The nanostructural catalytic composition CuMoO$_4$/TiO$_2$ + SiO$_2$/Ti for combustion of diesel soot

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ABSTRACT

The combination of two methods, the plasma electrolytic oxidation (PEO) technique for the oxide film formation on titanium and the extraction-pyrolytic (EP) technique for catalytic active layers coating are suggested to use. After covering with Cu and Mo by equimolar mixture of extracts and subsequent pyrolysis the copper molybdate phase grains with diameter up to 200 nm are observed. Three-fivefold covering leads to the formation of copper molybdate continuous layer. The composition CuMoO$_4$/TiO$_2$ + SiO$_2$/Ti has the most high catalytic ability; after twofold treatment (EP) of oxidized titanium surface, diesel soot oxidation takes place in lower temperature range (the initiation temperature of combustion, T_i = 270 °C) than powder molybdate sample (T_i = 340 °C). In subsurface layer of CuMoO$_4$ (~3 nm) the presence of Cu$^+$ and Mo^{4+} was observed, which can explain the high reactivity of the compositions CuMoO$_4$/TiO$_2$ + SiO$_2$/Ti on initial stage of soot combustion.

1. Introduction

Searching efficient catalysts for combustion of soot emitted by diesel engines is one of the main problems of environment protection from toxic car transport surges. The interest in diesel exhaust after-treatment systems is ever-growing in view of the increasingly stringent US and European emission standards. The main pollutants emitted by this type of engine are soot particles and nitrogen oxides. Diesel exhaust particles consist mainly of highly agglomerated solid carbonaceous material, volatile organic and sulfur compounds. Removal of the particulate matter with adsorbed polycyclic aromatic hydrocarbons is the problem of great concern in view of the established carcinogenic and mutagenic effects of these hydrocarbons. Typically, temperature range of diesel gases changes from 120 to 360 °C at the starting moment of the cold engine and increases to 500–800 °C in the positioned normal regime [1,2]. The uncatalyzed combustion of soot occurs at temperatures of 550–650 °C. Since the soot ignition temperature is very high, it should be lowered to the temperature of exhaust. One of the methods, proposed to lower the level of particulate matter emission, is based on the use of the oxidation catalysts that decrease the combustion temperature of soot down to the diesel exhaust temperature. An active search has been under way in the last several years to find active catalysts for the abatement of diesel exhaust contaminants. Reportedly, transition metal oxides (CeO$_2$, MoO$_3$, V$_2$O$_5$, Co$_3$O$_4$, Fe$_2$O$_3$, CuO) [3,4] and some their binary oxides compounds (LiCrO$_2$, CsV$_2$O$_7$) [5,6] also oxide composites (Au–VOx/TiO$_2$, Cu/K/V/Cl, La$_{0.8}$K$_{0.2}$Cu$_x$Mn$_{1-x}$O$_3$, K$_x$/La$_2$O$_3$, Cu/Ce/Al/O) [7–11] are active catalysts for oxidation of carbonaceous materials in air. Earlier we have shown that CuMoO$_4$ prepared by the pyrolysis of metals extracts mixture catalyze the combustion of soot efficiently too [12]. Also, the use of Ag deposited on ceria was found to increase the rate of soot oxidation in tight contact condition [13], but about a great decrease of its activity in loose contact of carbon particles and catalyst has been also reported [14]. However, loose contact is more representative of the real contact conditions occurring in a catalytic trap for diesel particulate removal [15,16]. A promising technique of diesel exhaust abatement lies in the development of a catalytic filter that combines filtration and oxidation of the emitted soot particulates [17]. Usually, the ceramic or metal filter's surface is covered by wash-coat (Al$_2$O$_3$ or SiO$_2$) with a high surface area on which a small amount of the catalyst is based. In this work the combination of two methods is

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applied to formation of catalytic coatings for soot filters. A plasma electrolytic oxidation (PEO) technique was used to derive an oxide film of the certain structure on the metal surface, and extraction-pyrolytic method was employed for forming a catalytically active layer. The PEO method allows one to receive a complex oxide layers on a surface of valve metals under electric spark or arc discharges in aqueous solutions of electrolytes [18]. The essence of extraction-pyrolytic (EP) method consists in mixing of required relations of the metal organic extracts and their subsequent pyrolysis on air till formation of complex oxide compounds [19]. The aim of this work is research of soot combustion at presence of catalytic compositions $CuMoO_4/TiO_2 + SiO_2/Ti$ prepared by use of extraction-pyrolytic method and plasma electrolytic oxidation method.

