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Catalytic Activity of Ce-, Zr- and Mn-Containing Oxide Layers on Titanium in the Process of Biomass Gasification

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Abstract

Composition, surface structure (including those after annealing at high temperature) and the catalytic activity in the steam conversion of naphthalene were studied for Ce-, Zr- and Mn-containing oxide layers obtained on titanium by means of plasma electrolytic oxidation. The composition and structure of oxide systems were studied by means of XRD phase analysis, energy dispersion analysis and scanning electron microscopy. It was demonstrated that Ce-, Zr-containing structures exhibit a rather high thermal stability: the elemental and phase composition, the structure of their surface remain almost unchanged after annealing in atmospheric air at the temperature values up to 800 °C. The catalytic studies demonstrated a rather high activity of Ce-, Zr-containing coatings in the reaction of naphthalene steam conversion at the temperature values up to 850 °C. Mn-containing oxide structures have developed surface covered with nanowhiskers those were not detected after thermal treatment. Mn-containing oxide systems exhibited a lower level of naphthalene conversion as compared to Ce-, Zr-containing coatings, which could be connected with substantial changing their surface and with the formation of low-active fused manganese silicates at high temperature values.

Key words: oxide coatings, titanium, plasma electrolytic oxidation, catalytic steam conversion of naphthalene

INTRODUCTION

For the last time, interest increased in studying the catalytic gasification of biomass, *i. e.* the conversion of biomass under oxygen deficiency at elevated temperature values (800–900 °C). This yields a gaseous energy carrier that represents a producer gas consisting of CO, H_2, CO_2, CH_4, H_2O and N_2 and a number of undesired organic and inorganic impurities (H_2S, HCl, NH_3, alkali metals). A complicated mixture of hydrocarbons (excluding gaseous ones) generated in the course of biomass gasification in a generalized manner is called “tar” [1]. Decreasing the yield of the latter mixture could be achieved by means of using catalytically active materials [2–5].

One of the most stable compounds difficult to decompose in the mentioned mixture is presented by naphthalene [6, 7], whereon it is often considered a model compound simulating the tar. Ni-containing catalysts with low cost and high activity with respect to the decomposition of resins [8, 9] are widely used for the catalytic decomposition of naphthalene. However, the use of Ni-containing catalysts is hindered by the deposition of carbon on the surface and/or by the metal sintering [10]. The catalysts studied oxidation Different metal oxide systems (CoO_x, MnO_x, CuO, ZnO, Fe_2O_3, CeO_2, TiO_2, Al_2O_3 and CuZnO) prepared via the precipitation method [11, 12] were studied as the catalysts for the oxidation of naphthalene. A high activity in the vapour-phase catalytic oxidation of naphthalene is exhibited by mixed oxide catalysts CeO_2-ZrO_2 [13]. Several studies have demonstrated that these systems are resistant with respect to carbon deposition due to a great number of oxygen vacancies and oxygen mobility [14, 15].

For the last time, supported oxide catalysts including those applied onto metal carriers, are increasingly considered as catalysts for heterogeneous processes [16, 17]. One of the non-traditional and promising methods for the preparation of supported catalytically active materials with controlled composition, porosity and surface structure is presented by the method of plasma electrolytic oxidation (PEO). It is based on the formation of oxide layers on metals under the action of spark and arc discharge at the metal/electrolyte interface [18–25]. The advantage of this method for catalysis consists in the ability of single-stage application of functional coatings onto complicatedly shaped metal structures within a relatively short time (from several minutes to tens of minutes) using an aqueous electrolyte at a temperature not exceeding 50 °C. Moreover, it should be noted that the mentioned compositions are resistant with respect to thermal shocks, and exhibit a high thermal and electrical conductivity of the metal substrate.

Catalysts active with respect to CO oxidation were prepared by means of impregnation of the systems $SiO_2 + TiO_2/Ti$ formed by means of PEO in the solutions of transition metal salts, with further annealing [21, 22].

Using the PEO of titanium in aqueous electrolytes with Ce(III) polyphosphate complexes there were obtained oxide compositions $TiO_2 + CePO_4/Ti$ [23]. In an aqueous electrolyte with $Zr(SO_4)_2$ there were prepared PEO coatings with the thickness of 200 μm with predominant ZrO_2 phase in monoclinic and tetragonal modifications [24]. The zirconium content in the fibres amounted up to 20 at. %. Coatings on titanium containing cerium and zirconium oxides are as a rule obtained using a plasma electrochemical method from an aqueous electrolyte containing cerium and zirconium sulphates in a molar ratio from 1 : 3 to 3 : 1 [25]. In the composition of the coatings there were found 2–3 at. % of cerium and 6–15 at. % of zirconium.

