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EFFECT OF THE POLYMER TEMPLATE MODIFICATION ON THE STUCTURE AND PROPERTIES OF THE COPPER NANOTUBES EMBEDDED IN COMPOSITE TRACK-ETCHED MEMBRANES

Abstract. This paper is devoted to the study of the preliminary oxidative modification effects as well as activation and sensitization conditions of PET track etched membranes (TeMs) on the structure of copper nanotubes (NTs) synthesized by the electroless deposition approach. The structure and composition of the synthesized composite membranes was studied by advanced methods such as: UV-Vis spectroscopy, energy dispersive analysis, scanning electron microscopy, X-ray diffraction and gas permeability.

The catalytic activity of Cu/PET TeM catalysts obtained under various deposition regimes has been studied using the benchmark reaction of the p-nitrophenol (p-NP) reduction in the presence of the sodium borohydride. It was shown that the highest value of the constant rate of the p-NP reduction reaction was determined for the composites prepared in the modified and double activated PET TeMs.

In the temperature range of 16-35 °C, the effect of temperature on the rate of the p-NP dehydrogenation reaction in the presence of composite catalysts based on copper NTs was studiedand the activation energy values were calculated. the lowest values of Ea were determined for samples synthesized in a matrix of unmodified and simple activated PET TeMs.

Keywords: copper nanotubes, electroless template synthesis, oxidation pretreatment, track-etched composite membranes, p-nitrophenol reduction

Introduction. Composite track-etched membranes (TeMs) with deposited nanotubes (NTs), nanowires (NWs) or nanoparticles (NP) form a new class of composite nanomaterials and are subject of investigation in various fields of membrane materials science. Literature data analysis shows that such composite membranes are a promising material for the development of lead-acid batteries, nanosized energy generators, high-sensitivity electrodes, elements of nano- and microelectronics, nanosensorics and photovoltaics, and magnetic devices [1–5]. Composite materials based on TeM s and NTs, NWs or NPs deposited by various methods have a large catalytically active specific surface, high mechanical strength, which allows them to be used for several consecutive reaction cycles without purification and activation. In most of the previously published works devoted to the study of the catalytic properties of the composite membranes a reduction reaction of p-nitrophenol (p-NF) is used [6,7]. The catalytic properties of monocomponent composites based on TeMs and gold NTs [8], AgNTs [9], Pt NTs [10], Au [11] and Pd [12], composites of mixed composition of Ni-Co Ni-Co [13], Ag/Au [14]. Moreover, in a number of works the authors managed to achieve an increase in the activity of composite materials by carrying out a preliminary modification of the polymeric template [11,15]. However, despite the diversity of the types of studied composite membranes, a limited amount of data on the reduction ability of copper NTs in composites has been found in the literature, although a number of review articles [16,17] indicate a significant potential for using nanosized copper and its compounds in organic synthesis as effective catalysts. In addition, nanostructures (NSs) based on copper and its oxide forms are objects of close study due to their surprising properties in the nanoscale state[18].

The purpose of this work is to study the effect of a preliminary oxidative modification of the activation conditions and sensitization of PET TM on the structure of copper NTs obtained by chemical deposition. It is of interest to consider the change in the catalytic properties of Cu/PET TeMs composite catalysts obtained under different deposition regimes.

EXPERIMENTAL

Chemicals. Copper (II) sulfate pentahydrate, sodium potassium tartrate, sodium hydroxide, palladium chloride, p-nitrophenol (4-NP) and sodium borohydride (Sigma) and all the other chemicals were of the analytical or reagent grade and were used without further purification.

Oxidation pretreatment of PET template. PET TeM samples were oxidized in H_2O_2/UV system. Details of the method were described elsewhere [3]. Membranes were immersed in 300 mM H_2O_2 water solution at pH=3 (HCl) for 180 min under UV irradiation at 254 nm. After oxidation the samples were washed twice in deionized water, dried in air at room temperature for 5 h.