2. Materials and methods

2.1. Catalyst preparation

The bulk copper molybdate was prepared using an extraction-pyrolysis process, by mixing appropriate ratios of organic metal extracts, followed by pyrolysis in air until the formation of a mixed oxide compound. The molybdenum was extracted from an ammonium paramolybdate solution in hydrochloric acid by isoamyl alcohol. The copper was extracted from appropriate nitrate solutions by n-caprylic acid using standard techniques [19]. The concentrations of Cu (determined by helatometry titration) and of Mo (determined by thiocyanate method) in organic extracts were equal to 3.25, 0.01 and 1.10 $mol \cdot l^{-1}$, respectively. The metals extracts were taken at molar rations Cu:Mo 1:1 and were mixed thoroughly. The organic solvents were evaporated at temperature 40 °C and at the vacuum condition up to a formation of homogeneous paste. Subsequently, the paste was heated in the air atmosphere at 200 °C for 2 hours and then additionally at 550 °C for 2 hours. High purity chemical reagents corresponding to 99.9–99.99% (MERCK, Germany) were used.

The oxide coatings were formed on the wires ($\varnothing$ 1.2 mm) and plates ($25 \times 5 \times 1$ mm) of the titanium alloy VT1-0 (0.2 Fe, 0.1 Si, 0.07 C, 0.04 N, 0.12 O, 0.01 H and Ti >99.6%) by PEO technique. Prior to coating deposition, the substrates were stripped with emery buff and polished chemically in a mixture of concentrated acids (the volume ratio $HF:HNO_3 = 1:1$) at a temperature of about 70 °C followed by rinsing in distilled water and drying. The PEO treatment was conducted in aqueous electrolyte containing 0.05 $mol \cdot l^{-1}$ Na_2SiO_3 and 0.16 $mol \cdot c^1$ NaOH. PEO coatings were formed on the titanium substrates being in an anodic polarization for 10 min at an average current density of 0.2 $A cm^{-2}$. The electrochemical cell consisted of a thermal glass with a spiral-shaped nickel cathode. The system was cooled by cold water pumped through the cathode to keep the electrolyte temperature below 35 °C. The final formation voltage was about 280 V. After anodic sparking treatment, the samples were rinsed by distilled water and air-dried at room temperature.

The oxidized titanium plates and wires were put in the organic solution of the capryl extract Cu and the isoamyl extract Mo diluted by used organic solvents up to total concentration of metals 2 wt.%. Further the samples were placed into an oven and heated in the air atmosphere at 150 °C for 1 hour for removal of organic solvents and then at 550 °C for 2 hours for decomposition of extractable substances and formation of oxide phases. The amount of supported molybdate was ~0.03 wt.%.

2.2. Catalyst characterization

The phase composition of reaction products was determined by X-ray diffraction (XRD) using the D8 Advance Bruker diffractometer with CuK_α radiation. The phases were identified using JCPDS data. The particle size distribution was evaluated using Analyzette 22 Comfort FRITSCH laser analyzer. The morphology of the prepared bulk copper molybdate was determined by scanning electron microscopy (SEM) using the LEO-1420 OXFORD instrument. Specific surface area (BET) was defined by conventional N_2 adsorption at 77 K using a Sorbi 4.1 META apparatus. The surface structural characteristics of the supported catalysts were investigated by means of atomic force microscopy (AFM) with an instrument NTEGRA PRIMA. The elemental composition of PEO coatings (X-ray spectrum analysis, XSA) was determined by an electron probe micro-analyzer JXA 8100 with an INCA energy spectrum analyzer. To prevent surface charging in this context, a thin graphite layer was deposited on the samples prior to measuring. X-ray photoelectron spectroscopy (XPS) was used for surface analysis. The XPS spectra were measured on a SPECS ultrahigh-vacuum system using a 150-mm electrostatic hemispherical analyzer. Ionization was performed using MgK_α radiation. The working vacuum was 2×10^{-7} Pa. The spectra were calibrated using the C1s lines of hydrocarbons, whose energy was taken equal to 285.0 eV. Relative quantity of elements (at.%) were defined according to integrated intensity of strips with taking into account of corresponding electrons photoionization profiles using standard means of program XI-SDP v4.2. The surface was etched by a bombardment with argon ions of an energy of 5 keV.

