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Platinum-Niobium(V) Oxide/Carbon Nanocomposites Prepared By Microwave Synthesis For Ethanol Oxidation

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In the present work, Pt nanoparticles were deposited by means of microwave synthesis on the primary carbon supported Nb_2O_5 composite which was prepared in two different ways: (A) by dispersion of Nb_2O_5 and carbon with the mass ratio equal to 1:1 in a 2-propanol solution by ultrasonication for 30 min. with further desiccation of the mixture and (B) by heating the Nb_2O_5/C composite obtained according to the procedure (A) at 500 °C for 2 h. The transmission electron microscopy was used to determine the shape and the size of catalyst particles. X-ray diffraction and inductively coupled plasma optical emission spectroscopy were employed to characterize the structure and composition of the synthesized catalysts. The electrocatalytic activity of the synthesized catalysts towards the oxidation of ethanol in an alkaline medium was investigated by means of cyclic voltammetry.

Keywords: platinum, niobium(V) oxide, nanocomposite, microwave synthesis, ethanol oxidation.

1. INTRODUCTION

Among different types of fuel cells, alkaline fuel cells (AFCs) are the best studied [1 – 5]. Alkaline direct ethanol fuel cells (DEFCs), which promise to be a clean and efficient energy production technology, have recently attracted worldwide attention, primarily because ethanol is sustainable fuel. It also possesses many unique physicochemical properties including a high energy density as well as ease of transportation, storage and handling [6 – 9]. Platinum is a good catalyst for the oxidation of alcohols [6, 10 – 13], but the use of it as an electrode material is limited by its high price.

Recently, metal oxide (Al_2O_3, Fe_2O_3, CeO_2, TiO_2 et. al) promoted Pt electrocatalysts have been considered for direct electro-oxidation of alcohols [14 – 19]. The n-type niobium pentoxide (Nb_2O_5) semiconductor is a remarkable material having application in catalysis, because of its excellent microtextural, chemical stability and corrosion resistance properties [20 – 23]. Pt-based catalysts with metal oxides ($Pt – M_xO_y$) and transition metals (PtM (Fe, Ni, Co)) allow reducing the amount of Pt. It has been determined that the Pt-based catalysts exhibit a better catalytic stability and a higher activity for the oxidation of alcohols [24, 25] and reduction of oxygen [26 – 30] than the bare Pt catalyst. The catalytic enhancement of Pt-based catalysts with transition metals has been attributed to the PtM alloy formation and the change in Pt electronic structure due to the presence of metal, Pt – Pt distance, and d-electron density in Pt [31 – 34].

Creating of fast, simple and cost-effective technologies with the aim to produce catalysts with a small particle size and high distribution on the support and with tailored properties, is still in progress. Over the last few decades, material synthesis techniques based on microwave chemistry have received considerable attention as a new promising method for the one-pot synthesis of metallic nanostructures in solutions. The greatest advantage of using microwave irradiation is that it allows exact control of reaction conditions with the purpose to tailor the resulting nanoparticles according to requirements [35 – 37].

The aim of this study was to investigate the dependence of the activity of the niobium (V) oxide/carbon supported platinum catalysts (denoted as Pt-Nb_2O_5/C) towards the oxidation of ethanol in an alkaline medium on the conditions of preparation of primary Nb_2O_5/C composites. The electrocatalytic activity of the Pt-Nb_2O_5/C catalysts with respect to ethanol oxidation was investigated by means of cyclic voltammetry. The electrochemical behavior of the Pt-Nb_2O_5/C catalysts towards the oxidation of ethanol was compared with that of carbon supported bare Pt catalyst (denoted as Pt/C). The transmission electron microscopy (TEM) was used to determine the shape and the size of catalyst particles. X-ray diffraction (XRD) and inductively coupled plasma optical emission spectroscopy (ICP-OES) were employed to characterize the structure and composition of the synthesized catalysts.

