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ZEOLITE-BASED CATALYSTS FOR SYNTHESIS OF CARBON NANOTUBES

G.T. Smagulova[1,2*], N.G. Prikhod'ko[1,3], N.R. Guseinov[1,4], R. Nemkayeva[1,4], B.T. Lesbayev[1,2], A.A.Zakhidov[5], Z.A. Mansurov[1,2]

[1]Institute of Combustion Problems, 172 Bogenbaybatyr str. Almaty, Kazakhstan
[2]Al - Farabi Kazakh National University, 71al - Farabi av., Almaty, Kazakhstan
[3]Almaty University of Energetic and Communications, 126, Baitursynov str. Almaty, Kazakhstan
[4]National Nanotechnology Laboratory of Open Type, 71al - Farabi av., Almaty, Kazakhstan
[5]University of Texas at Dallas,NanoTech Institute, West Campbell Road 800, Richardson, Texas, USA
*e-mail: smagulova.gauhar@inbox.ru

Abstract
Supported transition-metal catalysts were prepared on zeolite by self-propagating high-temperature synthesis method and were tested upon receipt of carbon nanotubes by CVD. The effectiveness of zeolite as matrix for catalysts in chemical vapor deposition synthesis of multiwall carbon nanotubesis is presented here. Obtaining of carbon nanotubes on zeolite-based catalysts was characterized by the transmission and scanning electron microscopy as well as Raman spectroscopy. For catalyst of zeolite-Co_3O_4 the carbon nanotubes have a diameter of 11 nm. For catalyst of zeolite-Fe_2O_3 the carbon nanotubes have a diameter from 7 to 21 nm. Raman spectrum indicates at low defectiveness of obtained carbon nanotubes.

Key words: zeolite, catalyst, self-propagating surface thermosynthesis, carbon nanotube

Introduction

Carbon nanotubes due to their unique physico-chemical properties are called as «materials of the future» [1] it's triggered an exceptional splash during investigating of the carbon nanomaterials. Carbon nanotubes are used in many application fields such as energy, biotechnology, microelectronics, textile, etc. [2-4]. The producing of composite materials on the basis of carbon nanotubes is one of the main application fields. There are many methods for the synthesis of carbon nanotubes such as electro arc, CVD synthesis, flame synthesis [5], etc. Currently, CVD method is recognized as the leader in synthesizing of CNTs.

CVD method is an inexpensive system, and there is a feasibility to use different catalysts and various carbon containing sources in solid, liquid and gas forms.Structure and properties of carbon nanotubes depends on many factors: initial components, composition and structure of catalyst, synthesis conditions and other. The catalysts methods are applied for synthesis of carbon nanotubes.

Frequently, the catalyst is the complex of matrix and active phases. The catalysts on the basis of transition metal particles from fine metal or their compounds such as salts and oxides are the most effective in the synthesis process of carbon nanotubes. The silicon wafers [6], aerogels, quartz, mesoporous silica [7] are used as matrixes for the catalyst. Carbonaceous precursors are decomposed into catalytic nanoparticles but the carbon is diffuse through a catalytic nanoparticle and sprout into CNTs. There are two main model of carbon nanotubes growth: «tip-growth model» and «base-growth model».

Depending on composition and structure of the catalyst there is one or the other growth mechanism. The choice of matrix for catalysts, its structure predetermines the properties of final product. Creation of new catalytic systems with various composition of active phases and matrix allows obtaining the carbon nanotubes with different morphology and properties.

Experimental

Obtaining of catalyst

It must be considered the nature of transition metal when choosing the catalyst. In series of transition metals from Ti to Ni, the bonding force M-C with filled electrons of d-level is rising [8]. The formation of strong bindings such as Ti, V, Cr with carbon is determine their low catalytic activity. For this reason such catalyst as oxides of cobalt and iron were used.

For preparation of catalysts the synthetic zeolite (80 % is silicon oxides) with apparent density of about 0.9187 g/cm^3 was used. The zeolite has a structure of thin scaly plates. Previously, the zeolite was heated at a temperature of 1000 °C for the removing of volatile compounds, and in synthesis process of CNT the zeolite leave unchanged its composition and structure. After thermal treatment, investigations on zeolite with the help of XRD and SEM methods were carried out (Fig. 1).