2.3. Catalyst activity investigation

All experiments were performed by using of real diesel soot emitted at a torch flame from combustion of diesel fuel; the BET surface area of diesel soot amounted to 62 m^2/g. The catalyst–carbon mixture was prepared according to two different procedures: (1) tight contact, by mixing of soot and powder catalyst (1:20 mass basis) in agate mortar for 10 min; and (2) loose contact, by placing the titanium wires or powder catalyst over a metal grid (the copper sieve with mesh dimension 0.2 μm) and covering with soot emitted by a flame from combustion of diesel fuel up to increase in weight of the sample not less than 0.2–0.4 wt.%. The activity of the prepared catalyst toward soot combustion was analyzed in a dynamic gas atmosphere (50 ml/min) of the air at heating rate 5 °C/min by using thermoanalyzer STA 449F3 NETZSCH. The catalytic test was carried out by gravimetric thermal analysis (TG) and differential scanning calorimetry (DSC). The initiation temperature for soot oxidation (T_i) was estimated from the intercept of a linear fit to the observed weight decrease with the zero line. The catalytic activity for the combustion of soot was determined as the temperature of maximum intensity (T_m) of exothermic DSC-curve. The waste gases at the combustion of soot were investigated with use of Infracar M-1 Alpha-dynamica gas analyzer, a range of emission measurements: $CO - 0 \div 7 \pm 0.42\%$, $CO_2 - 0 \div 16 \pm 0.96\%$. The selectivity of oxidizing reaction $\eta(CO_2)$ was calculated as the ratio $\frac{CO_2}{CO + CO_2} \cdot 100\%$.

3. Results and discussion

The sequence of phase formation at pyrolysis conditions of the mixture extracts (molar rations Cu:Mo 1:1) is represented in Fig. 1. In the pyrolysis products only copper (I) chloride diffraction peaks are revealed at 300 °C (Fig. 1a). As is shown in Fig. 1b, copper (I) chloride undergoes reduction at 350 °C. Also, in XRD pattern appears the halo that may be due to amorphous pyrolysis products of molybdenum extracts. The temperature growth to 400 °C is enough for oxidation of Cu up to Cu_2OCl_2 and up to CuO, and for $Cu_3Mo_2O_9$ formation (Fig. 1c). Both the absence of the peaks of MoO_3 phase and the formation of orthorhombic $Cu_3Mo_2O_9$ phase (orthorhombic, ASTM: 24–55) can be an evidence of oxide interaction, which is occurring during MoO_3 crystallization, because of its high reactivity. The heat treatment at 450 °C (Fig. 1d) leads to the formation of $CuMoO_4$ phase (trigonal, ASTM: 22–242). The elemental composition analysis of $CuMoO_4$ phase showed an identical quantity of copper and molybdenum (at.%); presence of chlorine was not detected. SEM image of the $CuMoO_4$ prepared by extraction-pyrolytic method at 550 °C is
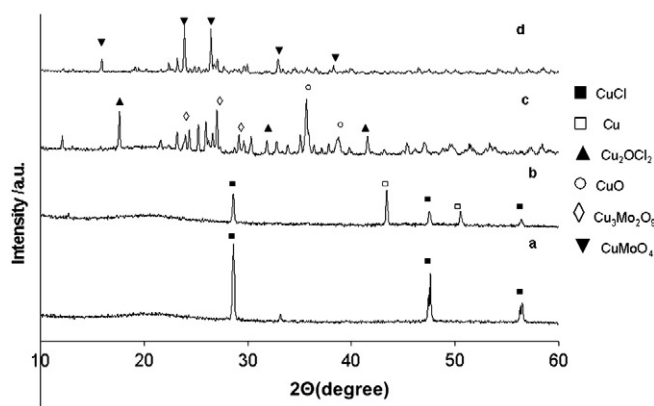
Fig. 1. XRD patterns of the samples obtained by pyrolysis of equimolar mixture of Cu and Mo extracts at 300 (a), 350 (b), 400 (c), and 450 °C (d).