2. MATERIALS AND METHODS

2. 1. Chemicals

H_2PtCl_6 (37.5 % of Pt), Nb_2O_5 powder (purity 99.9 %) and graphite powder (99,9995 %) were purchased from Alfa-Aesar Supply. Nafion (5 wt.%, D521, 1100 EW) was purchased from Ion Power Inc. Supply. H_2SO_4 (96 %), NaOH (98.8 %), ethanol (96 %), glycerol and acetone were purchased from Chempur Company. All chemicals were of analytical grade. Ultra-pure water with the resistivity of 18.2 MΩ cm^{-1} was used to prepare all the solutions.

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2. 2. Fabrication of catalysts

The primary Nb_2O_5/C composite was prepared according to the following procedures: (A) by dispersion of Nb_2O_5 and carbon (mass ratio being 1:1) in a 2-propanol solution by ultrasonication for 30 min. with further desiccation of the mixture and (B) by heating the Nb_2O_5:C composite obtained according to the procedure (A) in a muffle furnace at 500 °C for 2 h in air atmosphere. Then Pt nanoparticles were dispersed over Nb_2O_5/C composites by the rapid microwave heating method. Typical preparation consists of the following steps: at first, the solution containing 1.9 mM of H_2PtCl_6 and 1 M of glycerol was prepared. pH of the solution was adjusted to 11.65 by adding dropwise a 0.4 M NaOH solution. Then 100 mg of Nb_2O_5/C prepared by (A) and (B) procedures were added to the reaction mixture and sonicated for 20 min. For the microwave irradiation, the reaction mixture was put into a microwave reactor Monowave 300 (Anton Paar). The reduction of Pt nanoparticles was carried out at a temperature of 170 °C for 30 s. For comparison, the carbon supported Pt catalyst was also prepared at 170 °C for 30 s. After preparation, the synthesized catalysts were washed with acetone, ultra-pure water with the resistivity of 18.2 MΩ cm^{-1}, then filtered and dried in a vacuum oven at 80 °C for 2 h.

2. 3. Characterization of catalysts

A shape and size of catalyst particles were examined using a transmission electron microscope Tecnai G2 F20 X-TWIN equipped with EDAX spectrometer with r-TEM detector. For microscopic examinations, 10 mg of sample was first sonicated in 1 ml of ethanol for 1 h and then deposited on the Cu grid covered with a continuous carbon film.

X-ray diffraction patterns were recorded using a D8 diffractometer (Bruker AXS, Germany, 2003) with Cu Kα radiation using a Ni/graphite monochromator. A step-scan mode was used in the 2-theta range from 20° to 90° with a step length of 0.02° and a counting time of 5 s per step.

The Pt metal loadings were estimated from ICP-OES measurements. The ICP optical emission spectra were recorded using an ICP optical emission spectrometer Optima 7000DV (Perkin Elmer).

2. 4. Electrochemical measurements

The working electrode was a thin layer of Nafion-impregnated catalyst cast on a glassy carbon electrode, a Pt sheet was used as a counter electrode and an Ag/AgCl/KCl (3 M KCl) electrode was used as reference. The catalyst layer was obtained according to the following steps: at first the 10 mg of Pt-Nb_2O_5/C or Pt/C catalysts were dispersed ultrasonically for 1 hour in a solution containing 0.25 μl of 5 wt.% Nafion and 0.75 μl deionized H_2O to produce a homogeneous slurry. Then 5 μl of the prepared suspension mixture was pipetted onto the polished surface of a glassy carbon electrode with a geometric area of 0.07 cm^2 and dried in air for 12 h.