Thus, with the use of one-stage PEO method on titanium surface there can be formed layers involving transition metal oxides including the oxides of manganese, zirconium and cerium. There were studied the composition and structure of PEO layers on titanium comprising transition metal compounds, in some cases their catalytic activity in the oxidation of CO within the temperature range of 20–500 °C. However, there is no information available from the literature concerning the activity of the mentioned catalytic systems obtained using the PEO technique in the processes of biomass gasification.

The aim of this work consisted in studying the composition, surface structure including that after high-temperature annealing of Ce-, Zr- and Mn-containing layers applied onto titanium oxide obtained *via* the PEO technique, as well as the catalytic activity of these compositions with respect to the model reaction of steam naphthalene conversion.

MATERIALS AND METHODS

In order to perform the plasma electrolytic oxidation we used samples made of titanium wire VT1-0 0.2 cm in diameter and 40 cm long. The samples were chemically polished in a mixture of acids, $HF/HNO_3 = 1 : 3$ at a temperature of 60–80 °C for 2–3 s. The samples were then washed with distilled water and dried in atmospheric air.

The cell for PEO procedure was presented by a beaker made of heat-resistant glass with the volume capacity of 1 L. The oxide coatings were formed in a galvanostatic mode on titanium under anodic polarization immersed in electrolyte. As a power source we used a TER4-

63/460N thyristor unit (Russia) with a unipolar pulse shape of current.

The compositions $CeO_x + ZrO_2 + TiO_2/Ti$ were prepared by means of a procedure described in [25]. In order to prepare the manganese oxide layers $MnO_x + SiO_2 + TiO_2/Ti$, we preliminarily oxidized titanium samples in an aqueous electrolyte containing 0.05 M Na_2SiO_3, during 10 min at a current density of 5 A/dm^2. Oxide systems $SiO_2 + TiO_2/Ti$ formed were further impregnated in a solution of manganese nitrate and calcined in atmospheric air at 500 °C for 4 h.

In order to determine the thermal influence on the properties of the coatings, the samples were annealed in atmospheric air for 24 h at separate temperature values amounting to 600, 800, 850, 900 °C. After cooling, they were studied by means of a scanning electron microscope (FESEM ZEISS ULTRA 55) with a Thermo Scientific system of energy dispersion X-ray microanalysis (EDX). The studies were conducted at the Chair of Surface and Materials Technology of the Institute of Materials Engineering (Siegen, Germany).

The phase composition was determined by means of D8 ADVANCE X-ray diffractometer (Germany) according to the Bragg–Brentano method with the rotation of a sample in the field CuK_α radiation.

The tests of the catalytic activity of PEO layers on titanium with respect to the gasification of biomass were performed at the Chair of Environmental Processes Energy Engineering of the Institute Energy Technique attached to the University of Siegen, Germany. For modelling tar compounds we used naphthalene. A laboratory-scale catalytic unit consisted of saturators, a tubular reactor, a unit for the condensation and absorption of naphthalene. In order to avoid the sublimation of naphthalene the gas pipeline system and other parts of the installation were preliminary heated up to 250 °C. In saturators made of stainless steel, there occurred the process of nitrogen saturation with naphthalene and water vapour. The model gas mixture contained about 1.7 vol. % of naphthalene, 30 vol. % of H_2O, and the rest was nitrogen. In order to maintain a constant temperature value inside the saturators the entire system was thermally isolated by means of mineral fibres and aluminum layer. After mixing, a homogeneous mixture of nitrogen, steam and naphthalene entered the reactor. The reactor represented a stainless steel tube with an inner diameter of 4.25 cm, placed into a furnace with electronic temperature control up to 1000 °C. In order to perform catalytic testing, we cut the wire coated with active layer into pieces 1 cm long. The total volume of the catalytic material was equal to 100 cm^3. The pieces of wire placed within the reactor onto a porous plate and a substrate consisting quartz fibres. From above the catalyst layer was covered by a layer of quartz fibres and a filter. The duration of contacting between the gas mixture and the catalyst layer (contact time) was the same for all the samples of the catalyst amounting to 0.4 s. The gas flow through the reactor was controlled by two independent Bronkhorst EL-Flow-F201C mass flow controllers; the gas flow rate was equal to 0.48 Nm^3/h.