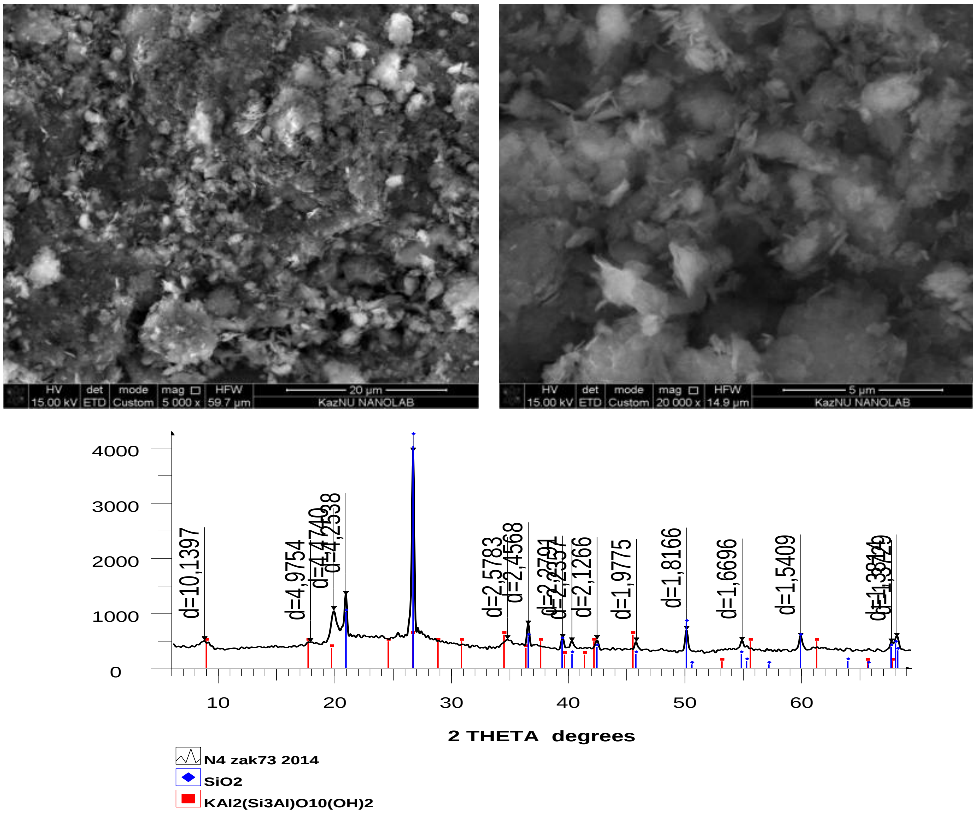

Fig. 1 – SEM images and XRD diffractogram of pure zeolite

The base phase of zeolite is SiO_2 (80 %) and small part of illite is $KAl_2(Si_3Al)O_{10}(OH)_2$. The concentration of the active components of zeolite was 3 wt. %. For preparation of zeolite-based catalyst, a pure zeolite in amounts of 1 g was introduced in aqueous solution of cobaltous nitrate or ferrous chloride as well as glycine in stoichiometric ratio.

After that the sample was dried for 30 minutes in air at 100 °C. Then the catalyst was placed in a furnace where it was heated for 1 hour at a temperature of 500 - 600 °C. The high temperature initiates the self-propagating surface thermosynthesis, the result of which is the formation of cobalt oxide (Co_3O_4) or iron oxide (Fe_2O_3) and ultradisperse particles [9].

$$3Co(NO_3)_2{\cdot}6H_2O + 6C_2H_5NO_2 + 0.5O_2 = 12CO + 33H_2O + 6N_2 + Co_3O_4$$

XRD analysis of obtained metals showed that cobaltous oxide has the following formula Co_3O_4 and the ferrous oxide - Fe_2O_3 (Fig. 2).

Synthesis of carbon nanotubes on the zeolite-based catalysts by chemical vapor deposition

The chemical vapor deposition apparatus was used for synthesis of carbon nanotubes. Gas flow is - 650 cm^3/min, H_2 - 150 cm^3/min, C_2H_2 – 19.5 cm^3/min. The synthesis temperature is 710 °C, the synthesis time is - 20 minutes.

