Photocatalytic and adsorptive properties of titanium dioxide prepared by thermal decomposition of metatitanic acid

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Several types of titania-based photocatalysts were prepared by the thermal decomposition of metatitanic acid. The obtained photocatalysts were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and thermal analysis. The photoreduction of potassium dichromate was used as a model reaction in order to evaluate the photocatalytic activity of the prepared catalysts. The influence of methanol on the rate of photoreduction was also investigated. It was determined that the most active catalyst is obtained during annealing of metatitanic acid at 400 °C and contains 69.3% of rutile and 30.7% of anatase. Cr(VI) adsorption is best described by the Langmuir adsorption isotherm. Titania catalyst modified with copper, cobalt, zinc or tungsten additives has larger adsorption capacity for Cr(VI), but smaller photoreduction rate as compared to pure TiO_2.

Key words: photocatalysis, adsorption, titanium dioxide, thermal decomposition, metatitanic acid

INTRODUCTION

TiO_2-based heterogeneous photocatalysis continues to be a very actively developing field of fundamental and applied research [1–4]. It has been established that the nanostructured TiO_2 can be used as an efficient photocatalyst for the oxidation of various organic compounds, the removal of some metal ions, the photosplitting of water, the manufacture of dye-sensitized solar cells. The main disadvantage of TiO_2 is its ability to act as a photocatalyst only under UV irradiation. For this reason, there is a need for new TiO_2-based materials which could be sensitive to visible light. One of the possible ways to extend the spectral response of TiO_2 is its modification with narrow band-gap semiconductors, such as Cu_2O, Fe_2O_3, CdSe.

Under UV irradiation, the photoelectrons and holes are generated in TiO_2 particles. These charge carriers are characterized by very strong redox properties and are able to oxidize and reduce many organic and inorganic substances on the surface of photocatalyst. Recently, an increased attention has been paid to the simultaneous oxidation of organic pollutants and the reduction of toxic metal ions, such as Cr(VI) [5–7]. For example, it has been shown in numerous papers that highly toxic, mutagenic and carcinogenic Cr(VI) ions can be photocatalytically reduced to less harmful Cr(III) ions [8–28]. The contamination of wastewater by Cr(VI) ions usually originates from industrial processes such as paint production, leather tanning or electroplating. The preferred treatment is the reduction of Cr(VI) to Cr(III) upon the addition of sodium thiosulfate, ferrous sulfate, sulfur dioxide gas or sodium bisulfate / metabisulfite. Afterwards, Cr(III) ions can be precipitated as $Cr(OH)_3$. However, these methods require extensive use of chemicals and heterogeneous photocatalytic reduction may be used as an alternative.

The aim of the current work was to obtain new TiO_2-based photocatalysts and to study their adsorbtion capacity and photocatalytic activity. The photoactivity of the prepared

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catalysts was evaluated using Cr(VI) ions photoreduction as a test reaction. The choice of this reaction is mainly related to these reasons:

• Cr(VI) ions are highly toxic contaminants, thus, their removal is a persistent environmental problem. Heterogeneous photocatalytic reduction permits the reduction of Cr(VI) to less harmful Cr(III);

• Kinetics of Cr(VI) photoreduction in the presence of organic compounds provide some insights about photoredox properties of the photocatalysts. This information is very important in the search of highly efficient photocatalysts suitable for various processes, such as water photosplitting or oxidation of organic compounds.

MATERIALS AND METHODS

The titania-based catalysts were prepared by the thermal decomposition of metatitanic acid (H_2TiO_3, Reachim, Russia, 99% purity,) in the air at 400, 600 and 800 °C for 1 h (throughout the paper, the produced photocatalysts are denoted as T400, T600 and T800, respectively). In order to prepare the composite catalysts (denoted as Ti–O–Co Ti–O–Zn, Ti–O–Cu and Ti–O–W), H_2TiO_3 was impregnated using aqueous solutions containing $Co(CH_3COO)_2$, $Zn(CH_3COO)_2$, $Cu(CH_3COO)_2$ (all from Reachim, Russia, >97% purity) or tungsten(VI)-peroxocomplex. The latter was prepared by dissolving tungsten powder (Sigma-Aldrich, 99%) in 30% hydrogen peroxide (Lach-Ner, Czech Republic). The metal : Ti ratio was varied in the range of 0.5–5% (wt). In addition, commercial Degussa P25 titanium dioxide was used in the experiments due to its well-documented photoactivity and known physical properties (~80% of anatase, ~20% of rutile, small amount of amorphous phase, specific surface area ~50 m²/g, particle size ~20 nm [29]).

