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# Visible light driven photocatalysis in chromate(VI)/$TiO_2$ systems—Improving stability of the photocatalyst

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ABSTRACT

Titanium dioxide photosensitization to visible light can be observed in the presence of chromate(VI) ions adsorbed at the surface of $TiO_2$. The resulting materials do not show, however, sufficient stability and photostability—chromium(VI) species desorb from the surface and can be reduced to chromium(III). The stability of such systems has been improved by $TiO_2$ impregnation with fluorochromate(VI), $K[CrO_3F]$, instead of $K_2Cr_2O_7$, yielding yellow F-$Cr^{VI}$@$TiO_2$ material. Fluorides playing the role of anchors enable stronger adsorption of chromates at titanium dioxide. Also composites of water insoluble chromates(VI) with $TiO_2$ release significantly lower amounts of $Cr^{VI}$ ions. Such materials have been synthesized according to two main strategies—the first one involves precipitation of water insoluble chromates in the presence of $TiO_2$ particles ($MCrO_4$@$TiO_2$) while the second strategy comprises of $TiO_2$ synthesis in the presence of insoluble chromate particles ($TiO_2$@$MCrO_4$). Visible light induced photocatalytic activity of synthesized materials was studied in the process of 4-chlorophenol (4-CP) oxidation. A considerable photocatalytic activity was observed in the case of F-$Cr^{VI}$@$TiO_2$ and $TiO_2$@$MCrO_4$ type materials ($M^{n+}$: $Ba^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Cr^{3+}$). Among the composites the highest photoreactivity was shown by $TiO_2$@$CoCrO_4$ (1.7% $Cr^{VI}$, mol/mol, calcined at 450 °C) and $TiO_2$@$Cr_2(CrO_4)_3$ (5% $Cr^{VI}$, mol/mol, calcined at 450 °C).

## 1. Introduction

Photocatalytic oxidation of organic compounds driven by visible light can be realized in various $TiO_2$-based systems. Photosensitization of titanium dioxide involving doping or surface modification with *p* (N [1–6], C [7–11], S [9,12], Cl, Br [13], I [14], Pb [15]), *d* (V [16], Cr [17,18], Au, Rh, Ni [19], Pt [19–23], *etc.*) or *f* (Eu, Pr, Yb [24], Ce [25], Nd [26], *etc.*) block elements, may facilitate visible-light induced electron injection into the conduction band of titanium dioxide. Consecutive secondary thermal reactions leading to formation of reactive oxygen species (ROS) are responsible for oxidation of organic matter [27–29]. Unfortunately, modified materials often suffer from a thermal instability, photocorrosion, or a low solar energy conversion efficiency.

There are several reports on photocatalytic activity of titanium dioxide suspensions in chromate(VI) solutions induced by UV light [30–37]. In these systems $Cr^{VI}$ is reduced by the electrons from the $TiO_2$ conduction band to $Cr^{V}$. In the presence of organic compounds (such as oxalate, phenols, salicylic acid, humic acids) the efficiency of photoinduced $Cr^{VI}$ reduction increases due to increased yields of holes consumption in the processes of organic molecules oxidation suppressing the electron-hole recombination. The same tendency was found in analogous systems irradiated with visible light [38,39]. Photoinduced oxidation of organic compounds was also studied in the aqueous solutions of chromates(VI) in the absence of titanium dioxide [40–43]. The simultaneous $Cr^{VI}$ reduction and organic compounds (containing hydroxyl or carboxylic groups) oxidation results from LMCT (ligand-to-metal charge transfer) excitation of chromate(VI) ions followed by photoinduced electron transfer from the electron donor (organic molecule) to chromate(VI).

The activity of combined $TiO_2$–$Cr^{VI}$-organic compound systems in visible light driven photodegradation of pollutants attracts the attention on the possibility of their future environmental applications. However, chromates(VI) are present mainly in the liquid phase, what is a serious disadvantage when considering the $TiO_2$–$Cr^{VI}$ systems as photocatalysts. In addition, $Cr^{VI}$ may undergo a subsequent reduction to chromium(III) [30]. Therefore, immobilization of chromates(VI) at $TiO_2$ should be considered. The simplest way of immobilization is an adsorption process, which may be controlled by pH of the solution, concentration of the adsorbate, ionic strength and temperature. The adsorption of chromium(VI) species at the $TiO_2$ surface results mainly from the electrostatic interactions. FTIR measurements excluded possibility of chromates(VI) chemisorption [44]. Thus, positively charged surface of $TiO_2$ at low pH (below ~6.5 [45,46]) should facilitate

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adsorption of the negatively charged $HCrO_4^-$ ions being the main form of chromate(VI) present at applied pH and low chromate concentrations [47]. Nevertheless, the equilibrium between adsorbed and desorbed $Cr^{VI}$ species assures continuous washing out of the chromates.