Results and Discussion

The obtained carbon nanotubes are grown on zeolite-based catalysts and were investigated by scanning (Quanta 3D 200i, FEI) and transmission electron microscopes (JEOL JEM-1011) as well as Raman spectrometer (Solver Spectrum, NT-MDT). Fig.3 shows the SEM and TEM images of carbon nanotubes are grown on zeolite with Co_3O_4.

According to TEM images, it can be seen that multi-walled carbon nanotubes have a diameter of about 11 nm.

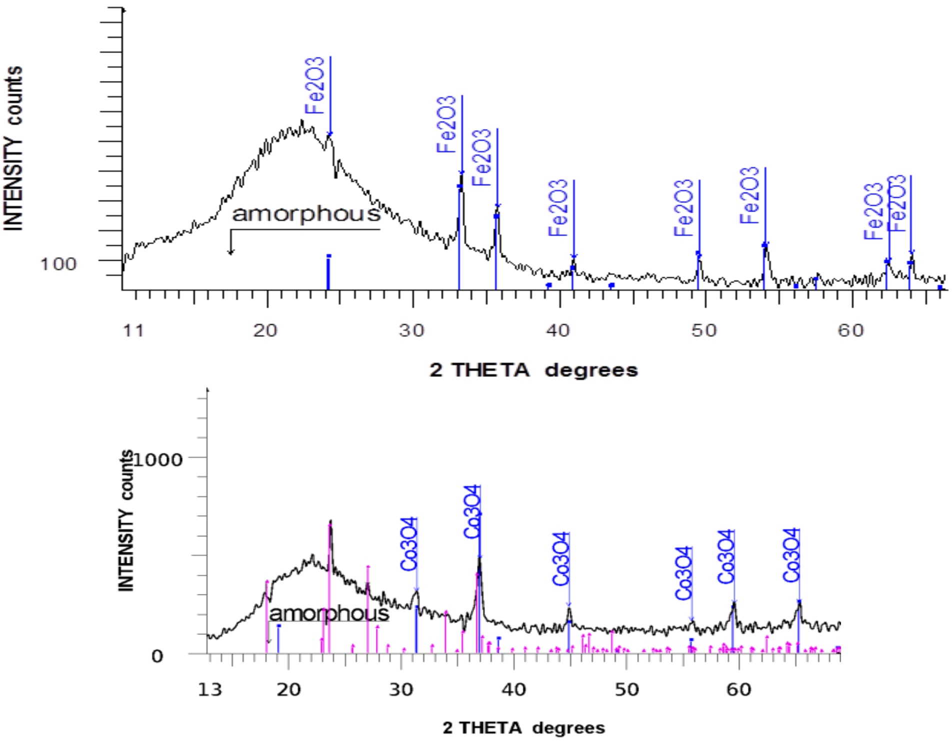

Fig. 2. XRD diffractograms of Fe_2O_3 and Co_3O_4 zeolite-based catalysts

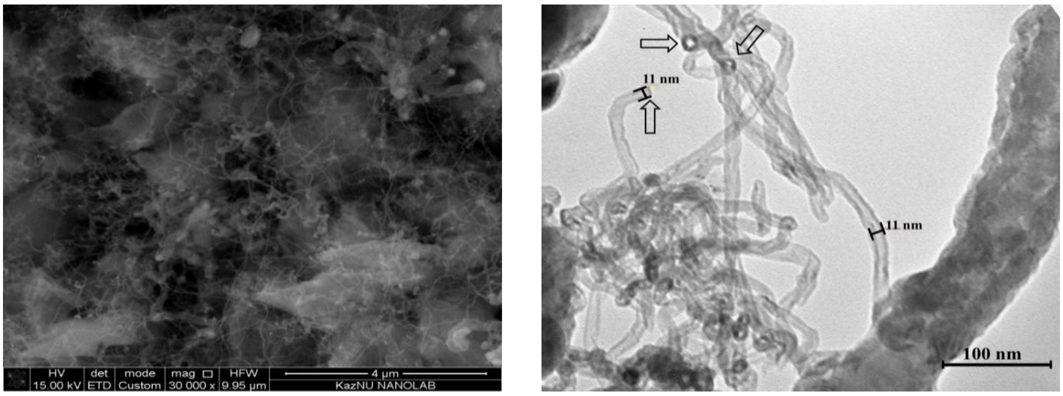

Fig.3.SEM and TEM images of carbon nanotubes on zeolite-based catalysts with Co_3O_4.