The changes in the concentration of potassium dichromate were determined with a Perkin Elmer Lambda 25 spectrometer by measuring the absorption at 352 nm wavelength.

The photoactivity of different catalyst samples was quantified in terms of the fractional conversion X of dichromate:

$$X = \frac{C_0 - C_t}{C_0} \cdot 100\%,\tag{1}$$

where C_0 and C_t are the concentration of potassium dichromate at the initial stage of the reaction and at the moment t, respectively.

The photoactivity tests were carried out using a thermostated annular glass photoreactor containing 100 mL of the stirred aqueous suspension of dichromate and catalysts. For all experimental runs performed at 25 °C, the initial concentration of photocatalyst was 5 g/L. The initial concentration of potassium bichromate ($K_2Cr_2O_7$, Reachim, Russia, 99%) was varied in the range of 0.1–0.5 mM, the initial pH being about 5.2. A 400 W high pressure metal halogen lamp (Philips 400/30S) was used as an UV irradiation source and fixed outside the reactor. The incident light intensity was evaluated by potassium ferioxalate actinometry [30] and was found to be $9 \cdot 10^{18}$ photons/s in the range of 300–430 nm. The influence of methanol (CH_3OH, Penta, Czech Republic, 99.8%) concentration on the rate of photoreduction was also investigated.

The adsorption capacity of the prepared catalysts was evaluated using the same experimental set-up in the absence of UV irradiation.

The X-ray powder diffraction (XRD) data were collected with a DRON-6 (Bourevestnik Inc., Russia) powder diffractometer with Bragg–Brentano geometry using Ni-filtered CuK$_\alpha$ radiation and a graphite monochromator. The crystallite size D_{hkl} was calculated from the line broadening using the Scherrer's equation [31]:

$$D_{hkl} = \frac{k \cdot \lambda}{B_{hkl} \cdot \cos\Theta},\tag{2}$$

where λ is the wavelength of the Cu K$_\alpha$ radiation (1.54056×10^{-10} m), θ is the Bragg diffraction angle, B_{hkl} is the full width at the half maximum intensity of the characteristic reflection peak ($2\theta = 25.3°$ for anatase and $2\theta = 27.5°$ for rutile) and k is a constant (the value used in this study was 0.94).

The amount of rutile in the prepared catalyst was evaluated using the following equation [32]:

$$x = \left(1 + 0.8\frac{I_A}{I_R}\right)^{-1},\tag{3}$$

where x is the amount of rutile in TiO_2 particles, I_A and I_R are the maximum intensity of the characteristic reflection peak of anatase and rutile, respectively.

Differential scanning calorimetry and thermogravimetry (DSC-TG) analysis was performed on a Netzsch STA 409 PC Luxx (Netzsch GmbH, Germany) simultaneous thermal analyzer. The heating was carried out in air, the rate of temperature increase was 15 K min⁻¹, and the temperature range from 30 to 1 000 °C was used.

Fourier transform infrared (IR) absorption analysis was performed on a Perkin Elmer FT-IR System (Perkin Elmer, USA). The vacuum mold was used to form a tablet (1 mg of substance mixed with 200 mg of KBr). The analysis was performed in the range of 4 000–400 cm⁻¹.

The value of pH was measured using a pH-meter 673 M.