Other approaches preventing chromate transfer to the solution might involve chemisorption of chromate(VI) at the surface of titanium dioxide by introducing the anchoring ligands to the chromium(VI) complex or synthesis of composites constituted of $TiO_2$ and water insoluble chromates(VI). In this paper we present synthesis and tests of photocatalytic activity of $TiO_2$/chromate(VI) systems characterized by a higher stability (hampered desorption of $Cr^{VI}$) compared to that of chromate(VI) adsorbed at suspended $TiO_2$. An additional benefit of using such materials could be related to reversibility of the $Cr^{VI}$ photoreduction in the presence of molecular oxygen [48,49].

## 2. Experimental

### 2.1. Materials

Barium chloride, manganese(II) sulfate, cobalt(II) nitrate hexahydrate, chromium(III) nitrate hexahydrate, potassium chromate and potassium dichromate (*Merck* and *POCh*), titanium isopropoxide (*Aldrich*), isopropanol (*Aldrich*) and barium sulfate (*Fluka*) were used as received. 4-Chlorophenol (4-CP, *Fluka*) was purified by distillation at low pressure. The fraction boiling at 355 K ($p = 5$ Torr) was collected. A commercially available titanium dioxide samples, *Degussa* P25 (anatase/rutile mixture, $50\,m^2\,g^{-1}$) and *Kerr-McGee* Titanhydrat-0 (TH-0, anatase, $330\,m^2\,g^{-1}$), were used.

### 2.2. Synthetic procedures

$K[CrO_3F]$ was synthesized according to the following procedure: 5 g of $K_2Cr_2O_7$ was dissolved in 50 ml of warm, concentrated HF. After cooling to the room temperature the crystalline red product was filtered and dried.

Titanium dioxide (TH-0) was modified by impregnation for 24 h at room temperature with chromium(VI) compounds: $K_2Cr_2O_7$ or $K[CrO_3F]$. The resulted powders, $Cr^{VI}@TiO_2$ and $F\text{-}Cr^{VI}@TiO_2$, were washed 7 times with water, centrifuged, dried and ground in the agate mortar.

Barium, manganese(II), cobalt(II) and chromium(III) chromates(VI) were precipitated from aqueous solutions of potassium chromate(VI) ($0.5\,mol\,dm^{-3}$, 3 ml) by addition of a proper salt (barium chloride, manganese(II) sulfate, cobalt(II) nitrate ($0.5\,mol\,dm^{-3}$, 3 ml), chromium(III) nitrate ($0.75\,mol\,dm^{-3}$, 3 ml)). The obtained materials were rinsed 6–8 times with water, centrifuged, dried at room temperature and calcined in air at various temperature programs: 300 °C for 3 h or 300 °C for 3 h followed by 600 °C for 10 h.

$MCrO_4@TiO_2$ composites were prepared by the impregnation of P25 with $CrO_4^{2-}$ ions followed by precipitation of the water insoluble salts. P25 (0.1 g) was suspended in aqueous solution of $K_2CrO_4$ ($0.2\,mol\,dm^{-3}$, 5 ml), sonicated for 1 h and rinsed 2 times with water. The obtained samples were treated with aqueous solutions of barium chloride, manganese(II) sulfate, cobalt(II) nitrate ($0.15\,mol\,dm^{-3}$, 5 ml) and chromium(III) nitrate ($0.3\,mol\,dm^{-3}$, 5 ml). Obtained materials were rinsed 6–7 times with water, centrifuged and dried at room temperature. The composites were used for photocatalytic tests as received or they were additionally calcined at 450 °C for 5 h in air.

$TiO_2@MCrO_4$ composites, with various amounts of chromates(VI) (from 0.5 to 5%; $Cr^{VI}$:$Ti^{IV}$, mol/mol), were prepared using proper amounts (6–50 mg) of water insoluble chromates (*vide supra*) as precursors: $BaCrO_4$, $MnCrO_4$, $CoCrO_4$, or $Cr_2(CrO_4)_3$. New materials were synthesized by a slow hydrolysis of titanium isopropoxide (2 ml) added to the suspension of an appropriate chromate(VI) in isopropanol (8 ml), in humid atmosphere. After two days formed materials were slowly dried at room temperature and calcined at temperatures: 350 °C for 5 h or 450 °C for 5 h or 450 °C for 5 h followed by calcination at 540 °C for 4 h. As a reference material neat $TiO_2$ was synthesized according to the same procedure.