Determination of change in carboxyl groups on the surface of PET TeMs before and after oxidation was made according to the procedure were described elsewhere [4] using toluidine blue dye. The calculation is based on the assumption that 1 M of dye complexed with 1 M of carboxyl groups.

Electroless template synthesis of copper NTs. TeMs were prepared from 12.0 µm PET film by irradiation with$^{+15}Kr^{84}$ ions (energy = 1.75 MeV per nucleon, fluence = $4 \cdot 10^7$ ions/cm^2) at the DC-60 heavy ion accelerator in Astana, Kazakhstan. Subsequently, the irradiated film was etched 4.0 min in 2.2 M NaOH solution at 85 ± 1°C. The pore size did not exceed 395±5 nm.

Prior to electroless deposition (ELD) of copper, the PET template was exposed to activation and sensitization procedures [38]. On the first stage a sample of PET TeM was immersed in a solution containing 50 g/l of $SnCl_2$ and 60 ml/l of 37% HCl for 6 minutes, afterword it was thoroughly rinsed for 10 min under flowing warm water. At the next activation stage, the sensitized membrane was immersed for 6 min into solution of 0.1g/l of $PdCl_2$ and 10 ml/l of HCl to provide formation of the thin layer of Pd nuclei and finally dried on the air [32].

To study the effect of activation treatment on the copper NTs deposition process, sensitization and activation stages were repeated twice for a series of sample.

Deposition was carried out at the temperature of 10°C. The activated polymer matrix was immersed in a thermostated deposition solution ($KNaC_4H_4O_6 \cdot 4H_2O$ - 18 g/l, $CuSO_4 \cdot 5H_2O$ - 5 g/l, NaOH - 7 g/l) and carefully fixed to avoid its expulsion by bubbles of evolved hydrogen. The desired pH = 12.45 was adjusted by the addition of sulfuric acid. The copper deposition process started immediately after the addition of 0.13M formaldehyde, for all the regimes, the deposition time did not exceed 40 min. At the end of the ELD, the samples were washed in a 96% ethanol solution and in deionized water and dried in an inert atmosphere.

Characterization. The structure of the copper NTs deposited in PET TeMs was investigated using a scanning electron microscope (SEM) JEOL JFC-7500F. Hitachi TeM3030 SEM equipped with a BrukerXFlash MIN SVE microanalysis system was used to elucidate the chemical composition of the resulting NTs. X-ray diffraction (XRD) measurements of the “as-prepared” composite membrane samples were obtained on a D8 Advance (Bruker, Germany). X-ray was generated at 40 mA and 40 kV and the scanning position ranged from 15-90˚ 2(θ). The crystal grain sizes were calculated using Scherrer equation.

Catalysis. A sample of Cu NTs composite membrane of size 2×2 cm was immersed into the stirred reaction mixture of 10 ml of $7.82 \cdot 10^{-6}$ M 4-NP and the $7.82 \cdot 10^{-3}$ M $NaBH_4$ aqueous solution [5]. The reaction was monitored at a temperature of 25±0.1 °C every 5-7 minutes using UV-Vis spectrophotometer in the wavelength range 200-600 nm. All samples were tested 3 times. Pseudo-first order reaction rate constants were calculated by plotting $\ln(A_t/A_0)$ versus time (A_t and A_0 is absorbance at $\lambda = 400$ at time t and in t=0). The slope of the line of best fit in the plot gives the pseudo-first order rate constant.

RESULTS AND DISCUSSION

In this study, copper NTs deposition was carried out in etched (Etch-PET TM) as well as oxidized (OX-PET TeMs). Previously [21] was found that the treatment of PET TeMs in oxidation systems based on hydrogen peroxide allows to significant increase the concentration of terminal carboxyl groups. Within this study we have obtained modified PET templates with a concentration of terminal carboxyl groups on the surface and in channels of the membrane equal to 14.9 ± 0.8 nM/cm^2 (for only etched PET TM this value is 6.0 ± 0.1 nM/cm^2).