Naphthalene and other hydrocarbons were first collected on the outlet of the reactor, via condensing them in vessels placed in a cooling bath at −20 °C. For absorbing the remaining hydrocarbons we used a system composed of several impingers with a capacity of 100 mL, filled with 30 mL of isopropanol and placed in a cooling bath at −30 °C. The condensate and the innage of impingers were poured into a flask to evaporate isopropanol using a standard rotary evaporator. The flask with a dry solid residue was weighed accurate within 0.1 mg to measure the mass of gravimetrically determined hydrocarbons after catalytic testing. The conversion level of naphthalene (X_{naph}, %) was determined according to the formula

$$X_{\text{naph}} = (m_0 - m)/m_0$$

where m_0 is the mass of naphthalene placed into the reactor, g; m is the mass of hydrocarbons measured gravimetrically after the catalytic tests, g.

RESULTS AND DISCUSSION

Table 1 demonstrates the results of elemental analysis of the initial Ce-, Zr-containing samples and annealed ones at the temperature ranging within 800–900 °C. On the surface of Ce-, Zr-containing samples not subjected to heat treatment, there were detected carbon,

TABLE 1

Elemental composition of Ce-, Zr-containing samples annealed at different temperature

Elements	Atomic fraction, %			
	at the annealing temperature, °C			
	Initial	800	850	900
C	7.6	–	–	4.5
O	68.3	73.3	76.2	64.5
Ti	18.8	20.4	21.2	31.0
Zr	4.0	4.6	2.6	–
Ce	1.4	1.6	–	–

oxygen, titanium, zirconium and cerium. Zirconium content on the surface of the initial samples is insignificant (4.0 at. %) being 2.9 times higher than the cerium content.

After annealing the samples at the temperature lower than 800 °C, no carbon was revealed on the surface of oxide structures, whereas the content of the other elements did not exhibit any substantial change. According to the XRD phase analysis, the initial samples and ones annealed at 800 °C contain TiO_2 in rutile and anatase modifications and a complex oxide of the spinel type such as $ZrTiO_4$ in the film structure. A significant reduction in or absence of Ce and Zr is observed after sample annealing at 850 °C and higher. So, the zirconium content is 1.5 times reduced, with no cerium detected on the surface of the samples annealed at 850 °C. The surface of the samples annealed at 900 °C exhibited no cerium and zirconium. Furthermore, in the latter case, an increase in the titanium content of 10 at. % is observed on the surface, and the oxygen/titanium ratio corresponds to TiO_2. Thus, annealing at high temperature values (850 °C or higher), to all appearance, results in the redistribution of the elements, thermal diffusion onto the surface of the titanium coating and, consequently, the crystallization of titanium oxide.

Changes in the elemental composition of Ce-, Zr-containing coatings correlate with changing their surface structure proceeding in the course of a high temperature processing of the samples. The SEM images of the surface of Ce-, Zr-