### 2.3. Diffuse reflectance spectra

The diffuse reflectance spectra were recorded using UV–Vis Perkin-Elmer Lambda 35 spectrophotometer equipped with 5 cm dia. integrating sphere. Samples were prepared by grinding the tested materials with barium sulphate powder used also as a reference material. The obtained reflectance spectra were converted to Kubelka-Munk function values, $F(R_\infty)$, defined as $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$; where $R_\infty$ stands for reflectance.

### 2.4. XRD measurements

Crystal structures of investigated materials were confirmed by XRD phase analysis using an *X'PERT PRO MPD* diffractometer, *X'PERT Highscore* software and *PDF-4+* database.

### 2.5. Photoreactivity tests

Photodegradation of 4-chlorophenol (4-CP) in the presence of new materials irradiated with visible light was tested. Stirred suspensions of a modified titanium dioxide ($0.5\,g\,dm^{-3}$) in 20 ml 4-CP solutions ($2.5 \times 10^{-4}\,mol\,dm^{-3}$) were irradiated in a round 2 cm quartz quvette with a high-pressure mercury lamp (HBO-500, 500 W) equipped with 455 nm cut-off and 10 cm $CuSO_4$-solution ($0.1\,mol\,dm^{-3}$) filters. The intensity of incident light in the range of 455–700 nm was $100 \pm 10\,mW\,cm^{-2}$ (the initial area of irradiated suspension was $10\,cm^2$). pH values of the suspensions were within the range of *ca.* 5.5–7.0. During the experiment run 2 ml samples were collected and filtered through a Millipore membrane filter ($0.22\,\mu m$). The absorption spectra of filtrates were recorded at UV–Vis Hewlett Packard HP8453 spectrophotometer. Absorption spectrum of 4-CP consists of two peaks at 225 and 280 nm. The degree of 4-CP decomposition was determined from the absorbance changes measured at 225 nm (measured molar absorption coefficient of 4-CP at 225 nm is $7700\,dm^3\,mol^{-1}\,cm^{-1}$).

### 2.6. Stability of materials (chromium species release)

The stability of prepared materials was estimated on the basis of absorption spectra of samples collected during photocatalytic tests. Appearance of a peak at ∼360 nm was an evidence of the chromium(VI) species present in solution. In neutral and low concentrated $K_2CrO_4$ solutions two main ionic forms of $Cr^{VI}$ coexist: $HCrO_4^-$ with absorption maxima at 260 nm ($2600\,dm^3\,mol^{-1}\,cm^{-1}$) and 350 nm ($1600\,dm^3\,mol^{-1}\,cm^{-1}$) [50], and $CrO_4^{2-}$ with maxima at 275 nm ($3600\,dm^3\,mol^{-1}\,cm^{-1}$) and 373 nm ($4800\,dm^3\,mol^{-1}\,cm^{-1}$) [51].

## 3. Results and discussion

### 3.1. Synthesis of new materials

The surface modified materials were obtained by impregnation of commercially available $TiO_2$ sample TH0 with $K_2Cr_2O_7$ or

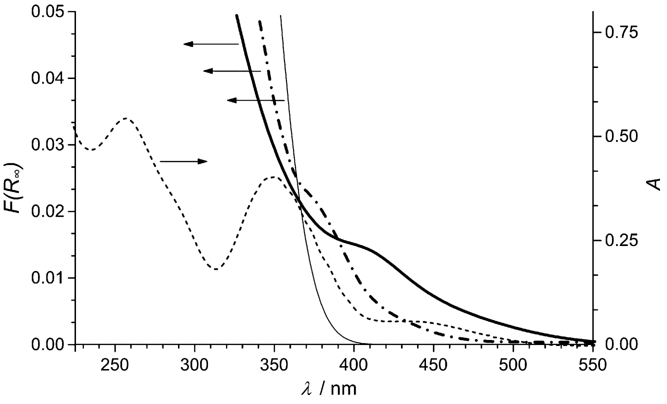

**Fig. 1.** Diffuse reflectance spectra (Kubelka-Munk function) of F-$Cr^{VI}$@$TiO_2$ (thick line), $Cr^{VI}$@$TiO_2$ (-·-·- line) and neat $TiO_2$ (TH0, thin line). For comparison an absorption spectrum of 0.25 mmol $dm^{-3}$ K[$CrO_3F$] aqueous solution is also shown (dotted line).