RESULTS AND DISCUSSION

Photocatalytic activity and structure of TiO_2

The results presented in Fig. 1 show that the prepared T400 sample is the most active among other studied photocatalysts. It was determined that after 15 min of irradiation the fractional conversion of Cr(VI) ions is 55% (the concentration of dichromate decreased from 0.25 mM to 0.11 mM). No changes in chromium(VI) concentration were obtained under irradiation in the absence of photocatalysts. It was determined [15, 16] that the photochemical reduction of Cr(VI) proceeds at appreciable rate only in strongly acidic solutions. The control
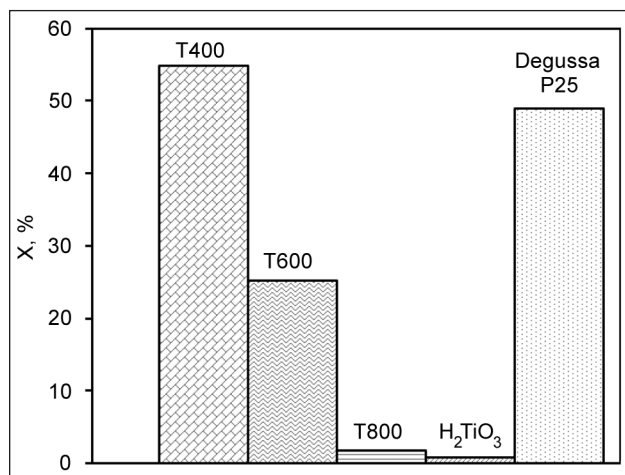
Fig. 1. Photocatalytic activity of various catalysts in the reduction of Cr(VI). X is fractional conversion (%) after 15 min.

experiments revealed that the direct photolysis and chemical reduction of Cr(VI) do not present considerable contributions to the observed concentration variations during the used experimental conditions. Metatitanic acid H_2TiO_3 is characterized by a very low photocatalytic activity. It is worth to note that T400 catalyst is more effective than commercial P25 TiO_2 which is often used as the standard to evaluate the activity of new UV light-sensitive photocatalysts. The decrease in Cr(VI) concentration may be associated with photocatalytic redox processes occurring on the surface of TiO_2 [1]. Under UV irradiation the generation of photoelectrons (e^-) and holes (h^+) takes place in TiO_2 particle. The interaction between photoelectrons e^- and $Cr_2O_7^-$ ions may lead to the formation of Cr^{3+} ions [12]:

$$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O. \quad (4)$$
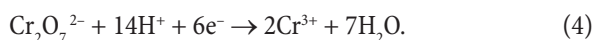
It is known that in aqueous solutions Cr(VI) ions can exist in several forms: H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$ or CrO_4^{2-} depending on pH. Our experiments were carried out at an initial pH 5.2. On the basis of thermodynamic calculations [22], we presume that under such experimental conditions the reaction

mixture consists of 75% $HCrO_4^-$, 15% CrO_4^{2-} and 10% $Cr_2O_7^{2-}$. As a result, (4) equation may be transformed to:

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O. \quad (5)$$
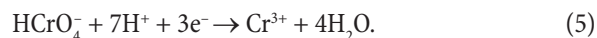
Photogenerated holes h^+ oxidize water molecules with a formation of $^\bullet OH$ radicals:

$$H_2O + h^+ \rightarrow {}^\bullet OH + H^+ \quad (6)$$
or
$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+. \quad (7)$$

Hereby, chromium(VI) reduction to chromium(III) and oxygen release are the main processes in this system. At the kinetic point of view, these processes are slow because more than one electron must be transferred.

During experimental tests it was observed that particles acquire a slightly greenish color. It could be due to the formation of Cr(III) compounds, as it is known that the green color is typical to Cr_2O_3 while Cr(IV) oxide is dark brown or even black.

The increase in the heat treatment temperature of the metatitanic acid sample decreases markedly the photoactivity of the catalysts. For instance, the fractional conversion of Cr(VI) ions is only 1.8% in a case of the T800 sample (Fig. 1). The decrease in photocatalytic activity should be primarily associated with changes of the crystalline structure in TiO_2 and explained using the Ohtani model [33]. According to this model, a high photocatalytic activity of TiO_2 can be achieved with the catalyst having a large specific surface area for the effective adsorption of organic or inorganic substances and a high degree of particle crystallinity in order to slow down the recombination of photogenerated charge carriers.

Those both requirements can only be partially satisfied at moderate temperatures (<500 °C) as the calcination at higher temperatures results in better crystallinity, but lower specific surface area.