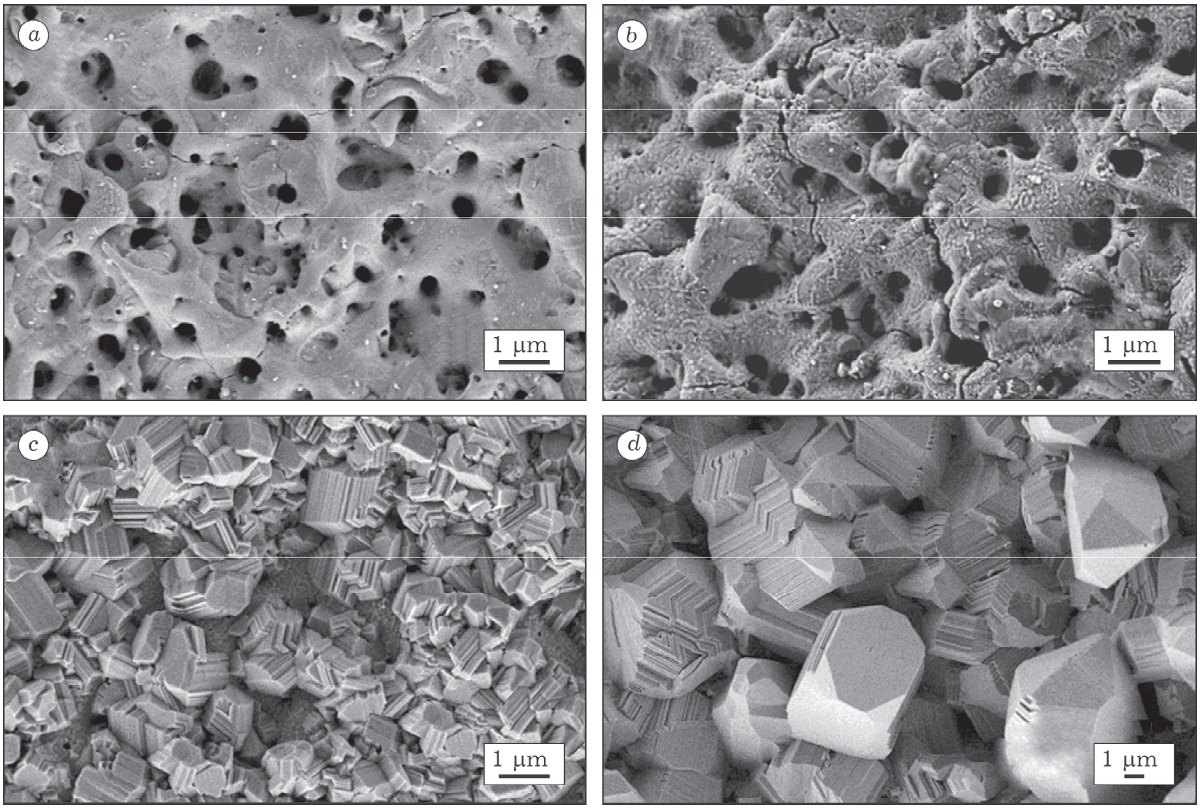

Fig. 1. SEM images for Ce-, Zr-containing oxide coating on titanium, annealed at different temperature values, °C: initial (*a*), 800 (*b*), 850 (*c*), 900 (*d*).

containing samples annealed at different temperature values (Fig. 1) demonstrate that the surface of the initial samples is quite uniform, porous (see Fig. 1, *a*). The pore size ranges from 1 μm to several tens of nanometres.

At low magnifications it is seen that annealing the samples at the temperature of 800 °C results in cracking the surface and its fragmentation (see Fig. 1, *b*).

The surface of the samples after annealing at higher temperature values exhibits changing to a significant extent (see Fig. 1, *c*, *d*). So, the surface of the samples annealed at 850 °C is partially covered with regular-shape crystals with the size up to 1 μm, between those there are fragmented portions of the surface observed. After annealing at 900 °C the sample surface is completely covered with much larger, well faceted crystals with the size up to 10 μm (see Fig. 1, *d*).

Thus, the surface structure and the distribution of elements are rather insignificantly different for initial Ce-, Zr-containing samples and the samples annealed at 800 °C. Significant changes in the composition and structure of the surface occurs after sample annealing at 850 °C and above. This fact indicates a relatively high thermal stability of Ce-, Zr-containing samples and the possibility of their use as catalysts for high-temperature processes. Considerable changing after annealing at the temperature values higher than 850 °C such as occurring thermal diffusion to the titanium surface (to all appearance, through the pores) and its oxidation by atmospheric air. In this case one can observe the formation of geometrically regular crystals.

TABLE 2

Elemental composition of $MnO_x + SiO_2 + TiO_2/Ti$ structures annealed at different temperature

T, °C	Elemental composition, at. %					
	C	O	Si	Ti	Mn	Na
Initial	3.1	63.8	17.3	3.5	11.9	0.5
800	3.9	62.4	17.0	5.7	11.0	–
900	1.8	67.2	8.8	15.9	6.3	–