K[$CrO_3F$]. An adsorption of chromate(VI) at the titanium dioxide surface from acidic solutions allows application of this simple preparative procedure to obtain a yellow material, $Cr^{VI}$@$TiO_2$, although continuous washing causes its bleaching. Substitution of one oxo ligand with fluoride anion affording $[CrO_3F]^-$ enhanced the affinity of the complex to the $TiO_2$ surface as expected from a high affinity of $F^-$ to $TiO_2$ [52]. Obtained F-$Cr^{VI}$@$TiO_2$ powder was also yellow. The $Cr^{VI}$ release to solution from F-$Cr^{VI}$@$TiO_2$ was partially suppressed when compared to $Cr^{VI}$@$TiO_2$.

The composite materials were obtained using two different procedures. The composites from the first group ($MCrO_4$@$TiO_2$, $M^{n+}$: $Ba^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Cr^{3+}$) were synthesized by precipitation of water insoluble chromium(VI) salts from $CrO_4{}^{2-}$ ions adsorbed at $TiO_2$. The second group of materials ($TiO_2$@$MCrO_4$) was obtained by a slow hydrolysis of the $TiO_2$ precursor in the presence of water insoluble chromates(VI). The colour of synthesized composites depended on the $M^{n+}$ ions and calcination temperature. All obtained materials were subjected to spectral characterization and photocatalytic tests.

### 3.2. Diffuse reflectance spectra of materials

Yellow F-$Cr^{VI}$@$TiO_2$ material is characterized by the electronic spectrum presented in Fig. 1. Beside the absorption edge starting around 400 nm characteristic for titanium dioxide, the absorption maximum at 415 nm is pronounced. A significant shift of the absorption maximum points at a significant electronic interaction between the adsorbed (chemisorbed) complex and titanium dioxide surface. For comparison, spectrum of adsorbed chromate(VI) ions resembles that of chromate(VI) ions in solution; the latter does not differ significantly from absorption spectrum of dissolved $[CrO_3F]^-$.

Covering of $TiO_2$ with water insoluble chromium(VI) complexes allowed synthesis of colored materials resistant to bleaching during washing. Diffuse reflectance spectra of the composite materials and unmodified P25 are shown in Fig. 2. All received materials were characterized by a typical $TiO_2$ absorption below 400 nm accompanied by long tails extending to 500–850 nm. Only absorption of $BaCrO_4$@$TiO_2$ above 470 nm is negligible.

The slow hydrolysis of titanium(IV) isopropoxide in the presence of water insoluble chromates(VI) synthesized according to the procedure described in Section 2 resulted in formation of composites with absorption spectra extended towards visible light (Fig. 3). All materials show a bathochromic shift of the typical $TiO_2$ absorption, which in case of $BaCrO_4$@$TiO_2$, $CoCrO_4$@$TiO_2$, $MnCrO_4$@$TiO_2$ materials is additionally accompanied by tails extending to 600–850 nm.

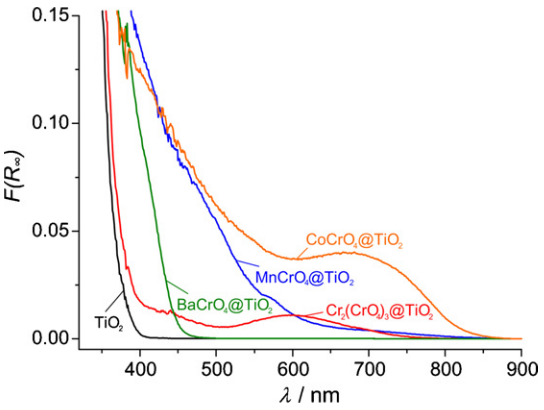

**Fig. 2.** Diffuse reflectance spectra (Kubelka-Munk function) of $MCrO_4$@$TiO_2$ composites and neat $TiO_2$ (P25).

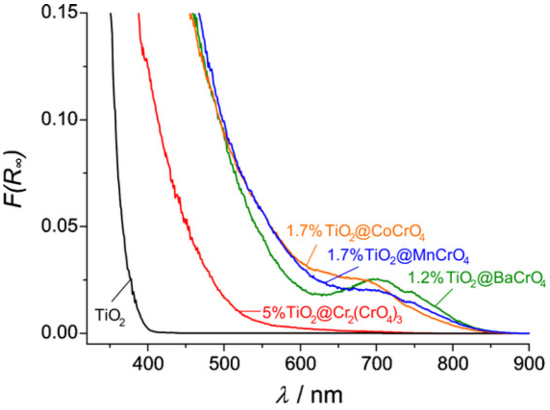

**Fig. 3.** Diffuse reflectance spectra (Kubelka-Munk function) of $TiO_2$@$MCrO_4$ composites calcined at 450 °C and neat $TiO_2$ (P25).