DSC-TG analysis was used to elucidate the structural changes of metatitanic acid during heat treatment (Fig. 2).
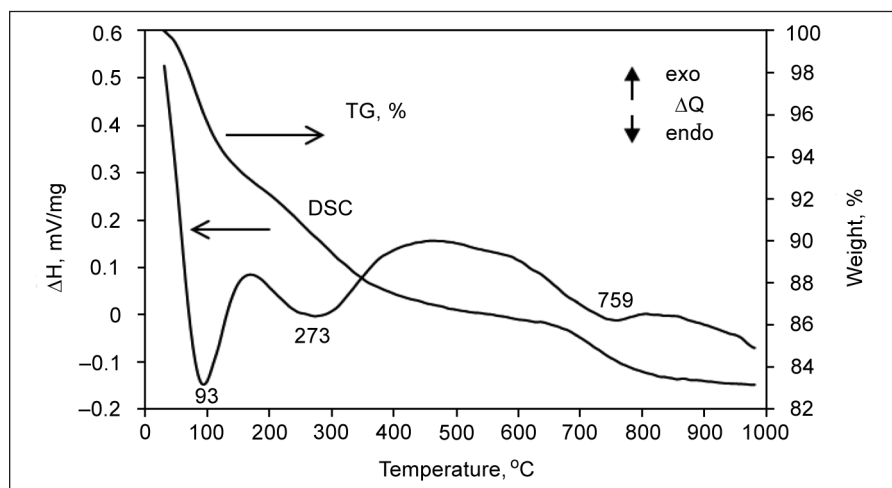

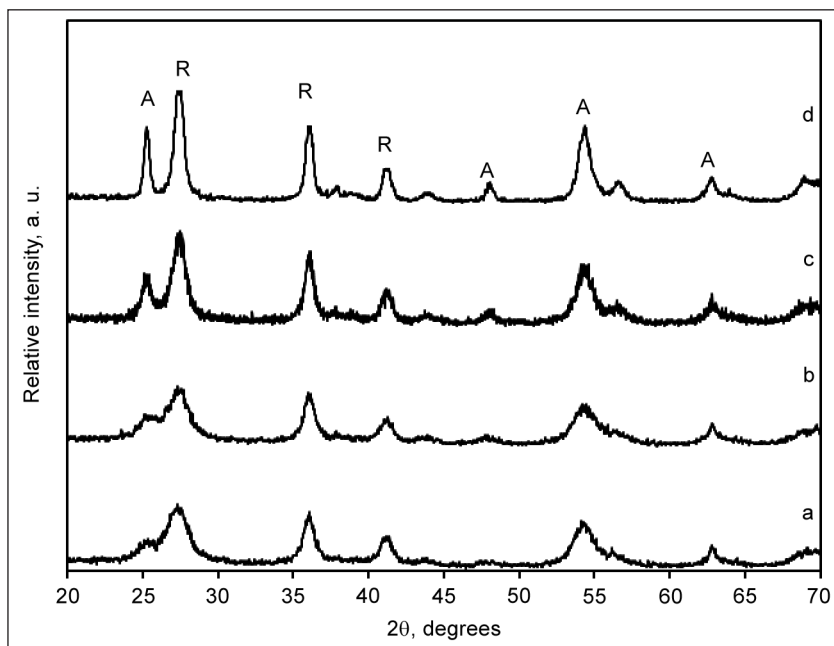**Fig. 2.** TG–DSC patterns for H_2TiO_3

Fig. 3. XRD patterns of various catalysts: a) H₂TiO₃;
b) T200; c) T400; d) T600. Indexes: A — anatase,
R – rutile

Three endothermic effects at 93, 273 and 759 °C may be defined from the DSC curve and could be associated with the desorption of physically adsorbed water molecules, the loss of crystallization water and anatase transformation to rutile. Data of the TG analysis show the total weight loss of 16.8%, most of it is due to removal of physically adsorbed and crystalline water (~7.1 and ~5%, respectively).

It is interesting to note that the XRD spectrum of H_2TiO_3 shows the presence of anatase and rutile phases (Fig. 3). XRD data reveal that T400 photocatalyst is composed of 69.3% of rutile and 21.7% of anatase, as it is calculated by Equation (3). According to the Scherrer equation, the average crystallite size of anatase and rutile is 24 and 19 nm, respectively.

FTIR spectra of metatitanic acid, T400 and T800 samples are presented in Figure 4. Absorption peaks at 525 and 545 cm^{-1} correspond well to Ti–O and Ti–OH vibrations, which usually occur at 450–800 cm^{-1} [34]. A broad absorption band (peak at 3 310 cm^{-1}) is associated with OH$^-$ and water molecules adsorbed on the surface of metatitanic acid. The absorption peak at 1 614 cm^{-1} appears as a result of deformation vibrations of physically adsorbed water molecules. The existence of Ti–OH is confirmed by absorption at 1 200–1 071 cm^{-1}. The intensity of these peaks decreases upon heat-treatment of metatitanic acid.