Fig. 3. XRD pattern of oxidized titanium plate three times covered by $CuMoO_4$.

illustrating that the powder consists of faceted crystallites with diameter up to 2–3 μm (Fig. 2).

The thickness of the coatings produced by PEO method in silicate electrolyte reaches 10 μm. The elemental composition analysis of coatings showed presence (at %) 70.9—O, 15.6—Si, 13.1—Ti, and 0.4—Na. According to XRD (Fig. 1a), the coatings include titanium oxide, which is represented in structural modifications of rutile and anatase. None of the diffraction patterns show reflections from crystallized siliceous phases, indicating that the silicon is presented in the coating in the form of the amorphous silica. The XRD pattern of samples obtained by the triple treatment of the oxidized titanium plate in equimolar solution of the metal extracts with subsequent pyrolysis at 550 °C shows a diffraction peaks of the Ti, TiO_2 and the triclinic structure $CuMoO_4$ (Fig. 1b). The morphology of the compositions $TiO_2 + SiO_2/Ti$ and $CuMoO_4/TiO_2 + SiO_2/Ti$ is demonstrated in Fig. 4. The typical surface of a titanium plate after PEO treatment (Fig. 4a) is rough enough; there are raisings, hollows, and pores which may be the traces of electric breakdowns or of a gas bubbles outlets. The oxide film uniformly covering the surface of the titanium consists of the crystallites with the size of 3 up to 10 μm; a diameter of the pores reaches 5–7 μm. The grains of the $CuMoO_4$ phase with a diameter up to 200 nm are observed on the surface of a porous oxide film after a primary treatment (Fig. 4b). The subsequent cycles of treatment result in significant increase of the crystallite sizes of the copper molybdate, till 7–10 μm after four cycles (Fig. 4c), which fill up large pores of the oxide layer.
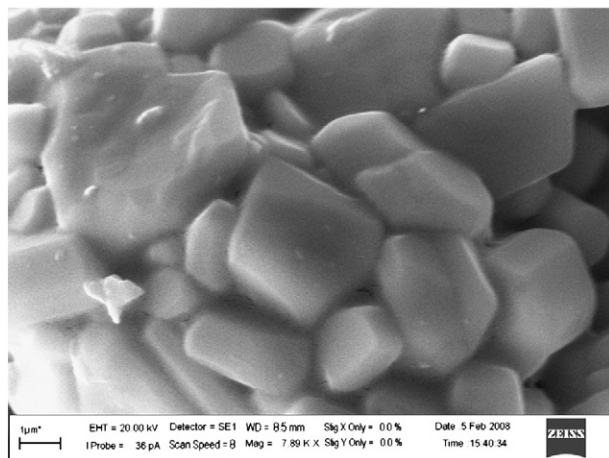

Fig. 2. Electron micrography of $CuMoO_4$ obtained by pyrolysis of equimolar mixture of Cu and Mo extracts at 550 °C.
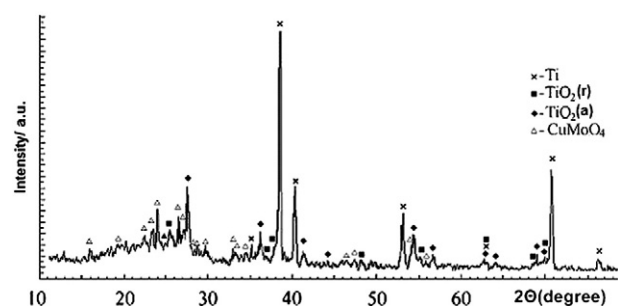
The results of catalytic activity investigation presented in Fig. 5 and in Table 1 show that the bulk molybdate the $CuMoO_4$ can greatly decrease the oxidation temperature range of diesel soot in comparison with uncatalyzed soot combustion. A significant increase of CO_2 selectivity was also noticed. The visible combustion initiation temperature which was defined by start of the mass loss is located in 330–350 °C range. However, the T_m value under loose contact conditions became above compared with tight contact conditions (405 versus 387 °C, respectively). The sample $TiO_2 + SiO_2/Ti$ provided long temperature range of the soot oxidation from 420 °C up to 570 °C and the T_m value up to 483 °C. The temperatures T_i and the T_m have become slightly less after single-stage covering by the $CuMoO_4$ of the $TiO_2 + SiO_2/Ti$ surface. The observed comparatively weak effect may be caused by a presence of small catalyst content in a structure of surface layer. The start of soot oxidation significantly drops up to 270 °C after two treatment cycles of the oxidized titanium surface by EP method. The samples begin to slowly lose mass, about 10 wt % of soot up to 350 °C, then the rate of mass loss is increasing and reaches a maximum at 410 °C (Fig. 5, curve 3). Nonsymmetric exotherms (Fig. 6) correlate to the TG signals and to the generation of combustion products in gas-phase. At the subsequent EP treatment (more than twofold covering of copper molybdate) the temperature of the process beginning does not change, but intensity of initial stage of the soot combustion process noticeably comes down.