### 3.3. Photocatalytic activity of photocatalysts

The photocatalytic activity of synthesized materials was tested in reaction of 4-CP photodegradation upon visible light irradiation. Decrease in absorbance at 225 nm was taken as the measure of the of 4-CP degradation degree.

Surface modified materials, $Cr^{VI}$@$TiO_2$ and F-$Cr^{VI}$@$TiO_2$, appeared to be active in the process of 4-CP degradation driven by visible light (Fig. 4). Both surface chromate(VI) and fluorochromate(VI) species photosensitize $TiO_2$. Chemisorption of fluorochromate(VI) yielded a more active photocatalyst.

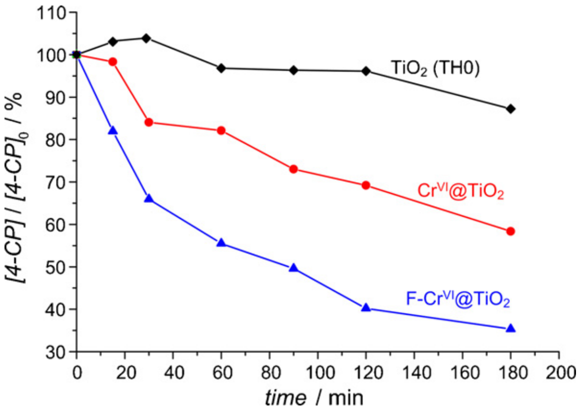

**Fig. 4.** Photodegradation of 4-CP upon irradiation with visible light (λ > 455 nm) in the presence of surface modified materials: $Cr^{VI}$@$TiO_2$ and F-$Cr^{VI}$@$TiO_2$.

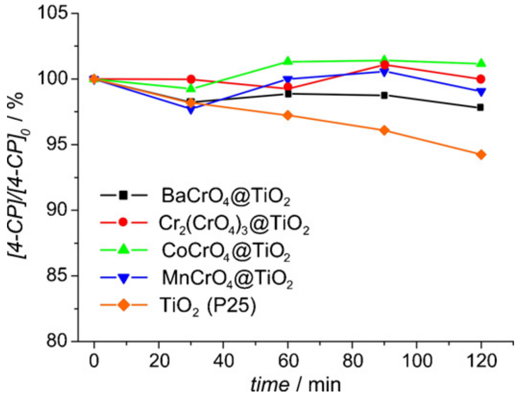

**Fig. 5.** Photodegradation of 4-CP upon irradiation with visible light (λ > 455 nm) in the presence of $MCrO_4@TiO_2$ composites.

The type of preparation procedure applied for synthesis of composites plays a key role in their photoreactivity. Decomposition of 4-CP illuminated with visible light in the presence of $MCrO_4@TiO_2$ composites or unmodified P25 is shown in Fig. 5. Titanium dioxide particles with precipitated water insoluble chromates(VI) showed only a negligible photoreactivity when irradiated with visible light, although all tested $MCrO_4@TiO_2$ materials were coloured. The most photoactive composite, $BaCrO_4@TiO_2$ (2% of degraded 4-CP after 2 h), appeared to be less active than unmodified P25 which was used as a reference material (5.5% of degraded 4-CP after 2 h). The lack of 4-CP photodegradation in the presence of $MCrO_4@TiO_2$-type materials during illumination with visible light points at a very low (if any) efficiency of $TiO_2$ photosensitization. The observed visible light activity of neat P25 may be, to some extent, associated with the formation of charge-transfer complexes between 4-CP and titanium(IV) surface centers acting as $TiO_2$ photosensitizers [53].

Calcination of examined materials at 450 °C for 5 h did not improve their photoreactivity.