Most nanotubes have an open end (the arrows on TEM images shows the open ends of the nanotubes); the absence of catalyst nanoparticles at the ends of nanotubes indicates on introduction of «base-growth model» where the interaction of the catalyst nanoparticles and substrate (here the zeolite particles) is strong. The rising carbon nanotube is unable to rend off the catalyst nanoparticle from substrate, and therefore the crystallization of carbon nanotube is occurred on top of metal particles [10].

Fig.4 shows the Raman spectrum of carbon nanotubes on zeolite-based catalysts with Co_3O_4.

The Raman spectrum of multi-walled nanotubes have two main maxima: at wave-length of 1300 - 1360 cm^{-1} (D-band) – is the «defective Raman zone» is conditioned by dispersion of nanostructured defects of carbon nanotubes, as well as at ~ 1580 cm^{-1} (G-band) is characterized by vibrations of sp^2 carbon-to-carbon bonds. The presence of these peaks is a result of the longitudinal oscillations of graphite layers [11].The ratio of the peak intensities I_D/I_G corresponds to a ratio of defect structures (sp^3 configuration of carbon) in the graphite-like structures (sp^2 configuration of carbon) in carbon nanotubes. For the sample of CNT the ratio of peak intensities is I_D/I_G is 0.80.

Fig. 5 shows the SEM and TEM images of carbon nanotubes are grown on zeolite with Fe_2O_3.

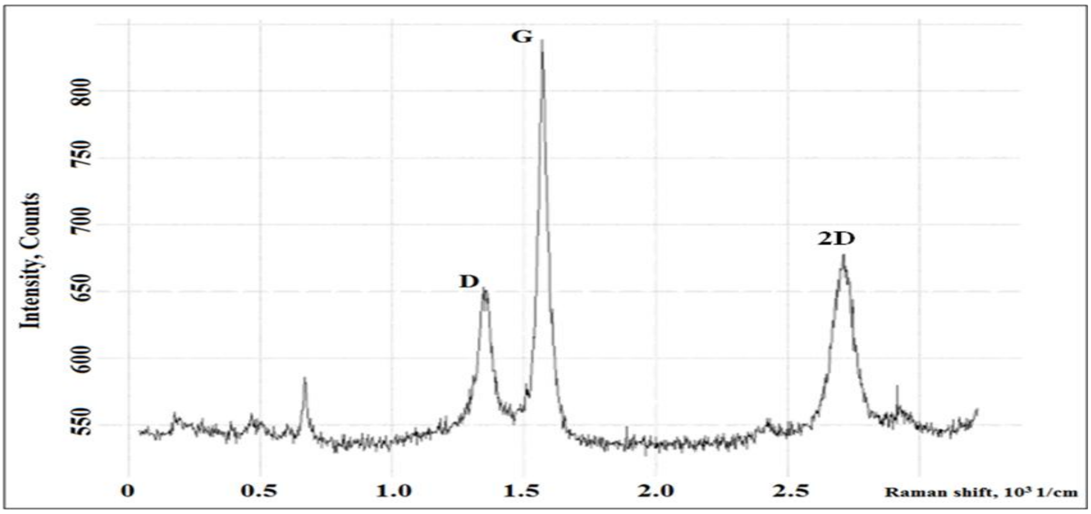

Fig.4.Ramanspectrumof carbon nanotubes on zeolite-based catalysts with Co_3O_4.