It is generally accepted that reaction between photogenerated holes and water molecules (Equations 6 and 7) is a limiting stage of photocatalytic processes. Therefore, photogenerated charge carriers tend to recombine, thus reducing the efficiency of photocatalysis. One possible way to decrease the recombination rate is the use of organic additives which can be readily oxidized on the surface of TiO₂.

With the addition of methanol, the rate of the photocatalytic reduction of potassium dichromate increases sig-

nificantly (Fig. 5). By comparing the results shown in Figs. 1 and 5, it is seen that the conversion of Cr(VI) after 15 min of irradiation increases from 55 to 99%. These results are in agreement with those obtained by other authors [7, 8, 12]. For example, the influence of different organic compounds (p-hydroxybenzoic acid, phenol, salicylic and citric acids) was studied [12]. The positive influence was found for all organic additives; however, the effect depends on the nature of organic compound. In a case of citric acid, the reduction rate constant increases more than 20 times. Wang et al. [8] determined that an addition of colorless organic acids resulted in the formation of a charge-transfer complex which is sensitive to visible light irradiation and induced the photocatalytic
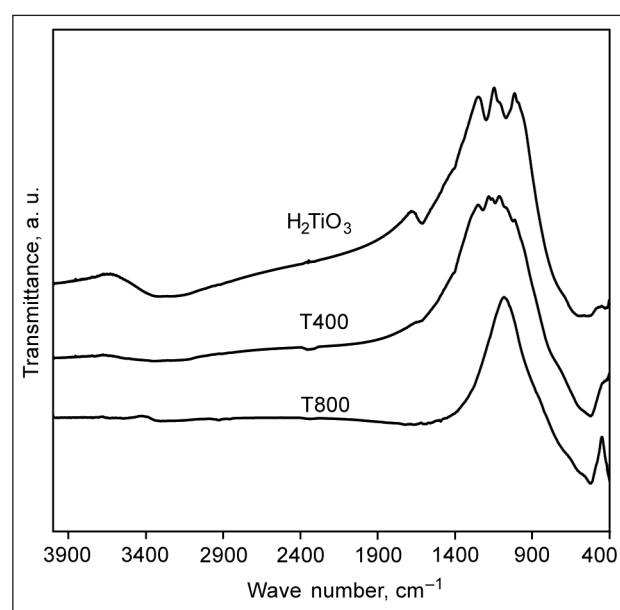

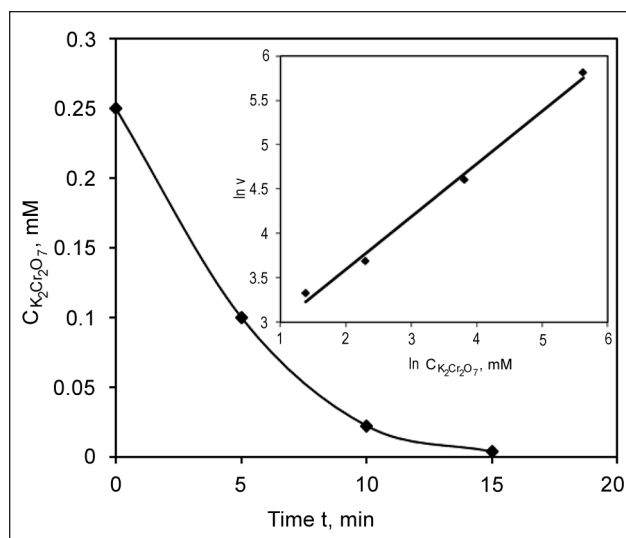**Fig. 4.** FTIR spectra of H₂TiO₃, T400 and T800 photocatalysts

Fig. 5. Kinetic curve of Cr(VI) photocatalytic reduction using T400 catalyst. $C^0_{K_2Cr_2O_7} = 0.25$ mM, $C^0_{CH_3OH} = 10$ mM. Inset: Plot for the calculation of reaction order

oxidation of organic acids and photoreduction of Cr(VI). Among the used acids, the tartaric acid was found to be the most efficient.

The calculated apparent reaction order with respect to the potassium dichromate concentration is 0.6 (inset of Fig. 5). Alam and Montalvo [22] reported that the reaction order of potassium dichromate reduction might vary from 0.5 to 1 depending on pH.