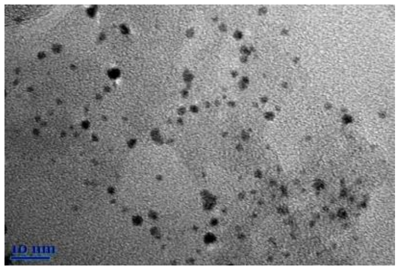
All electrochemical measurements were performed with a Zennium electrochemical workstation (ZAHNER-Elektrik GmbH & Co.KG). Steady state linear sweep voltammograms were recorded in a 1 M C_2H_5OH + 0.5 M NaOH solution at a linear potential sweep rate of 50 mV s^{-1} from -0.5 to 0.5 V at a temperature of 25 °C. The electrode potential is quoted versus the standard hydrogen electrode (SHE). The presented current densities are normalized with respect to the geometric area of catalysts.

All solutions were deaerated by argon for 15 min prior to measurements.

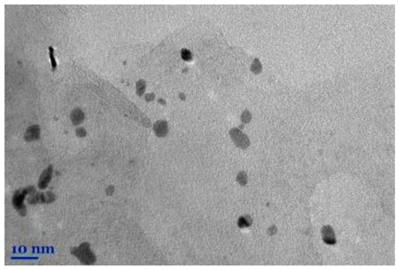
3. RESULTS AND DISCUSSION

The niobium (V) oxide/carbon and carbon supported Pt catalysts were prepared by means of rapid microwave heating. The niobium (V) oxide/carbon support for the deposition of Pt nanoparticles was prepared by dispersion of Nb_2O_5 and carbon with mass ratio being 1:1 in a 2-propanol solution with further desiccation of the mixture and the one heated at 500 °C for 2 h. The reaction mixture consisted of required amount of Pt (IV) salt, prepared Nb_2O_5/C supports and 1 M glycerol solution was kept at 170 °C for 30 s under microwave irradiation. The prepared catalysts were denoted depending on the preparation of primary Nb_2O_5/C composite i. e. A-Pt-Nb_2O_5/C, B-Pt-Nb_2O_5/C, or just A-, B-. The properties of these catalysts were compared with those of the Pt/C catalyst prepared in the same manner.

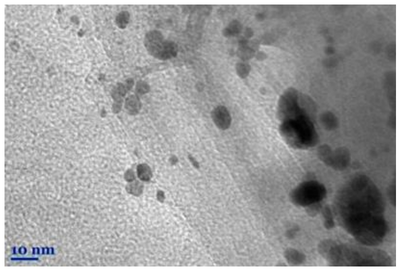
The Pt nanoparticles of ca. 4-7 nm in size were deposited on the surface of carbon in the A-, and B-Pt-Nb_2O_5/C catalysts (Fig. 1).



a



b



c

Fig. 1. TEM images of: a – the Pt/C; b – A-Pt-Nb_2O_5/C; c – B-Pt-Nb_2O_5/C catalysts

For comparison, the Pt/C catalyst was synthesized with Pt nanoparticles of ca. 3-5 nm in size as depicted from

Fig. 1 a. In all cases the Pt nanoparticles were uniform and well dispersed on the surface of carbon.

X-ray diffraction was used for the structural characterization of the niobium (V) oxide/carbon and carbon supported Pt catalysts. Fig. 2 presents the XRD patterns of the B-Pt-Nb_2O_5/C and Pt/C catalysts. The particle size of Pt nanoparticles was determined using Scherrer equation and values of full width at half maximum (FWHM) of Pt XRD peaks. According to the pattern of Pt/C (Fig. 2), the composition of the latter catalyst consists of small Pt (PDF 4-802) crystallites of ca. 9 nm in size. In the case of the niobium (V) oxide/carbon supported Pt catalyst, the crystallites of Pt reach ca. 12 nm in size (Fig. 2), whereas the orthorombic (PDF 27-1003) and monoclinic (PDF 19-862) niobium pentoxide with particles in size of ca. 48 and 18 nm, respectively, are predominant.

The Pt loading of the synthesized catalysts was determined by ICP-OES. It was found that the Pt loadings were 0.128, 0.185 and 0.114 mg Pt cm^{-2} in the Pt/C, A-Pt-Nb_2O_5/C and B-Pt-Nb_2O_5/C catalysts, respectively.