Determination of the synthesis optimal conditions is the quietly important issue due its impact not only on the structure of nanomaterials but also on properties. Thus, sensitization stage the adsorption of Sn^{2+} ions occurs on the surface and in the pore channels of the PETTeMs (figure 1).

Further on the activation stage, Sn^{2+} acts as the reductant of Pd^{2+} ions afterward the formation of dense layer of nanosizedPdnanoparticles as a catalytic nuclei was observed.

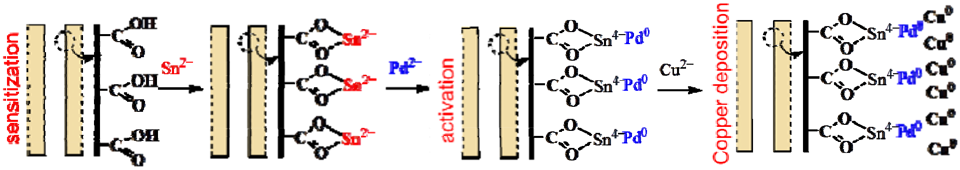

Figure 1 – General scheme of copper electroless deposition in the PET template

The formation of palladium nanoparticles at the activation stage (figure 2) was confirmed by X-ray diffraction (JCPDS 05-0681). And the dimension of nanoparticles (6.7±0.05) nm remains practically unchanged with several repeated procedures. Visual observation of the activated samples showed that multiple stages of sensitization and activation provide a denser layer of catalytic nucleation centers for palladium throughout the entire volume of the template.

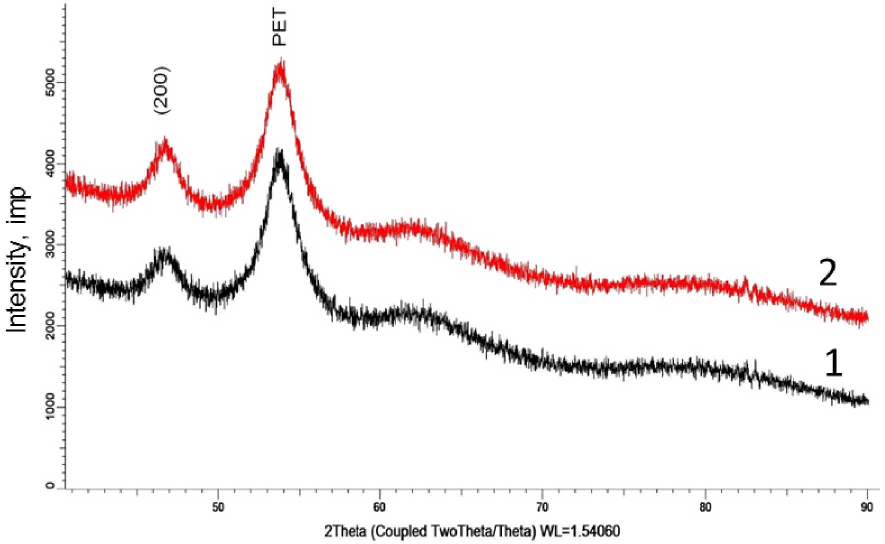

Figure 2 – XRD patterns of the PET TeM after single and double activation treatment

The energy-dispersive analysis was carried out to determine the chemical composition of copper NTs immediately after plating. It was found that the synthesized Cu NTs consist entirely of copper; the minor peak at 1.5 keV corresponds to SEM sample holder, peaks related to the carbon and oxygen are belong to the PET.

According to the XRD analysis data, all synthesized samples of the Cu NTs has afcclattice of copper and XRD pattern contained the(111), (200), (220) и (311), peaks related to the Cu^0. XRD data as well as copper deposition rate (R) and the structural parameters of final copper NTs are presented in the table 1. It’s should be noted that samples deposited in modified template possess a higher crystallinity.

