NEW SUBSTANCES, MATERIALS, AND COATINGS

Catalytic Properties of K₂Ti₂O₅ + K₂Ti₄O₉/TiO₂/TiO₂ + SiO₂/Ti Composites and Their Resistance to Environment Effects during the Process of Carbon Black Oxidation

P. G. Chigrin^{a, *}, E. A. Kirichenko^a, V. S. Rudnev^{a, b, c, **}, I. V. Lukiyanchuk^b, and T. P. Yarovaya^b

^aInstitute of Materials Science, Khabarovsk Scientific Center, Far East Branch, Russian Academy of Sciences, Khabarovsk, 680042 Russia ^bInstitute of Chemistry, Far East Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia ^cFar Eastern Federal University, Vladivostok, 690950 Russia *e-mail: pal_chig@mail.ru **e-mail: rudnevvs@ich.dvo.ru

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Abstract—A catalyst for oxidation of carbon black based on potassium dititanate has been synthesized. The catalyst has been fabricated by impregnation of oxidized titanium surface additionally modified with a sublayer of anatase nanoparticles by potassium hydroxide. It has been shown that the synthesized composites exhibit high capacity for oxidation of diesel carbon black, while the applied catalytic layer is characterized by resistance to adhesive and cohesive destruction along with a satisfactory resistance to thermal shock and impact of catalyst poisons. The temperatures of initiation and termination of the catalytic process are in the range 340–550°C and comply with the temperature ranges of the practically applied catalysts.

Keywords: potassium dititanate, thermochemical stability, carbon black particles, oxidation catalysts **DOI:** 10.1134/S2070205119010088

INTRODUCTION

In view of the annual increase of consumption of energy from carbon-containing fuel and environmental degradation due to emission of hazardous substances contained in combustion products, the development of efficient treatment methods for exhaust automotive and combustion gases constitutes a crucial ecological challenge.

Reduction of toxic environmental impact of combustion products of organic fuel can be achieved by decontamination of exhaust gases. Catalytic oxidation of the incomplete combustion products, in particular, semivolatile organic compounds and carbon black exhaust products, which are extremely hazardous for living organisms, is of special interest among other detoxification techniques.

Ceric oxide systems (Co–Ce, Mn–Ce, Cu–Ce, and Sm–Ce) are presently the most thoroughly investigated highly efficient catalysts for carbon oxidation [1-4]. In spite of the obvious advantages of the suggested catalysts, they exhibit low thermal and mechanical resistance [5]. These disadvantages are partly compensated by applying the catalysts on a support [6] and stabilizing them by introduction of ZrO₂ catalyst into the structure [7]. However, introduction of zirconium oxide reduces the catalytic activity of the sug-

gested compounds substantially. In addition, ceric oxide catalysts demonstrate low resistance to sulfur acid anhydride and water vapor, which inevitably hampers their extensive application [8, 9].

According to [3, 10-14], introduction of potassium ions to a structure of widely known oxide catalysts dramatically improves their catalytic activity. The authors of some recently published works [15-17] provided the results, which demonstrated good prospects of application of potassium titanates ($K_6Ti_4O_{11}, K_2Ti_2O_5$, $K_2Ti_4O_9$, and $K_2Ti_6O_{13}$) in the function of oxidation catalysts of carbon black, since they are characterized with high level of catalytic properties, thermal stability, and resistance to exposure to water vapor and gaseous SO_2 . These properties make potassium titanates promising materials for application as decontamination catalysts for exhaust gases, including diesel engine exhaust emission. It is worth mentioning that potassium titanates catalyze carbon oxidation under the conditions of both "close" and "loose" contact of carbon black with their surfaces [17]. However, an overwhelming majority of the studies of catalytic properties of potassium titanates were carried out using powdered samples. No published data were found on the activity of catalysts based on potassium titanates fixed on the support surface. Meanwhile, these deposited catalysts were used in practice in design of carbon black filters. The impact of catalyst poisons and thermal and mechanical loads on phase composition and mechanical resistance of the deposited catalyst remains unclear as well.