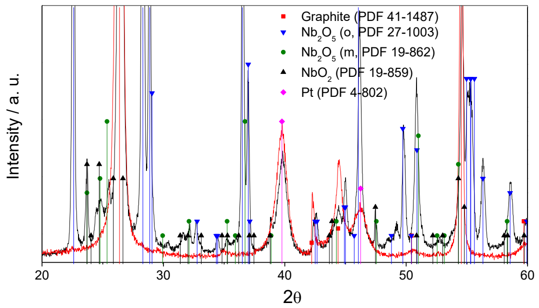


Fig. 2. XRD patterns of the Pt/C and B-Pt-Nb_2O_5/C catalysts synthesized by the microwave irradiation method

The electrochemically active surface areas (*ESAs*) of Pt in the synthesized catalysts were determined from the cyclic voltammograms of the A-Pt-Nb_2O_5/C, B-Pt-Nb_2O_5/C and Pt/C catalysts recorded in a deaerated 0.5 M H_2SO_4 solution at a sweep rate of 50 mV s^{-1} (Fig. 3).

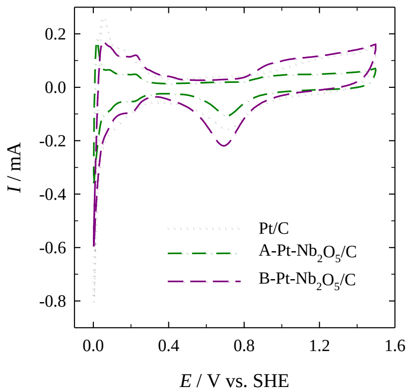


Fig. 3. Cyclic voltammograms of the A-Pt-Nb_2O_5/C, B-Pt-Nb_2O_5/C and Pt/C catalysts recorded in 0.5 M H_2SO_4 at a sweep rate of 50 mV s^{-1}

The *ESAs* for the catalysts were estimated from the integrated charge of the hydrogen adsorption region (Q_H) in the cyclic voltammograms according to Eq. 1 [38]:

$$ESA\ (cm^2) = Q_H\ (\mu C) / 220\ (\mu C\ cm^{-2}), \quad (1)$$

where 220 μC cm^{-2} is the charge required to oxidize a monolayer of hydrogen adsorbed on Pt. The *ESA* values ($m^2\ g^{-1}$) were calculated according to Eq. 2:

$$ESA\ (m^2\ g^{-1}) = Q_H / Pt\ \text{loading} \times 220 \quad (2)$$

It has been determined that the values of *ESA* are 1.8 cm^2 for Pt/C and 1.7 and 3.5 cm^2 for A- and B-Pt-Nb_2O_5/C catalysts, respectively. The specific activity has been determined to be 20 $m^2\ g^{-1}$ Pt for Pt/C, 13 $m^2\ g^{-1}$ Pt for A-Pt-Nb_2O_5/C and 20 $m^2\ g^{-1}$ Pt for B-Pt-Nb_2O_5/C.

The electrocatalytic activity of the A-, B-Pt-Nb_2O_5/C and Pt/C catalysts with respect to the oxidation of ethanol was investigated by cyclic voltammetry. Fig. 4 shows long-term cyclic voltammograms for A-, B-Pt-Nb_2O_5/C and Pt/C catalysts recorded in a 1 M C_2H_5OH + 0.5 M NaOH solution at a sweep rate of 50 mV s^{-1}.