Table 1 – Structural parameters of the copper NTs

№	Template	Number of activation	L Nm	a, Å	Crystal-linity, %	R, mg/cm^2·h	Structural parameters of NTs	
							Wall thickness, nm	Inner diameter, nm
1	Etch-PET TeMs	1	18,0±2,7	3,602	43,8	5,72	73,7	249
2	Etch- PET TeMs	2	19,9±2,9	3,594	52,5	5,632	88,15	203,3
3	Ox- PET TeMs	1	15,0±2,8	3,604	42,8	5,448	64,0	268,2
4	Ox- PET TeMs	2	21,4±3,2	3,597	53,1	5,748	79,5	237,3

SEMimages of the composites surface after copper deposition in the Etch-PET TeMa and Ox-PET TeMs samples after single and double activation treatment are presented on the figure 3. The sample code is given in accordance with table 2.

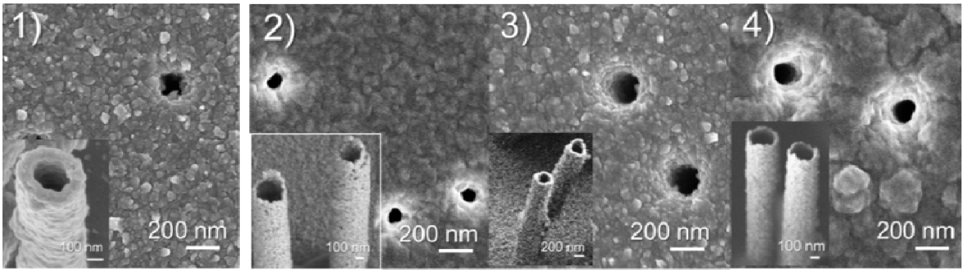

Figure 3 – SEM front side images of the Cu NTs composite membranes and magnified images of the released Cu NTs

As could be seen from SEM images of Cu-2 and Cu-4 a double repeated activation of the oxidized template surface provides the formation a copper layer consisting of more coarse-grained NPs, the wall thickness is almost 20% larger than in samples deposited in Etch-PET TeM templates.

Starting from Pradhan [28] reduction of 4-NP by sodium borohydride reaction has been used as a benchmark reaction for the evaluation of catalytic ability of nanosized catalysts [22].This reaction could be easily monitored by UV-vis spectroscopy: 4-NP shows a characteristic absorption peak at 400 nm in water solution from another hand the product, *p*-aminophenol (4-AP), exhibits a weak absorption peak at around 299 nm.The studied reaction has the pseudo-first order in the presence of excess of NaBH4, that allows to study the kinetics of the reaction to change the amount of the starting reagent 4-NP (figure 4).

As can be seen from the presented data, the preliminary oxidative modification of the PET template facilitates an increase in the catalytic activity of the composite membrane. In addition, for the OX-PET TeM sample (double activated) the of p-NPconstant rate increases by more than 40% compared to the sample prepared according to a standard procedure (Etch-PET TM, single activated).

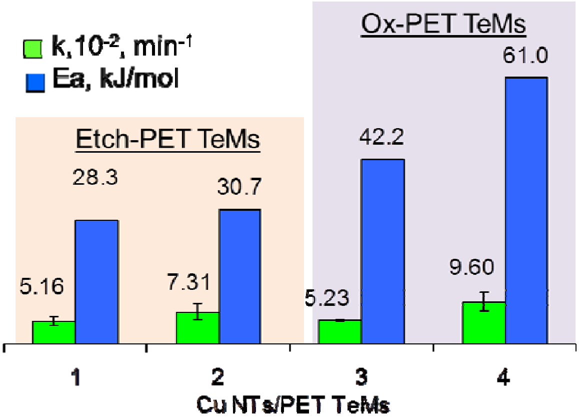

Figure 4 – The changes of constant rate and activation energy of the 4-NP reduction reaction in the presence of the composite membranes with embedded copper nanotubes

The impact of testing temperature on the catalyticability of the synthesized composite membranes were studied in the temperature range of 16-35 °C and the activation energy was calculated based on the Arrhenius plot (also presented in the figure 4).

