkomponente Katalisatoren für die Synthese der Kohlennanoröhren durch die Methode der chemischen Ablagerung aus der Gasphase

Zusammenfassung: Für die Synthese der Kohlelennanoröhren durch die Methode der chemischen Ablagerung aus der Gasphase wurden die vielkomponenten Katalisatoren ausgearbeitet. Die effektiven Katalisatoren wurden auf Grund der gemischten metallaktiven Systeme $(Fe,Co)/MgO–Al_2O_3$, $(Fe,Mo)/MgO–Al_2O_3$, $(Co,Mo)/MgO–Al_2O_3$, $(Fe,Co,Mo)/MgO–Al_2O_3$, $(Fe,Co,Mo)/Al_2O_3$ synthesiert. Es wurde den Effekt des Sinergismus der Metalle in den vielkomponenten Katalisatoren besprochen.

Catalyseurs muticomposants pour la synthèse des nanotubes carboniques par la méthode de la précipitation chimique à partir de la phase gazeuse

Résumé: Pour la synthèse des nanotubes carboniques par la méthode de la précipitation chimique à partir de la phase gazeuse ont été élaborés les catalyseurs muticomposants. Les catalyseurs efficaces ont été synthésés à la base des systèmes métallooxydes $(Fe,Co)/MgO–Al_2O_3$, $(Fe,Mo)/MgO–Al_2O_3$, $(Co,Mo)/MgO–Al_2O_3$, $(Fe,Co,Mo)/MgO–Al_2O_3$, $(Fe,Co,Mo)/Al_2O_3$. A été discuté l'effet de synergie des métaux dans les catalyseurs muticomposants.

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