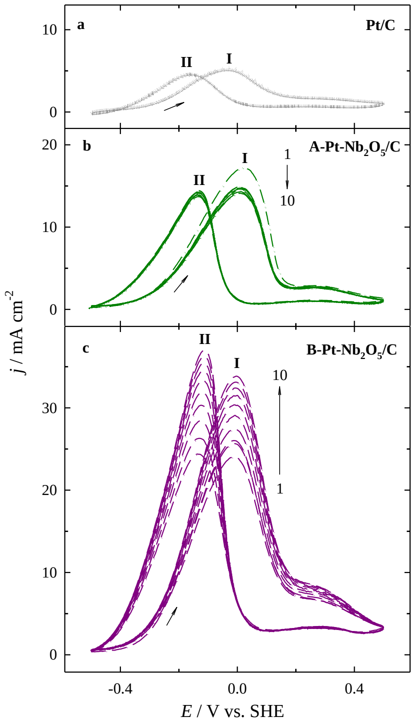


Fig. 4. CVs of: a – the Pt/C; b – A-Pt-Nb_2O_5/C; c – B-Pt-Nb_2O_5/C catalysts recorded in 1 M C_2H_5OH + 0.5 M NaOH at a sweep rate of 50 mVs^{-1}; at 25 °C

In the forward sweep, anodic peaks I are observed at ca. -0.03 V for Pt/C and ca. 0 V for A- and B-Pt-Nb_2O_5/C catalysts (Fig. 4). Peak I is related with the direct oxidation of ethanol in an alkaline medium. In the reverse sweep, anodic peaks II were detected at ca. -0.15 V for the Pt/C and ca. -0.1 for the both Pt-Nb_2O_5/C catalysts. This peak II in the reverse sweep is attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward sweep [39].

During long-term cycling the ethanol electro-oxidation current density values (anodic peak I) recorded at the B-Pt-Nb_2O_5/C catalyst increase in contrast to those at the Pt/C and A-Pt-Nb_2O_5/C catalysts. However, it should be noted that the obtained stabilized 10th cycle of ethanol oxidation current densities are also greater at the B-Pt-Nb_2O_5/C catalyst as compared to those at the Pt/C and A-Pt-Nb_2O_5/C catalysts.

Fig. 5 presents positive potential-going scans of investigated catalysts recorded in 1 M C_2H_5OH + 0.5 M NaOH at a sweep rate of 50 mVs^{-1}.

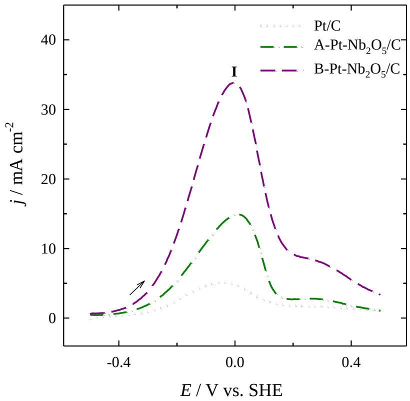


Fig. 5. Stabilized positive-potential going scans (10th cycles) of the A-Pt-Nb_2O_5/C, B-Pt-Nb_2O_5/C and Pt/C catalysts recorded in 1 M C_2H_5OH + 0.5 M NaOH at a sweep rate of 50 mV s^{-1}