The Langmuir-Hinshelwood model is usually used to describe kinetics of photocatalytic processes [1]. According to this model, the rate is proportional to the amounts of the reacting molecules that are adsorbed. The rate first increases, then passes through a maximum, and finally de-
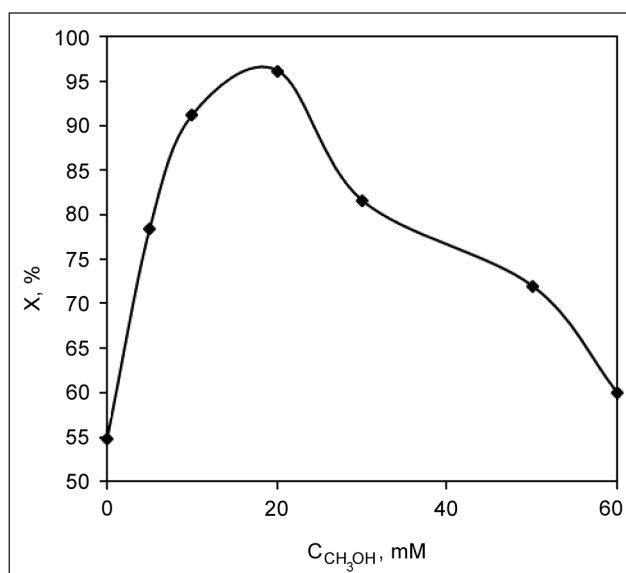
creases. Theoretically, the maximum rate corresponds to the optimum number of reacting species. This trend is observed in the obtained kinetic curve (Fig. 6). The maximum rate of the chromium(VI) reduction is reached when the initial concentration of methanol is 20 mM.

Adsorption characteristics of TiO₂ catalysts

The equilibrium of Cr(VI) adsorption in the dark is achieved within 20 min under the tested conditions. This can be attributed to the strong electrostatic attraction between negatively charged chromate species ($HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$) and the positively charged TiO₂ surface. The preliminary results showed that the presence of methanol slightly decreased the observed amount of adsorbed potassium dichromate due to the competitive adsorption. The results indicate that T400 catalyst adsorbs the largest amount of Cr(VI) ions (2.84 mg/g), followed by Degussa P25 TiO₂ (2.63 mg/g). Other catalysts which were prepared at higher temperatures showed much lower ability to adsorb Cr(VI) ions. These experimental results confirm the importance of catalyst capacity to adsorb potassium dichromate on the rate of photocatalytic reduction. However, there is no linear dependency between these two values, because other factors such as particle size, amount of impurities, defects also influence the efficiency of photochemical processes.

Fig. 7 presents an isotherm of potassium dichromate adsorption on TiO₂ P25 sample. The amount of adsorbed Cr(VI) is increasing when initial concentration is changed from 0 to 0.25 mM, then it reaches the maximum. These results are best described by the Langmuir adsorption isotherm. The calculated adsorption parameters are as follows: the maximum amount of adsorbate is 5.05 mg/g, the equilibrium constant of adsorption is 0.11 l/mg.
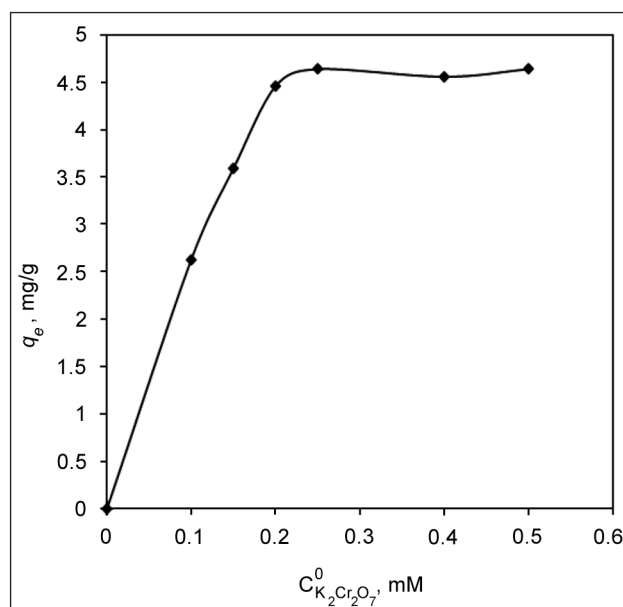