The increased value of Ea for sample № 4 is caused by bigger size of copper crystallites than in other studied samples.

It is very difficult to carry out a comparative analysis of the Ea data obtained with the earlier studies of the temperature dependence of the catalytic activity of copper nanostructures, since the different shape of the copper tested NSs, their dimensionality, the type of substrate, the fixing method and test conditions may differ. Thus, for a hybrid microgel based on nanosized copper and a copolymer of N-isopropylacrylamide and acrylic acid, the Ea value in the reduction reaction of p-NP was claimed to be 0.8 kJ/mol [22], for an analogous reaction in the presence of nanosized copper stabilized with polyvinipyrrolidone, Ea equal to 45.76 and 82.96 kJ/mol for NPs with size of 9 and 11 nm respectively [23].

The main conclusions that can be drawn from thepresented above results are:

– A preliminary oxidative modification of the PET TeMs template allows a significant increase in the concentration of terminal carbonyl groups and, correspondingly, an increase in the amount of palladium NPs as active nuclei of the copper NTs growth.

– The highest value of the p-NP reduction reaction rate constant was determined for samples of composites synthesized in modified and double activated PET TeMs. However, the largest value of Ea was also calculated for this sample. We assume that main reason isa sharp increase of the reaction rate: with an increase in temperature from 16 to 35 ° C, the reaction rate increases by 9 times for sample №1, but for samples with a minimal Ea value this parameter increases only by 1.75 times in the same temperature range.

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REFERENCES

[1] Stassi S., Cauda V., Ottone C., Chiodoni A., Pirri C.F., Canavese G. Flexible piezoelectric energy nanogenerator based on ZnO nanotubes hosted in a polycarbonate membrane // Nano Energy. 2015. Vol. 13. P. 474-481.

[2] Davenport M., Healy K., Siwy Z.S. Ag nanotubes and Ag/AgCl electrodes in nanoporous membranes // Nanotechnology. 2011. Vol. 22, N 15. P. 155301.

[3] Navitski A., Müller G., Sakharuk V., Cornelius T.W., Trautmann C., Karim S. Efficient field emission from structured gold nanowire cathodes // Eur Phys J Appl Phys. 2009. Vol. 48, N 3. P. 30502.

[4] Clochard M.C., El Jouad M., Bizière N., Chung P. Do, Drouhin H.J., Balanzat E., Lairez D., Viret M., Wegrowe J.E. Magnetic nanoconstrictions made from nickel electrodeposition in polymeric bi-conical tracks: Magneto-transport behavior // Radiat Phys Chem. 2014. Vol. 94, N 1. P. 66-71.

[5] Roh D.K., Patel R., Ahn S.H., Kim D.J., Kim J.H. Preparation of TiO_2 nanowires/nanotubes using polycarbonate membranes and their uses in dye-sensitized solar cells // Nanoscale. 2011. Vol. 3, N 10. P. 4162.

[6] Aditya T., Pal A., Pal T. Nitroarene reduction: a trusted model reaction to test nanoparticle catalysts // Chem Commun. 2015. Vol. 51, N 46. P. 9410-9431.

[7] Pozun Z.D., Rodenbusch S.E., Keller E., Tran K., Tang W., Stevenson K.J., Henkelman G. A systematic investigation of p-nitrophenol reduction by bimetallic dendrimer encapsulated nanoparticles // J Phys Chem C. 2013. Vol. 117, N 15. P. 7598–7604.

[8] Dotzauer D.M., Bhattacharjee S., Wen Y., Bruening M.L. Nanoparticle-containing membranes for the catalytic reduction of nitroaromatic compounds // Langmuir. 2009. Vol. 25, N 3. P. 1865-1871.