Supports for catalysts and methods of their preparation are of special interest. Ideally, these supports are supposed to combine high thermal stability and mechanical strength with sufficiently large surface area and chemical compatibility with catalytically active components. From this point of view, it is of interest to apply corrosion-resistant metals as supports that will be specially pretreated to produce an intermediate oxide layer with adhesion to the support metal, the thickness, chemical composition, and porosity of which can be easily controlled. The plasma electrolytic oxidation (PEO) is considered one of the most advanced and ecologically safe methods to apply oxide layers with controlled thickness, composition, and morphology on the surface of metals and alloys. The method consists in controlled anode oxidation of a metal electrode in the electrolyte medium due to the energy of plasma electric discharges. It was demonstrated that the PEO method was a promising way both to produce metal-oxide carriers of catalytically active compounds and to synthesize oxide catalysts on metal substrates [18–22].

For instance, CuMoO₄/TiO₂ + SiO₂/Ti composites were formed by means of combination of PEO and pyrolysis of the metal extracts mixtures. These composites were active during afterburning of carbon black at temperatures exceeding 270°C with maximum burning rate at 410°C under the conditions of weak contact of the carbon black particles with the catalyst surface [23]. Formation of an additional layer of the anatase particles of sizes of 30–50 nm on the PEO coating by means of solvothermal treatment resulted in reduction of the size of the copper molybdate particles, increase of the mechanical stability of CuMoO₄/TiO₂/TiO₂ + SiO₂/Ti composites, and decrease of the maximum burning rate temperature by ~50°C [24].

In view of the above, the objective of the present work was to form coatings containing potassium titanates on titanium supports preliminarily treated by the PEO and solvothermal methods and to investigate their catalytic capacity in carbon black afterburning, thermal stability, and resistance to mechanical loads and catalytic poisons.

EXPERIMENTAL

The PEO-coatings on wire samples of technical titanium of the VT1-0 grade were formed under the galvanostatic mode at the effective current density $i = 0.2 \text{ A/cm}^2$ for 10 min in a silicate electrolyte containing 0.05 mol/L of Na₂SiO₃ and 0.05 mol/L of NaOH. The thickness of the formed coatings ranged within 10–12 µm.

Prior to the synthesis of potassium-titanate coatings, oxidized titanium was treated by a colloidal suspension, which was prepared via hydrothermal synthesis [25] and contained anatase nanoparticles (30– 40 nm). The suspension was applied by dipping, its excess was removed, and then the titanium oxide samples were subject to gradual thermal treatment for 2 h at temperatures of 120, 350, and 550°C.

The alkaline synthesis was applied to form catalytic composites $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ [26]: the modified PEO-coating, which contained TiO₂ nanoparticles in its structure, was impregnated in 40% KOH solution, then the alkali excess was removed by ashless filter paper (Blue ribbon), after which the coating was thermally treated in Ar medium for 2 h at a temperature up to 900°C. The suggested method allowed to synthesize titanate phases at high rate and relatively low temperature in the inert atmosphere, avoiding destruction of the titanium substrate.

Excesses of hydroxides and potassium silicates were removed from $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 +$ SiO₂/Ti samples by washing with distilled water until neutral reaction of the flush water medium. Thereafter, the samples were dried in a muffle furnace at 150°C for 1 h and transported into a vacuum dessicator, where they were stored at room temperature.

Catalytic burning of carbon black was examined using a NETZSCH STA 449 F3 scanning thermogravimetric device in the air flow (50 mL/min) at a heating rate of 5°/min. $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 +$ SiO₂/Ti composites were coated by carbon black in the burner flame upon combustion of the diesel fuel (*GOST* (State Standard) 305-82). The temperature of the carbon black burning initiation (T_0) was determined according to the thermogravimetric (TG) curves and the temperature of the maximum burning rate (T_{max}) according to the extreme points of differential calorimetric (DSC) curves with an accuracy of $\pm 2^{\circ}C$.

The morphology and element composition of the samples were investigated by means of scanning electron microscopy (SEM) (an EVO 40 microscope equipped with a Rontec energy-dispersive spectrometer) with specification of the elements content using a 35-SDS JEOL spectrometer with wavelength dispersion. The molar ratio K : Ti in the potassium—titanate phases was calculated based on the elements atomic concentrations, which were determined by means of microprobe analysis.

Resistance of the applied layer to adhesive and cohesive destruction was estimated via the gravimetric method by weighting the samples before and after ultrasonic (US) exposure in aqueous media (generator power 100 W, sound vibration frequency 35 kHz), as was shown in [23]. The character of the coatings destruction was examined by visualization of the SEM images.