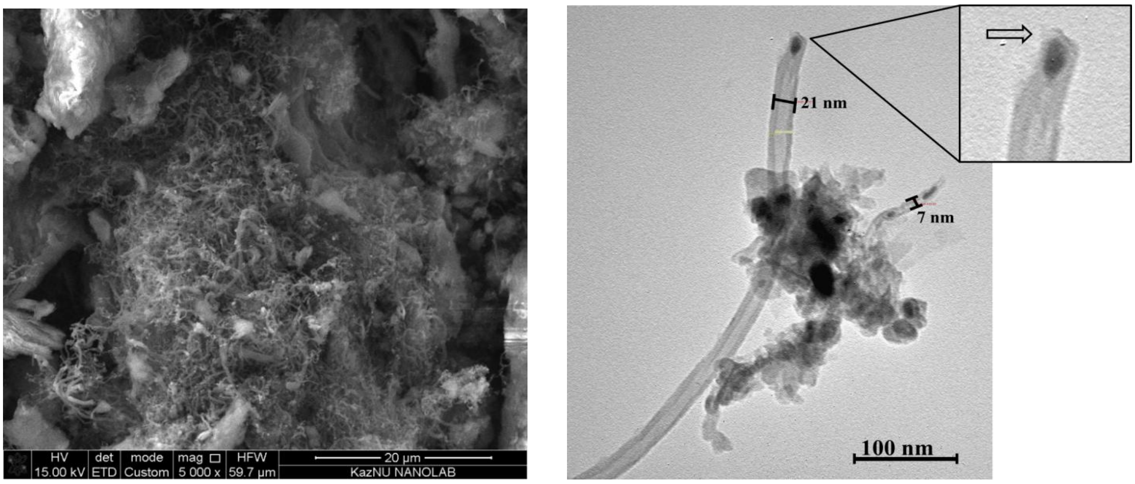

Fig. 5.SEM and TEM images of carbon nanotubes on zeolite-based catalysts with Fe_2O_3.

With the help of TEM images, it can be seen that multiwall carbon nanotubes have a diameters of about 7 and 21 nm respectively; also the image clearly shows the platelet shape of zeolite particles. As seen from the picture, the catalyst particles are at the top of MWCNTs and some catalyst particles are fixed at certain length of the nanotube. The fact that this is a top but not the basis of carbon nanotubes indicates a «cap» on the upper part of catalysts particles. This case illustrates the «tip-growth model», where the interaction of the catalyst and substrate is weak. The hydrocarbon is decomposed on the upper surface of catalyst particles and carbon nanotube crystallizes in place of coalescence of particles of catalysts and substrate, after that the catalysts particle is rend off from substrate, and further crystallization of carbon nanotube leads to migration of catalyst particles to upward. Until the top part of the metal particles is open for access and decomposition of hydrocarbon, the concentration gradient in the metal particle enables to diffuse the carbon and therefore provides a further growth of the carbon nanotube [10]. Availability of a «cap» on top of the catalyst indicates a cessation of growth and deactivation of the catalyst particles. Fig. 6 shows the Raman spectrum of carbon nanotubes on zeolite-based catalysts with Fe_2O_3.

The spectrum of this sample has the following peaks, peak D at a wave-length has 1355 cm^{-1}, G maximum has 1572 cm^{-1}**.** For this sample of CNT the ratio of peak intensity is I_D/I_G is 0.67. This ratio indicates at low defectiveness of obtained carbon nanotubes. Raman defectiveness of D-peak in graphite and nanotubes is similar. The difference is the width at half height (FWHM – full width at half maximum – standard expression).

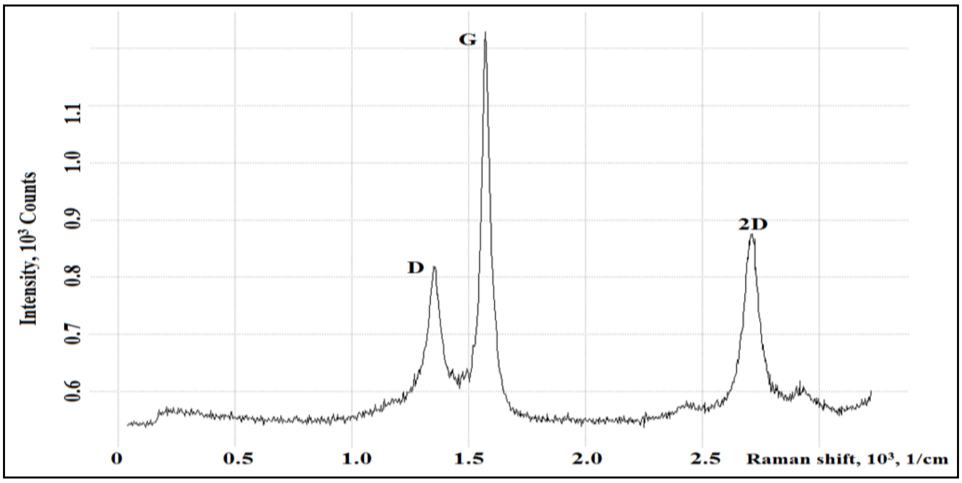

Fig. 6.Ramanspectrumof carbon nanotubes on zeolite-based catalysts with Fe_2O_3.