According to Neeft and co-workers [20] with the similar double peaks on kinetic curves it is possible to explain by the presence of soot part which is in direct contact to a surface of the catalyst (tight contact) and of another part of soot removed from the catalyst (loose contact). However the activity of compositions $CuMoO_4/TiO_2 + SiO_2/Ti$ at initial stage of diesel soot combustion was a lot higher than for the bulk copper molybdate under tight contact conditions (Table 1). Such factors as the number of active sites, on which catalytic reactions are localized and a rate of their formation as well as surface porosity of catalyst may have an influence on the initiation temperature of soot combustion. Earlier we have shown that high catalytic activity $CuMoO_4$ is caused by redox interaction between the particles surface of copper molybdate and soot [21]. The reduction of copper ions from 330 °C is accompanied by the formation of active $CuMoO_{4-x}$ phases, where catalytic reaction occurs. The infill of oxygen vacancies can occur either by gaseous oxygen adsorption with subsequent dissociation up to atomic oxygen or by oxygen atom diffusion from the bulk of the crystal to its surface. During the catalytic combustion of soot, the adsorbed surface oxygen species should play more significant role [22]. The formation of O_2^- anion via a rapid adsorption of molecular external oxygen upon vacancies is well-documented for perovskite [23,24] and for CeO_2 [25] soot abatement catalysts. The oxygen vacancies can be again regenerated via oxygen species transfer to soot.

The XPS analysis has shown that the formation of the catalytic molybdate coating by EP method occurs differently than that of the powder copper molybdate of the same composition. Surface compositions of the bulk $CuMoO_4$ and $CuMoO_4$ coating received as a result of fivefold treatment of the oxidized titanium plate by EP method are
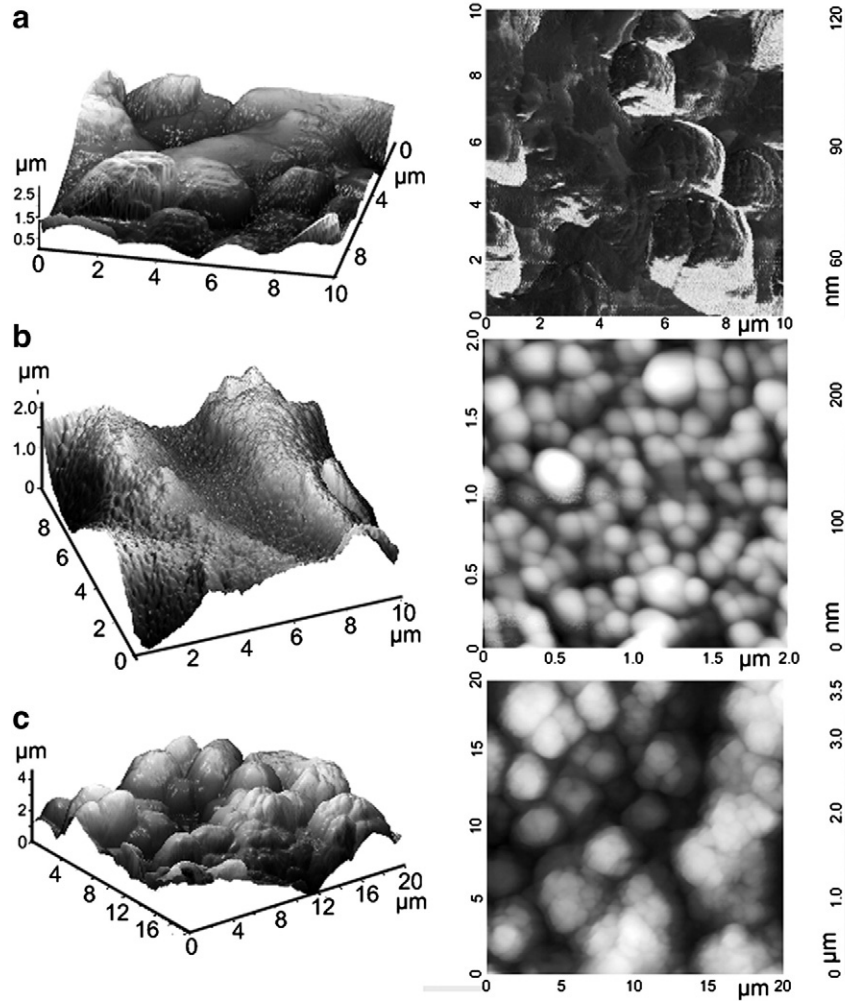
Fig. 4. AFM images of oxidized titanium surface microstructure (a), single-covered by CuMoO$_4$ (b), and four times covered by CuMoO$_4$ (c).
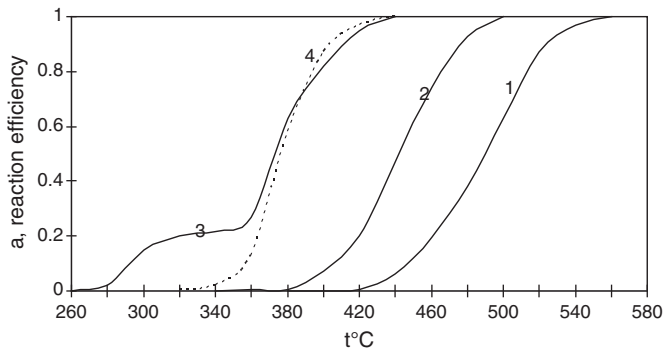