US treatment of the prepared samples was performed under the isothermal conditions at 25°C. The samples weight was measured using a NETZSCH STA 449 F3 balance with an accuracy of 10^{-6} g. The initial weight of the coating (m_0) was determined according to the weight difference between the weight of the coated wire and the same wire cleaned from the coating as deep as until metallic titanium. The wire was cleaned from the coating mechanically. The destructed coating weight (Δm) was estimated by weighing the sample before and after the US exposure, subsequent drying at 150°C, and cooling down to room temperature. Duration of an individual US exposure varied from 1 to 10 min: here, the total US exposure time for all the cycles per one sample equaled to 30 min.

Chemical stability of potassium titanates in the applied layer to sulfur dioxide (contact time 4 h) and vapor (1 h) was estimated by comparing catalytic properties of the initial samples and the ones that were intoxicated. The tests on exposure to the reactive gases were performed in an SNOL tubular furnace. The expenditures of SO₂ and H₂O were 0.14 and 10 g/min, respectively.

The thermal shock resistance of the samples was estimated based on the samples weight loss after one cycle of heating-cooling, as well as by comparing the catalytic capacity of the samples before and after the tests and changes in the surface morphology. Heating up to the preset temperature (800° C) was performed in an induction furnace at a rate of 60° /min. High thermal gradient was achieved by rapid cooling of the samples up to 0° C on the precooled solid metal plate. The cooling rate of the samples equaled ~ $100-150^{\circ}$ C/s.

RESULTS AND DISCUSSION

Composition and Structure of Coatings

According to the SEM data (Fig. 1a), during KOH solution treatment of the PEO coating modified by the anatase nanoparticles interlayer, a coating was formed, in which two main fragments can be identified: the first was represented by a fine crystalline phase homogeneously distributed along the surface, and the second by flat triangular-shaped crystals of a size of up to 5 μ m and a thickness from 0.5 to 1 μ m. According to the X-ray spectral microprobe analysis, the ratio of potassium and titanium ions, which corresponded to K₂Ti₂O₅ phases (10.6–10.7 at % of K, 12.2–12.3 at % of Ti, 3.7–3.9 at % of Si, the remaining part was oxygen), was observed in the first fragment, while K₂Ti₄O₉ phases (14.0–14.5 at % of K, 27.3–27.9 at % of Ti, 8.3–8.8 at % of Si, the remaining part was oxygen) was seen in the second one (Table 1). It is worth mentioning that the silicon concentration was substantially reduced in the composition of the composite coating, which may be related to the fact that the samples were washed after exposure to alkali and dissolv-



Fig. 1. SEM surface image of the catalytic $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ composite. (a) Initial coating, (b) subjected to 30 min of US exposure in water, and (c) after thermal shock.

able potassium silicates were removed along with the flush fluid.

The DSC curve, which corresponded to catalytic burning (Fig. 2, curve 1), had one peak of a symmetrical shape, which allowed concluding that the process occurred in a single stage, the temperature of the process initiation was 340°C, and the temperature of the maximum rate was 390°C. The obtained results on high catalytic activity of $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 +$ SiO₂/Ti composite were corroborated by the published data. For instance, according to [27], the decrease of the potassium molar ratio in the perovskite powder sample represented by the general formula $xK_2O \cdot yTiO_2$ resulted in the increase of the temperature of the maximum burning rate, since this process mechanism was determined by a formation of surface carbonate intermediates on K⁺ ions, so that the reduction of the potassium fraction in the titanate resulted in the decrease of the process rate.