The spectrum of D-band of multiwall carbon nanotubes (δ_v = 80-90 cm^{-1}) is 2 times wider than a similar spectrum of D-band of graphite (δ_v = 32-35 cm^{-1}).For MWNTs a sample is synthesized on zeolite with Fe_2O_3, have a half value width of D-band is δ_v = 52-75 cm^{-1}[12].

Conclusions

The results of investigation have shown the effectiveness of zeolite-based catalysts during synthesis of carbon nanotubes with the help of chemical vapor deposition method. The self-propagating surface thermo synthesis method promotes the producing of metal oxides particles on zeolite. Carbon nanotubes were synthesized on zeolite-based catalysts and were investigated by transmission and scanning electron microscopy as well as Raman spectroscopy. For the catalyst on zeolite-Co_3O_4 the carbon nanotubes have a diameter of 11 nm. For the catalyst on zeolite-Fe_2O_3 the carbon nanotubes have diameters from 7 to 21 nm. Raman spectrum indicates a low defectiveness of obtained carbon nanotubes. Obtained results are confirmed the perceptiveness of zeolite-based catalysts for synthesis of carbon nanotubes by CVD.

References

[1]. L. Forró, Ch. Schönenberger. Europhys. News, 32 (3) (2001) 86 – 90.

[2]. J. Riemenschneider, T. Mahrholz, J.Mosch, H.P. Monner and J. Melcher,“Carbon nanotubes - smart material of the future: Experimental investigation of the system response” in: II Eccomas thematic conference on smart structures and materials: Materials and Processes, 2005, July 18-21, Lisbon, Portugal.

[3]. M.F.L. De Volder, S.H. Tawfick, R.H. Baughman, A.J.Hart.Science, 339 (2013) 535-550.

[4]. R.H. Baughman, A.A. Zakhidov, A.W.de Heer. Science, 297 (2002) 787-792.

[5]. Z.A. Mansurov, T.A. Shabanova, N.N. Mofa.Sintezitekhnologiinanostrukturirovannykhmaterialov [Synthesis and technologies nanostructured materials]: Textbook. Kazak University, Almaty, 2012 (in Russian).

[6]. C.P. Huynh, S.C. Hawkins.Carbon, 48 (2010) 1105 –1115.

[7]. T. Abdel-Fattah, E.J. Siochi, R.E. Crooks. Fullerenes, Nanotubes, and Carbon Nanostructures, 14 (2006) 585 – 594.

[8]. V.S. Tkach, D.S. Suslov. Katalizatorynaosnovekompleksovperekhodnykhmetallov: aktual’nye problemiprimeryikheffektivnogoresheniya [Catalysts based on transition metal complexes: actual problems and examples of effective determination]: Textbook. Irkutsk State University, Irkutsk, 2011 (in Russian).

[9]. G.B. Aldashukurova, A.V. Mironenko, Z.A. Mansurov, N.V. Shikina, S.A. Yashnik, V.V. Kuznetsov, Z.R. Ismagilov. Journal of Energy Chemistry, 22 (2013) 811–818.

[10]. S. Yellampalli (editor) «Carbon Nanotubes – Synthesis, Characterization, Application», InTech, 2011.

[11].Z.A. Mansurov, N.G. Prikhod’ko, A.V. Savel’yev.Obrazovaniye PTSAU, fullerenov, uglerodnykhnanotrubokisazhi v processakhgoreniya [Formation PAHs, fullerenes, carbon nanotubes, and soot in combustion processes].Kazak University, Almaty, 2012 (in Russian).

[12].E.M. Baytinger, I.N. Kovalev, N.A. Vekesser, Yu.I. Ryabkov, V.V. Viktorov.Chemical Bulletin of Kazakh National University, 1 (69) (2013) 96 – 102.