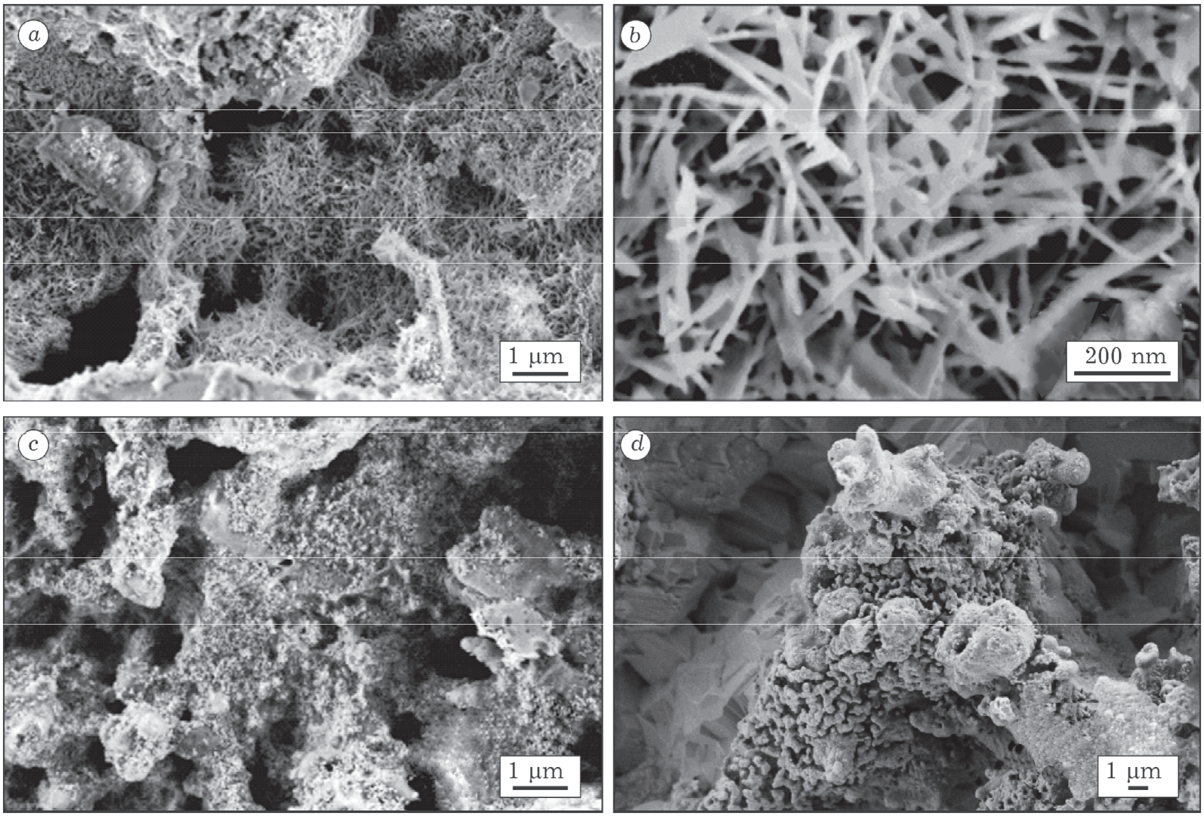

Fig. 2. SEM images of Mn-containing oxide coatings on titanium, annealed at different temperature values, °C: initial (*a*, *b*), 600 (*c*), 900 (*d*).

Table 2 demonstrates the results of elemental analysis for the surface of Mn-containing structures under investigation. It is seen that annealing the samples at 800 °C exerts no effect on the elemental composition of the surface. However, according to XRD phase analysis, the thermal effect on the phase composition of Mn-containing samples is rather significant. The initial Mn-containing structures involve manganese oxide Mn_2O_3 and TiO_2 in rutile modification. After annealing the samples at 800 °C there were found TiO_2 (rutile and anatase modifications) and complex compounds with the composition such as $Mn_7O_8(SiO_4)$. The surface of the samples annealed at 900 °C exhibit a marked redistribution of the elements: the amount of manganese and silicon decreases, whereas the amount of titanium demonstrates an increase. The XRD phase analysis revealed the presence of rutile TiO_2 modification only on the surface of the samples.

The SEM images of manganese containing oxide layers on titanium (Fig. 2) demonstrate that the surface of the manganese-containing heterogeneous structures is inhomogeneous. One can see caves and pores of different sizes, granules and complex structures in the hollows between those there are thin “feather-like” nanocrystals (whiskers) (see Fig. 2, *a*, *b*).

After annealing at 800 °C one could observe also changing the surface structure of manganese-containing samples (see Fig. 2, *c*, *d*). Nanowhiskers were not found, the surface was covered with fused entities. To all appearance, there occurs a thermo-chemical reaction associated with a partial dissolution of a substance inherent in the whiskers in the melt. This is in a good agreement with the results of XRD phase analysis according to those high-temperature annealing causes the formation of complex manganese silicate structures, whereas manganese oxide is absent. Thus, the annealing of manganese coatings results in the redistribution of the elements on the surface, the crystallization of titanium oxide and the formation of new complex structures, those, to all appearance, would exert a significant effect on the catalytic activity of the samples.