Table 1. Element composition of PEO-oxidized coatings

Composite	Element composition, at %			
	K	Ti	Si	
$SiO_2 + TiO_2/Ti$	_	15.4	18.7	
$TiO_2/SiO_2 + TiO_2/Ti$	—	20.3	12.4	
$\begin{array}{l} K_2 Ti_2 O_5 + K_2 Ti_4 O_9 / TiO_2 / TiO_2 + \\ SiO_2 / Ti \ Part \ 1 \end{array}$	10,6	12.3	3.8	
$\begin{array}{l} K_2 Ti_2 O_5 + K_2 Ti_4 O_9 / TiO_2 / TiO_2 + \\ SiO_2 / Ti \ Part \ 2 \end{array}$	14,3	27.6	8.5	

Estimation of Coating Stability to Adhesion and Cohesion Destruction

While in operation of applied oxidation catalysts for diesel carbon black under the actual conditions, flaking-off of the active coating according to the types of adhesion and cohesion destruction occurred due to varied mechanical loads (vibration, gas jet strokes etc.). In the present study, we suggest estimating the resistance of the synthesized composites to these types of destruction on the weight loss of the sample using the known technique [23]. US impact on catalytic



Fig. 2. DCM (continuous) and TG (dotted) curves of the carbon black oxidation in the presence of $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$. (1) Initial compositions, (2) compositions subjected to 30 min US exposure in water, and (3) compositions subjected to thermal shock.

 $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ composites (Table 2) was observed only after 5 min of the process start: here, the weight loss of the sample reached ~0.2% of the coating initial weight. The maximum weight loss of the coating of 0.3% occurred after 10 min of exposure to US, and there was no further weight loss observed even after 30 min of exposure to US. Apparently, an insignificant weight loss of the composite occurred due to partial flaking-off of potassium titanates and unreacted nanoparticles of the anatase interlayer.

Comparative analysis of the SEM images of the initial samples (Fig. 1a) and those subjected to 30-min US exposure (Fig. 1b) did not demonstrate any substantial changes in the morphology of the catalytic layer surface.

Thermal analysis of the carbon black burning curves (curves I, 2 in Fig. 2) also demonstrated similarity of catalytic properties of the compared samples of K₂Ti₂O₅ + K₂Ti₄O₉/TiO₂/TiO₂ + SiO₂/Ti. The carbon black oxidation in both cases initiated at 340°C and proceeded within a single stage, T_{max} values of the carbon black burning, as well as the temperature of the process termination, were also compatible.

To sum up, the performed tests demonstrated that catalytic composites $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2 + TiO_2 + SiO_2/Ti$ exhibited resistance to mechanical loads.

Examination of Thermal Stability

Analysis of the SEM images of $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ samples subjected to thermal shock demonstrated that rapid cooling did not influence the morphology of the sample surface, the coating after the thermal tests remained continuous, and no destructions or cracks were observed (Fig. 1c).

According to [28, 29], no active percolation of oxygen to titanium through the coating was observed up to 700°C and there occurred neither oxidation of the thin transition layer nor of the substrate metal. At temperatures of around 750°C and higher, active diffusion of titanium towards surface along the fractures and pores is initiated, as well as oxidation of titanium up to formation of rutile crystals. The investigated coatings also demonstrated a diffusion of potassium ions into a depth of the titanium oxide layer and the subsequent decrease of the potassium concentration on the surface.

Indeed, the element analysis of the surface of the $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ catalyst thermally treated up to 800°C, a compound was observed, whose composition was similar to $K_2Ti_4O_9$ (5.4–6.5 at % of K, 11.1–11.3 at % of Ti, 7.0–7.5 at % of Si, the rest was oxygen). Complete substitution of $K_2Ti_2O_5$ by $K_2Ti_4O_9$ in the catalytic layer resulted in substantial reduction of the catalytic activity reflected

in the increase of the temperature range of the carbon black burning by 70° C.

Thermogravimetric examination of DSC and TG oxidation curves of the $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ catalyst in air oxygen atmosphere is shown in Figure 3. Slow oxidation of titanium support was initiated as early as at 600°C. Phase transition of low-temperature α -Ti to high-temperature β -Ti was recorded at 882°C. Further heating, starting from 900°C, resulted in rapid increase of the oxidation rate of the titanium support and destruction of the catalyst.

Therefore, rapid heating up to 800° C and the following rapid cooling of the $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti composite resulted in partial oxidation of the$ metal substrate followed by reduction of the concentration of K⁺ ions on the surface and, subsequently, inthe decrease of the catalytic activity of the coating.Another fact worth mentioning is that this impact didnot interrupt the coating's integrity.