КАТАЛИЗАТОРЫ НА ОСНОВЕ ЦЕОЛИТОВ ДЛЯ СИНТЕЗА УГЛЕРОДНЫХ НАНОТРУБОК

Г.Т. Смагулова[1,2*], Н.Г. Приходько[1,3], Н.Р. Гусеинов[1,4], Р. Немкаева[1,4], Б.Т. Лесбаев[1,2], A.A. Zakhidov[5], З.А. Мансуров[1,2]

[1]Институт проблем горения, 050012, Казахстан, г. Алматы, ул. Богенбай батыра, 172
[2]Казахский Национальный университет им. аль – Фараби, Казахстан, г. Алматы, пр. аль – Фараби, 71
[3]Национальная нанотехнологическая лаборатория открытого типа, Казахстан, г. Алматы, пр. аль–Фараби, 71
[4]Алматинский университет энергетики и связи, Казахстан,г. Алматы, ул. Байтурсынова, 126
[5]University of Texas at Dallas, 800 W Campbell Rd, RL10, Richardson, TX 75080

Аннотация
Катализаторы переходных металлов на носителе были получены методом самораспространяющегося поверхностного термосинтеза на цеолите и были протестированы на процесс получения углеродных нанотрубок с помощью метода CVD. В работе представлены возможность применения и эффективность использования цеолита в качестве матрицы для катализаторов в синтезе одно- и многостенных углеродных нанотрубок методом химического парофазного осаждения. Углеродные нанотрубки, полученные на катализаторах на основе цеолита были исследованы с помощью, просвечивающей и сканирующей электронной микроскопии, и спектроскопии комбинационного рассеяния света. Для получения катализатора цеолита Co_3O_4 углеродные нанотрубки имеют диаметр 10,7-10,9 нм. Для катализатора цеолит-Fe_2O_3 были получены углеродные нанотрубки с диаметром от 6,8 до 20,9 нм. Спектр комбинационного рассеяния указывает на низкую дефектность полученных углеродных нанотрубок.
Ключевые слова: цеолит, катализатор, самораспространяющийся поверхностный термосинтез, углеродные нанотрубки

ЦЕОЛИТ НЕГІЗІНДЕ ЖАСАЛҒАН КАТАЛИЗАТОРЛАРДА КӨМІРТЕК НАНОТҮТІКШЕЛЕРДІҢ СИНТЕЗІ

Г.Т. Смағұлова[1,2*], Н.Г. Приходько[1,3], Н.Р. Гусеинов[1,4], Р. Немкаева[1,4], Б.Т. Лесбаев[1,2], A.A. Zakhidov[5], З.А. Мансұров[1,2]

[1]Жану проблемалары институты, 050012, Қазақстан, Алматы қ., Бөгенбай батыр көш., 172
[2]Казахский Национальный университет им. әл – Фараби, Қазақстан, Алматы қ., аль – Фараби даң., 71
[3]Ашық түрдегі ұлттық нанотехнологиялық зертхана, Қазақстан, Алматы қ., аль – Фараби даң., 71
[4]Алматы энергетика және байланыс университеті, Қазақстан, Алматы қ., Байтұрсынұлы көш., 126
[5]University of Texas at Dallas, 800 W Campbell Rd, RL10, Richardson, TX 75080

Аннотация
Тасымалдағыштағы ауыспалы металдардың катализаторлары өздігінен таралатын беттік термосинтез әдісімен цеолитте алынды және CVD тәсілі арқылы көміртекті нанотүтікше алу процесінде тексерілді. Осы жұмыста химиялық газфазалы тұндыру әдісімен бір және көпқабырғалы көміртекті нанотүтікше синтезі үшін катализатор матрицасы ретінде циолитті қолдану тиімділігі және мүмкіндігі көрсетілген. Циолит негізіндегі катализаторларда алынған нанотүтікшелер сәулелену және сканерлеу микроскопы, жарықты комбинациялық шашырату спектроскопиясы көмегімен зерттелді. Циолит-Co_3O_4 катализаторын алу үшін көміртекті нанотүтікшелер диаметрі 10,7-10,9 нм. Ал цеолит-Fe_2O_3 катализаторы үшін көміртекті нанотүтікшелер диаметрі 6,8 ден 20,9 нм дейін болды. Комбинациялық шашырату спектрлері алынған көміртекті нанотүтікшелердің дефектілігі төмен екенін көрсетті.
Түйінді сөздер: цеолит, катализатор, өздігінен таралатын беттік термосинтез, көміртекті нанотүтікше