Fig. 5. TG curves of diesel soot catalytic combustion in presence of uncovered oxidized titanium wire (1), single covered by CuMoO$_4$ (2), two times covered by CuMoO$_4$ (3) and bulk CuMoO$_4$ (4).

almost identical. There is a difference in small amount of silicon on coating surface due to PEO process conditions (Table 2). However, the presence of cations Cu$^+$ and Mo^{4+} is detected in near-surface

Table 1
Characteristics of catalytic combustion of diesel soot.

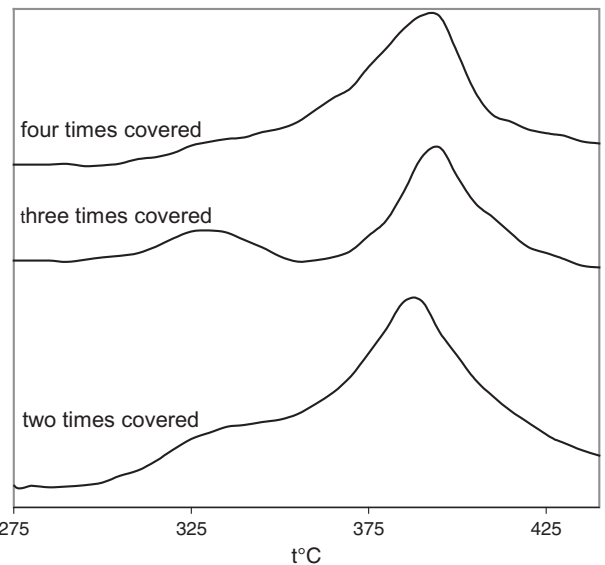| Catalyst	Under tight contact conditions			Under loose contact conditions		
	T_i °C	T_m °C	$\eta(CO_2)$, %	T_i °C	T_m °C	$\eta(CO_2)$, %
CuMoO$_4$ (bulk)	330	387	97.8	350	405	96.6
TiO$_2$ + SiO$_2$/Ti	–	–	–	420	483	92.8
CuMoO$_4$/TiO$_2$ + SiO$_2$/Ti (two times covered)	–	–	–	270	410	96.0
Noncatalytic	390	524	88.7	405	530	80.2

Fig. 6. DSC curves of diesel soot catalytic combustion in presence of oxidized titanium wire covered by CuMoO$_4$.

Table 2
Surface composition (at %) of the bulk $CuMoO_4$ and supported $CuMoO_4$ according to XPS analysis data.