Impact of Catalytic Poisons

The vapor impact on the $K_2Ti_2O_5$ + $K_2Ti_4O_9/TiO_2/TiO_2$ + SiO_2/Ti catalyst did not influence significantly the process of oxidation of carbon black. The temperature maximum of 389°C (curve *1* in Fig. 4) was close to that of the initial catalyst (curve *1* in Fig. 2): a slight difference fell within the device error. The element analysis of the composite surface did not reveal a substantial reduction of the potassium fraction in the coating composition compared to the initial one, which explains retaining of the catalytic activity typical for applied titanates $K_2Ti_2O_5$ and $K_2Ti_4O_9$.

Therefore, no substantial changes in the composition, morphology, and catalytic activity were observed in the $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ composite after the continuous vapor exposure.

Exposure to sulfur dioxide gas of the $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ composite resulted in a

TG, %

108

107

106

105

104

103

102

101

100

200

400



Temperature, °C

600

882°C

800

1000

Table 2. Influence of ultrasonic exposure time τ on relative weight loss of the coating made of $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti composite$

2 7 11 21 2		21	1			
τ, min	1	2	3	5	10	30
$\Delta m/m_0 \times 100\%, \%$	0	0	0	0.2	0.3	0.3

substantial increase of the temperature range of catalytic burning of carbon black—the reaction initiation temperature shifted by 50° C to higher temperatures (curve 2, Fig. 4). This indicates a decrease of the catalytic capacity of the composites.

Note that the average concentration of sulfur dioxide in diesel exhaust equaled to 80 ppm [8], so that a rate of the exhaust gas flow of ~300 L/min would correspond to the flow rate of sulfur dioxide of 0.076 g/min. The expenditure of SO_2 in the present study was 0.14 g/min, and the exposure time was 240 min.

The element analysis of the surface displayed the presence of chemisorbed sulfur in amounts from 1 to 2 at %. Sulfur dioxide must be able to form substantially more stable compounds with potassium than carbon dioxide, so that a formation of carbonate intermediates on the surface becomes less probable, which implies a decrease of the catalytic activity. However, it is worth mentioning that cerium dioxide CeO₂ extensively used as an afterburning catalyst for carbon black exhibits much more substantial reduction of activity after exposure to sulfur dioxide gas with the concentration more than three times lower. Particularly, a treatment of cerium catalysts by pure SO₂ flow for 40 min at a rate of 0.043 g/min resulted in the temperature decrease for maximum rate of the catalytic carbon black burning by 111°C [9]. Therefore, one can conclude that the $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 +$ SiO₂/Ti composite manifests much higher resistance to exposure to sulfur dioxide compared to cerium oxide catalysts that are extensively used at present.



Fig. 4. TG (dotted) and DCM (continuous) oxidation curves of soot carbon in the presence of $K_2Ti_2O_5$ + $K_2Ti_4O_9/TiO_2/TiO_2$ + SiO_2/Ti, subjected to (1) exposure to vapor and (2) inhibitive exposure to sulfur dioxide gas.

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DSC/(mV/mg)

2.0

1.5

1.0

0.5

0

1200

exo 🔺

CONCLUSIONS

Catalysts of the composition $K_2Ti_2O_5$ + $K_2Ti_4O_9/TiO_2/TiO_2$ + SiO_2/Ti have exhibited high catalytic capacity for oxidation of carbon black particles, which retained after mechanical tests and high-temperature exposure in vapor medium.

A substantial increase of the temperature of the maximum carbon black burning rate for the $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ composite after the isothermal holding at 800°C for 10 min has been demonstrated. This must be determined by the decrease of the surface potassium concentration upon temperature impact in air atmosphere due to redistribution of potassium between internal and external layers and partial transition of $K_2Ti_2O_5$ into less active titanate phase $K_2Ti_4O_9$. The obtained results have put restrictions on the temperature mode of the $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ catalyst operation.

It has been established that the exposure of $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ composite to sulfur hydroxide results in the decrease of the temperature of maximum catalytic burning rate for carbon black by ~50°C determined by chemisorption of sulfur and subsequent poisoning of the catalysts. However, these composites have appeared to be substantially more resistant to the exposure to SO₂ than extensively used oxide-cerium catalysts. Therefore, the catalytic composite $K_2Ti_2O_5 + K_2Ti_4O_9/TiO_2/TiO_2 + SiO_2/Ti$ represents a promising afterburning catalyst for carbon black among other catalysts presently applied in this field.

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