[9] Borgekov D., Mashentseva A., Kislitsin S., Kozlovskiy A., Russakova A., Zdorovets M. Temperature dependent catalytic activity of Ag/PET ion-Track membranes composites // Acta Phys Pol A. 2015. Vol. 128, N 5. P. 871-874.

[10] Muench F., Lauterbach S., Kleebe H.-J., Ensinger W. Deposition of Nanofilms inside a Polymer Template: Formation of Metal Nanotubes // e-Journal Surf Sci Nanotechnol. 2012. Vol. 10, N 0. P. 578-584.

[11] Korolkov I. V., Borgekov D.B., Mashentseva A.A., Güven O., Atlcl A.B., Kozlovskiy A.L., Zdorovets M. V. The effect of oxidation pretreatment of polymer template on the formation and catalytic activity of Au/PET membrane composites // Chem Pap. 2017. Vol. 71, N 12. P. 2353-2358.

[12] Muench F., Oezaslan M., Svoboda I., Ensinger W. Electroless plating of ultrathin palladium films: Self-initiated deposition and application in microreactor fabrication // Mater Res Express. 2015. Vol. 2, N 10. P. 105010.

[13] Schaefer S., Felix E.-M., Muench F., Antoni M., Lohaus C., Brötz J., Kunz U., Gärtner I., Ensinger W. NiCo nanotubes plated on Pd seeds as a designed magnetically recollectable catalyst with high noble metal utilisation // RSC Adv. 2016. Vol. 6, N 74. P. 70033-70039.

[14] Mashentseva A.A., Borgekov D.B., Niyazova D.T., Zdorovets M. V. Evaluation of the catalytic activity of the composite track-etched membranes for p-nitrophenol reduction reaction // Pet Chem. 2015. Vol. 55, N 10. P. 810-815.

[15] Kumar R., Kamakshi, Kumar M., Awasthi K. Functionalized Pd-decorated and aligned MWCNTs in polycarbonate as a selective membrane for hydrogen separation // Int J Hydrogen Energy. 2016. Vol. 41, N 48. P. 23057-23066.

[16] Ojha N.K., Zyryanov G. V., Majee A., Charushin V.N., Chupakhin O.N., Santra S. Copper nanoparticles as inexpensive and efficient catalyst: A valuable contribution in organic synthesis // Coord Chem Rev. 2017. Vol. 353. P. 1-57.

[17] Gawande M.B., Goswami A., Felpin F.-X., Asefa T., Huang X., Silva R., Zou X., Zboril R., Varma R.S. Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis // Chem Rev. 2016. Vol. 116, N 6. P. 3722-3811.

[18] Nam V., Lee D. Copper Nanowires and Their Applications for Flexible, Transparent Conducting Films: A Review // Nanomaterials. 2016. Vol. 6, N 3. P. 47.

[19] Korolkov I. V., Mashentseva A.A., Güven O., Zdorovets M. V., Taltenov A.A. Enhancing hydrophilicity and water permeability of PET track-etched membranes by advanced oxidation process // Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms. 2015. Vol. 365. P. 651-655.

[20] Bercu B., Enculescu I., Spohr R. Copper tubes prepared by electroless deposition in ion track templates // Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms. 2004. Vol. 225, N 4. P. 497-502.

[21] Korolkov I. V., Mashentseva A.A., Güven O., Niyazova D.T., Barsbay M., Zdorovets M.V. The effect of oxidizing agents/systems on the properties of track-etched PET membranes // Polym Degrad Stab. Elsevier Ltd, 2014. Vol. 107. P. 150-157.

[22] Farooqi Z.H., Sakhawat T., Rauf Khan S., Kanwal F., Usman M., Begum R. Synthesis, characterization and fabrication of copper nanoparticles in N-isopropylacrylamide based co-polymer microgels for degradation of p-nitrophenol // Mater Sci Pol. 2015. Vol. 33, N 1. P. 185-192.