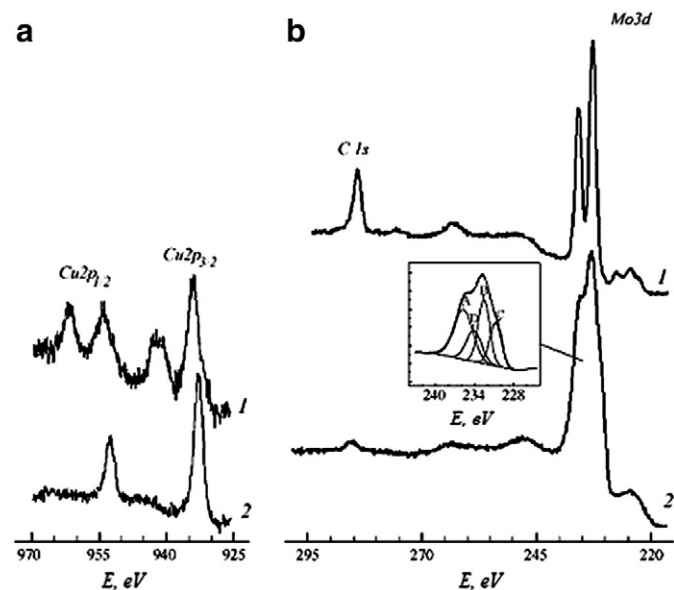| Sample	Cu2p3/2		O1s		C1s		Mo3d5/2		Si2p	
	E, eV	at %	E, eV	at %	E, eV	at %	E, eV	at %	E, eV	at %
Bulk $CuMoO_4$	934.9	6.7	531.0	41.9	285.0	37.4	233.1	14.0	–	–
Supported $CuMoO_4$ surface	934.7	4.4	530.8	48.3	285.0	26.8	232.7	13.6	104.2	7.0
Supported $CuMoO_4$ subsurface	932.4	4.5	530.9	61.2	285.2	3.6	232.5	24.0	104.3	6.7

*E—bond energy.

Fig. 7. Cu2p (a), C1s and Mo3d (b) spectra of the surface (1) and subsurface (2) layers of supported $CuMoO_4$. The insert shows the analysis of Mo3d spectrum of molybdenum after etching by bombardment with argon ions. A subsurface layer depth is ~3 nm.

layer of the composition $CuMoO_4/TiO_2 + SiO_2/Ti$ after etching on depth up to ~3 nm (Fig. 7, spectrum 2). According to the XRD data (Fig. 3), oxide phases of one-valent copper and quadrivalent molybdenum in the composition of the molybdate coating are not found. The formation in the structure $CuMoO_4$ of oxygen vacancies, caused by a presence of the ions Cu^+ and Mo^{4+}, can explain different catalytic activity of the composition $CuMoO_4/TiO_2 + SiO_2/Ti$ and bulk molybdate on initial stage of soot combustion. According to the received data about a microstructure of an oxidized titanium surface after coating by the copper molybdate (Fig. 4), the growth of the molybdate crystallites from quantity of cycles of EP processing leads to consecutive decrease of speed at the initial stage of soot oxidation. Thus, the high reactivity of the composition $CuMoO_4/TiO_2 + SiO_2/Ti$ can be caused by both the small size of the $CuMoO_4$ crystallites on an oxide surface, and high concentration of structural defects in the molybdate coating.

4. Conclusions

The composition $CuMoO_4/TiO_2 + SiO_2/Ti$ was formed by pyrolysis of the equimolar mixture of metal organic extracts supported on oxidized titanium surface. The composition $CuMoO_4/TiO_2 + SiO_2/Ti$ after twofold treatment (EP technique) of oxidized titanium surface has the most high catalytic ability for diesel soot oxidation. The oxidation process takes place in lower temperature range (the initiation temperature of combustion is 270 °C), than bulk copper molybdate under loose contact conditions of carbon particles and catalyst (the initiation temperature of combustion is 330 °C). The $CuMoO_4$ phase grains with diameter up to 200 nm in composition surface and Cu^+ and Mo^{4+} ions presence in composition subsurface layer of (~3 nm) were observed, which can explain the high reactivity of the compositions $CuMoO_4/TiO_2 + SiO_2/Ti$ on initial stage of soot combustion.

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