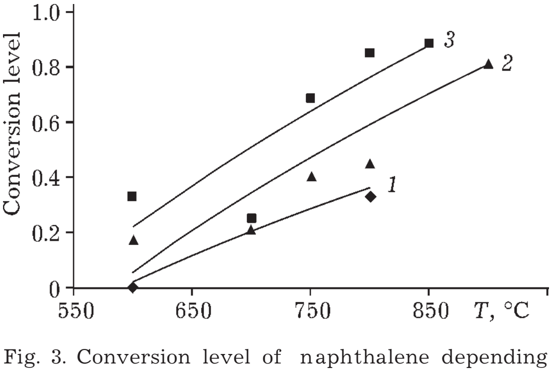

Fig. 3. Conversion level of naphthalene depending on temperature in the presence of different catalysts: *1* – without catalyst, *2* – $MnO_x + SiO_2 + TiO_2/Ti$, *3* – $ZrO_2 + CeO_x + TiO_2/Ti$.

The results obtained concerning the catalytic decomposition of naphthalene in the presence of systems $CeO_x + ZrO_2 + TiO_2/Ti$ and $MnO_x + SiO_2 + TiO_2/Ti$ are presented in Fig. 3. It is seen that the system $CeO_x + ZrO_2 + TiO_2/Ti$ exhibits a catalytic activity in the reaction of steam conversion of naphthalene within the temperature range of 800–850 °C there occurs an almost complete naphthalene decomposition as demonstrated by thermogravimetric analysis ($X_{\text{naph}} = 90\ \%$). A high activity of $CeO_x + ZrO_2 + TiO_2/Ti$ system, could be caused, to all appearance, by a great amount of active centres on its surface, those catalyze the reactions occurring in a heterolytic manner. On the surface of the Ce-, Zr- containing system there is the phase of $ZrTiO_4$ present, which phase, according to the authors of [26, 27] represents a solid acid that exhibits a catalytic activity with respect to different acid-catalyzed reactions such as the cracking and isomerization of alkanes, the hydration and polymerization of alkenes. In addition, TiO_2–ZrO_2 systems exhibit a developed surface area and a high mechanical strength [28, 29]. According to elemental analysis data (see Table 1), on the surface of the samples both original, and annealed at 800 °C, there are also mixed or individual compounds of zirconium and cerium. Mixed oxide system CeO_2–ZrO_2 is characterized by pronounced acidic properties (Zr^{4+} and Ce^{4+} act as Lewis acid sites) to catalyze the reaction those proceed according to heterolytic type. Furthermore, the presence of CeO_2 with a high oxygen storage capacity on the surface promotes decreasing the rate of catalyst carbonization [30, 31].

Manganese-containing catalysts exhibit a lower conversion level of naphthalene as to compare with Ce-, Zr-containing coatings, which could be connected both with a different nature of the catalytically active sites on the surface of Mn-containing layers, and with significant changing in their surface to form low-active fused manganese silicate under high temperature impact. Nevertheless, the presence of these systems contributes to increasing the level of naphthalene steam conversion. These data could be used for optimizing the obtaining conditions and properties of the coatings for using them in various catalytic processes including the gasification of biomass.

CONCLUSION

The present work reports the results of studying the composition, surface structure, including after the annealing at a high temperature, as well as the catalytic activity of Ce-, Zr- and Mn-containing oxide layers on titanium with respect to the reaction of naphthalene steam conversion. Oxide systems were formed by means of plasma electrolytic oxidation technique. It is demonstrated that the Ce-, Zr-containing structures exhibit a high thermal stability: elemental and phase composition as well as surface morphology does not change to a considerable extent after annealing at 800 °C. The Mn-containing oxide structures such as $MnO_x + SiO_2 + TiO_2/Ti$ obtained by means of the impregnation of silicon-containing PEO coatings on titanium an aqueous solution of manganese nitrate followed by annealing at 500 °C, exhibit a well-developed surface coated with nanowhiskers those are not detected after heat treatment. The presence of Mn-containing and Ge-, Zr-containing systems promotes enhancing the conversion level of naphthalene and could be useful for optimizing the production conditions and properties of the coatings for the purpose of using in various catalytic processes including the biomass gasification. Thus, the use of non-traditional, practically feasible PEO technique is demonstrated to be promising for the formation of catalytically active systems for the gasification of biomass.

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