Fig. 6. The influence of the methanol concentration on the reduction of Cr(VI) in the suspension of T400 catalyst. Experimental conditions: $t = 25$ °C, $C^0_{K_2Cr_2O_7} = 0.25$ mM, time = 10 min. X – Cr(VI) conversion ratio, %

Fig. 7. Adsorption capacity (q_e) of Degussa P25 TiO₂ as a function of the initial potassium dichromate concentration

Adsorption capacity and photocatalytic activity of composite catalysts

In order to improve the photocatalytic and adsorptive properties, T400 sample was modified with other metal oxides. Ti–O–Co, Ti–O–Zn, Ti–O–Cu and Ti–O–W mixed oxides were synthesized and their adsorption and photocatalytic properties were investigated. The experimental results are presented in Figures 8 and 9. They show that small amounts (0.5%) of any added component drastically decrease the photocatalytic activity of the pure T400 sample. Zinc effect is
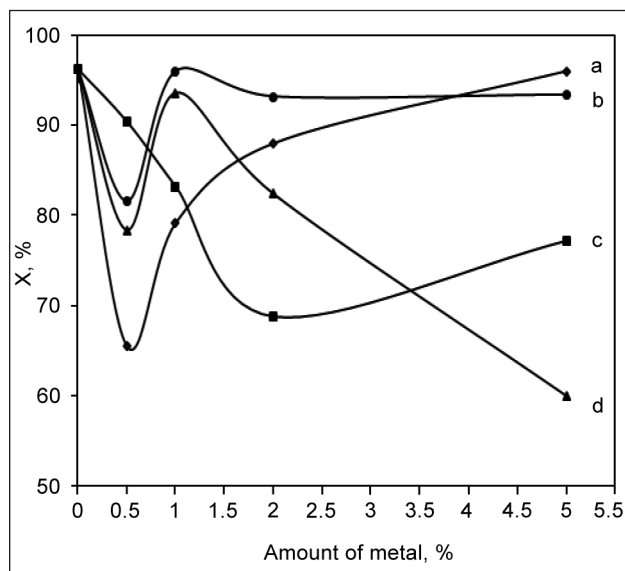

Fig. 8. Cr(VI) fractional conversion (X) as a function of the metal additive amount: a) Ti–O–Zn, b) Ti–O–W, c) Ti–O–Co, d) Ti–O–Cu. Experimental conditions: $t = 25\,°C$, $C^0_{K_2Cr_2O_7} = 0.25$ mM, $C^0_{CH_3OH} = 20$ mM, time = 10 min.
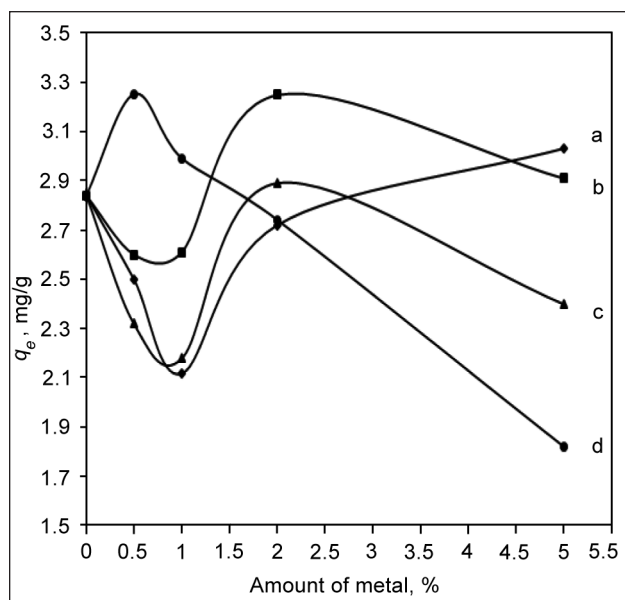

Fig. 9. Cr(VI) adsorption capacity (q_e) as a function of the metal additive amount: a) Ti–O–Zn, b) Ti–O–Co, c) Ti–O–Cu, d) Ti–O–W. Experimental conditions: $t = 25\,°C$, $C^0_{K_2Cr_2O_7} = 0.1$ mM, time = 30 min.

the worst: the photocatalytic conversion of Cr(VI) decreases from 96 to 66%. If 1–5% (wt) of zinc is added to T400 catalyst, its activity slightly increases, whereas cobalt and copper has a negative effect throughout all studied concentrations. Ti–O–W catalyst shows almost no changes in the conversion ratio (~94%) if more than 1% of tungsten is added to TiO_2 catalyst.