[23] Verma A.D., Mandal R.K., Sinha I. Kinetics of p-Nitrophenol Reduction Catalyzed by PVP Stabilized Copper Nanoparticles // Catal Letters. 2015. Vol. 145, N 10. P. 1885-1892.

Резюме

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ВЛИЯНИЕ МОДИФИКАЦИИ ПОЛИМЕРНОГО ТЕМПЛАТА НА СТРУКТУРУ И СВОЙСТВА НАНОТРУБОК МЕДИ В СОСТАВЕ КОМПОЗИТНЫХ ТРЕКОВЫХ МЕМБРАН

Работа посвящена изучению влияния предварительной окислительной модификации и условий активации и сенсибилизации ПЭТФ ТМ на структуру НТ меди, полученных методом химического осаждения. Структура и состав синтезированных композитных мембран была изучена методами: УФ-спектроскопия, энергодисперсионный анализ, растровая электронная микроскопия, рентгеновская дифрактометрия и метод газопроницаемости.

На примере классической реакции восстановления п-нитрофенола (п-НФ) в присутствии боргидрида натрия была изучена каталитическая активность катализаторов Cu/ПЭТФ ТМ, полученных при различных режимах осаждения. Показано, что наибольшее значение константы скорости реакции восстановления п-НФ было определено для образцов композитов, полученных в модифицированных и дважды активированных ПЭТФ ТМ.

В интервале температур 16-35 °С было исследовано влияние температуры на скорость реакции дегидрирования п-НФ в присутствии композитных катализаторов на основе НТ меди, на основании полученных данных были рассчитаны значения энергии активации. Наименьшее значение Еа было рассчитано для образцов, синтезированных в матрице не модифицированной ПЭТФ ТМ.

Ключевые слова: медные нанотрубки, синтез неорганических матриц, предварительная обработка окислением, композиционные мембраны с трек-травлением, снижение п-нитрофенола

Резюме

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КОМПОЗИТТІ ТРЕКТІ МЕМБРАНАЛАР ҚҰРАМЫНДАҒЫ МЫС НАНОТҮТІКШЕЛЕРІНІҢ ҚҰРАМЫ МЕН ҚҰРЫЛЫСЫНА ТҮРЛЕНГЕН ТЕМПЛАНТТЫ ПОЛИМЕРДІҢ ӘСЕРІ

Химиялық тұндыру әдісімен алынған мыснанотүтікшелерді (НТ) тотығу модификациясымен химиялық жауын шашын арқылы алынатын құрылымына ПЭТФ трективтік мембраналарның (ПЭТФТМ) белсендірудің және сенсибилизацияның әсерін зерттеуге арналған. Синтезделген композиттік мембраналардың құрамымен құрамы: УК-спектроскопия, энергетикалық дисперсті талдау, сканерден өтетін электрондық микроскопия, рентгендік дифрактометрия және газ өткізгіштігі әдістерімен зерттелді.

Түрлі тұндыру режимдерінде алынған Cu/ТМ ПЭТФ катализаторларының каталитикалық белсенділігі натрий бор гидридінің қатысуымен п-нитрофенолды (п-НФ) азайту үшін классикалық реакцияны қолдану арқылы зерттелді. п-НФ төмендету реакциясының жылдамдық тұрақты константасының мәнінің ең жоғары мәні модификацияланған және екі есе актив тендірілген ТМПЭТФ алынған композит үлгілері үшін анықталған.

16-35°С температурада мыс НТ негізделген композициялық катализаторлардың қатысуымен п-НФ дегидрирленген реакциясының жылдамдығына температураның әсері зерттелді және алынған мәндер негізінде активтендіру энергия мәндері есептелген. Синтезделген үлгілер үшін ТМПЭТФ модифицирленген емес матрицасында ең төменгі Еа мәндері есептелген.

Түйін сөздер: бейорганикалық матрицаның синтезі, тотығудың алдын ала емдеуі, трек-өңделген композициялық мембраналар, р-нитрофенолды азайту.