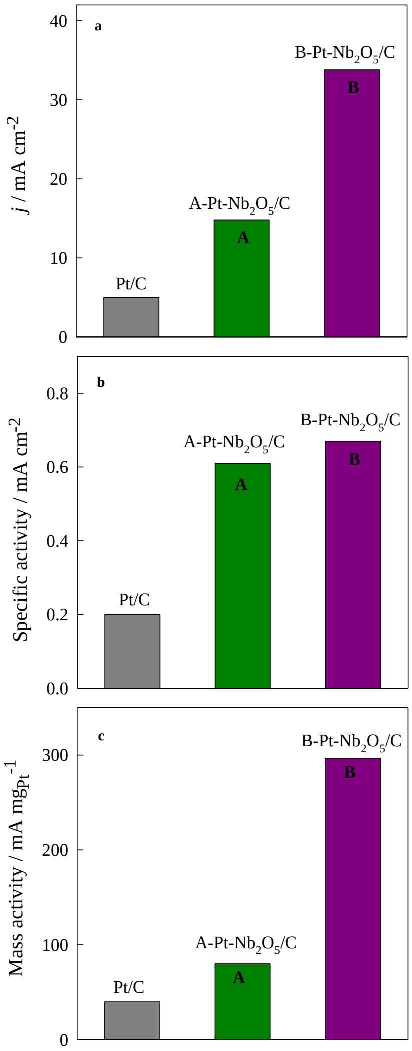


Fig. 6. Comparison of: a – current densities; b – specific activity; c – mass activity towards the oxidation of ethanol at 0 V vs. SHE for Pt/C, A-Pt-Nb_2O_5/C and B-Pt-Nb_2O_5/C recorded in 1 M C_2H_5OH + 0.5 M NaOH at 50 mV s^{-1}

Noteworthy, oxidation peaks on the A-Pt-Nb_2O_5/C and B-Pt-Nb_2O_5/C catalysts are much higher than those on Pt/C. Ethanol oxidation current densities on the A-Pt-Nb_2O_5/C and B-Pt-Nb_2O_5/C catalysts are ca. 3.0 – 6.0 times higher as compared to that of the bare Pt/C catalyst (Fig. 5).

To evaluate the electrocatalytic activity of investigated catalysts, ethanol oxidation current values were normalized by the electrochemically active surface areas for each catalyst to represent the specific activity (mA cm^{-2}). Mass activity of catalysts (mA mg^{-1}) was obtained by normalizing ethanol oxidation current density values by the Pt loadings for each catalyst. Assuming ca. 2.0 times higher *ESAs* value of the B-Pt-Nb_2O_5/C catalyst as compared with that of Pt/C, the surface area normalized ethanol oxidation current densities are ca. 3.4 times higher on the B-Pt-Nb_2O_5/C catalyst (Fig. 6 b). Assuming the similar ESAs value of the A-Pt-Nb_2O_5/C catalyst as compared with that of Pt/C, the surface area normalized ethanol oxidation current densities are ca. 3 times higher on the A-Pt-Nb_2O_5/C catalyst (Fig. 6 b).

The mass activities for ethanol oxidation are ca. 2 and 7 times higher at the A-Pt-Nb_2O_5/C and B-Pt-Nb_2O_5/C catalysts, respectively, as compared to those at the Pt/C catalysts (Fig. 6 c). It has been found that niobium (V) oxide/carbon supported Pt catalysts show an enhanced electrocatalytic activity towards the oxidation of ethanol in an alkaline medium as compared with that of the carbon supported bare Pt catalyst.

Notably, a higher activity towards the oxidation of ethanol shows the niobium (V) oxide/carbon supported Pt catalyst when the niobium (V) oxide/carbon support was heated at 500 °C for 2 h. Ca. 2.3 times greater ethanol oxidation current densities were recorded at the latter catalyst than those at A-Pt-Nb_2O_5/C when the niobium(V) oxide/carbon support was only dispersed in a 2-propanol solution. Mass activity for ethanol oxidation is ca. 4 times higher at B-Pt-Nb_2O_5/C as compared with that at A-Pt-Nb_2O_5/C.

4. CONCLUSIONS

A rapid microwave heating method was used to prepare the niobium (V) oxide/carbon supported platinum nanoparticles (Pt-Nb_2O_5/C) as electrocatalysts towards the oxidation of ethanol. The primary Nb_2O_5/C composite, used for the deposition of Pt nanoparticles, was prepared in two different ways: (A) by dispersion of Nb_2O_5 and carbon with the mass ratio equal to 1:1 in a 2-propanol solution by ultrasonication for 30 min. with further desiccation of the mixture and (B) by heating the Nb_2O_5/C composite obtained according to the procedure (A) at 500 °C for 2 h. It was found that higher catalytic activity with respect to the oxidation of ethanol show the B-Pt-Nb_2O_5/C catalyst when the primary support Nb_2O_5/C was dispersed in a 2-propanol solution followed by its heating at 500 °C for 2 h. It has been determined that the investigated Pt-Nb_2O_5/C catalysts outperformed the bare Pt/C catalyst.

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