It has to be mentioned that small amounts of tungsten (<1%) increase the adsorption capacity of catalyst (Fig. 9). The same effect appears if 2% of cobalt is present in the catalyst. It means that the adsorption capacity is not the only factor influencing the photocatalytic activity. For example, if a sample of T400 catalyst contains 5% of tungsten, it adsorbs almost 40% less than pure TiO_2 but the photocatalytic reduction rate remains the same (X = 94%).

XRD patterns of the synthesized composite catalyst with 5% of metal additive indicated only characteristic peaks of TiO_2 (not shown for the sake of brevity). In all cases anatase and rutile phases are formed, but their quantity depends on the additive (Table). Pure T400 catalyst has 69.3% of rutile. After impregnating H_2TiO_3 with zinc(II), cobalt(II) or copper(II) acetates and annealing at 400 °C, the final amount of rutile increased (up to 74.2% in a case of zinc). The addition of tungsten retarded anatase → rutile transformation rate.

Table. Rutile amount and crystallite size in the prepared catalysts

Catalyst	Rutile, %	Crystallite size, nm	
		Anatase	Rutile
T400	69.3	24	19
Ti–O–Zn	74.2	24	21
Ti–O–Co	69.9	28	17
Ti–O–Cu	71.2	34	19
Ti–O–W	64.8	28	17

CONCLUSIONS

TiO_2-based photocatalysts were prepared by thermal decomposition of metatitanic acid H_2TiO_3. The sample obtained at 400 °C showed the highest photocatalytic activity towards Cr(VI) photoreduction. X-ray diffraction analysis revealed that it comprises 69.3% of rutile and 30.7% of anatase. The prepared photocatalyst is more active than commercial Degussa P25 sample which is often used as a benchmark in the photocatalysis.

The equilibrium of Cr(VI) adsorption is reached within 20 minutes at 25 °C. The experimental data were best described by the Langmuir adsorption isotherm and the following adsorption parameters were calculated: the maximum amount of adsorbate is 5.05 mg/g, the adsorption equilibrium constant is 0.11 l/mg.

The photocatalytic reduction of Cr(VI) in the aqueous suspension of titania is 0.6 order reaction with respect to potassium dichromate concentration. The rate of photoreduc-

tion is increased in the presence of methanol as a sacrificial agent.

It was established that TiO_2 catalyst modified with copper, cobalt, zinc or tungsten oxides (0.5–5%) has larger adsorption capacity for Cr(VI) ions, but smaller photocatalytic reduction rate as compared to pure TiO_2.

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TITANO DIOKSIDO, GAUTO TERMIŠKAI SKAIDANT METATITANATO RŪGŠTĮ, FOTOKATALIZINĖS IR ADSORBCINĖS SAVYBĖS

S a n t r a u k a

Ištyrus titano dioksido, gauto termiškai skaidant titanato rūgštį, aktyvumą fotokatališkai redukuojant Cr(VI) jonus, nustatyta, kad aktyviausias yra 400 °C temperatūroje pagamintas katalizatorius, sudarytas iš 69,3 % rutilo ir 30,7 % anatazo. Pastebėta, kad Cr(VI) jonų adsorbcijos ant TiO_2 pusiausvyra nusistovi per 20 min. (esant 25 °C temperatūrai). Eksperimentiniams duomenims įvertinti geriausiai tinka Lengmiūro adsorbcijos izoterma, kurios nustatyti parametrai yra: maksimalus adsorbato kiekis – 5,05 mg/g, adsorbcijos pusiausvyros konstanta – 0,11 l/mg. Cr(VI) jonų fotokatalizinė redukcija TiO_2 vandeninėje suspensijoje yra 0,6 laipsnio reakcija $K_2Cr_2O_7$ atžvilgiu. Procesas paspartėja į reakcijos mišinį pridėjus metanolio. Nustatyta, kad titano dioksidą modifikuojant Cu, Co, Zn, W priedais (0,5–5 masės %) galima padidinti katalizatoriaus gebą adsorbuoti Cr(VI) jonus, tačiau jų fotokatalizinės redukcijos greitis sumažėja, palyginti su grynu TiO_2.