Materials prepared using the sol–gel procedure in the presence of water insoluble chromates ($TiO_2@MCrO_4$) showed higher photocatalytic activity as compared to $MCrO_4@TiO_2$ composites. The first two materials, $TiO_2@MnCrO_4$ and $TiO_2@BaCrO_4$, were only slightly photoactive, although they were relatively stable and nicely coloured. Measured fractions of degraded 4-CP amounted 4% and 8% after 2 h of irradiation with visible light in the presence of 1.7% $TiO_2@MnCrO_4$ and 1.2% $TiO_2@BaCrO_4$, respectively (both calcined at 450°C). The highest photocatalytic activity was found for 1.7% $TiO_2@CoCrO_4$ and for 5% $TiO_2@Cr_2(CrO_4)_3$ (Fig. 6). The fractions of 4-CP decomposition in the presence of these materials irradiated with visible light were 15% and 23% after 2 h of irradiation for $TiO_2@Cr_2(CrO_4)_3$ and $TiO_2@CoCrO_4$, respectively. Titanium dioxide samples prepared according to the same procedure but in the absence of any chromium(VI) salt did not show any photoreactivity under parallel conditions (Fig. 6).

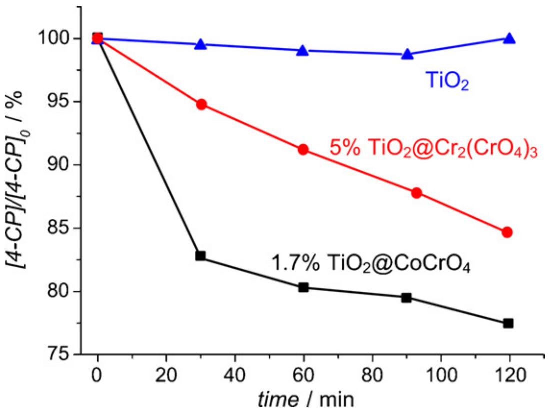

**Fig. 6.** Photodegradation of 4-CP upon irradiation with visible light (λ > 455 nm) in the presence of $TiO_2@CoCrO_4$ and $TiO_2@Cr_2(CrO_4)_3$ composites (calcined at 450 °C).

**Table 1**
The fraction of 4-CP decomposed after 120 min of irradiation of composites with various $Cr^{VI}$ content calcined at various temperatures.

| Composite | $Cr^{VI}:Ti^{IV}$ (mol:mol) [%] | $(1-[4\text{-CP}]_{120}/[4\text{-CP}]_0) \times 100$ [%] | | |
|---|---|---|---|---|
| | | 350 °C | 450 °C | 540 °C |
| $TiO_2@CoCrO_4$ | 0.5 | 4.4 | 6.0 | 2.6 |
| | 0.8 | – | 7.1 | – |
| | 1.7 | – | 22.6 | – |
| | 2.5 | 10.4 | 11.9 | – |
| $TiO_2@Cr_2(CrO_4)_3$ | 0.9 | – | 0.0 | – |
| | 2.0 | – | 8.0 | – |
| | 2.9 | 10.5 | 11.5 | – |
| | 4.0 | – | 14.2 | 6.6 |
| | 5.0 | – | 15.4 | – |
| $TiO_2@BaCrO_4$ | 0.5 | – | 7.9 | – |
| | 1.2 | – | 8.0 | – |
| $TiO_2@MnCrO_4$ | 1.7 | – | 4.1 | – |

In order to clarify the role of water insoluble chromium(VI) salts in the process of 4-CP photodegradation, the photoreactivity of these salts alone was tested. All prepared chromium(VI) salts, applied without calcination or calcined, appeared to be inactive when irradiated with visible or ultraviolet light—no degradation of 4-CP was observed during illumination in the presence of tested materials. In the case of $MnCrO_4$ and $Cr_2(CrO_4)_3$ a weak broad peak at 360 nm appeared after prolonged irradiation, what indicated the presence of certain amounts of dissolved chromium(VI) species. Calcination at 300 °C and 600 °C did not improve stability of these materials. $BaCrO_4$ and $CoCrO_4$ appeared to be less soluble under experimental conditions. The obtained results proved that opposite to the aqueous solution containing the excited $HCrO_4^-/CrO_4^{2-}$ ions [42] the photoinduced electron transfer from 4-chlorophenol to the excited $Cr^{VI}$ species in the solid phase is not effective. The photocatalytic activity of some composites did not result thus from intrinsic properties of chromium(VI) compounds alone, but from photosensitization of $TiO_2$ matrix with chromates (*vide infra*).

### 3.4. *Optimization of the photocatalysts*

Photoreactivity of $TiO_2@MCrO_4$ composites depends strongly on the chromate content. The best performance of the photocatalysts based on cobalt(II) chromate was achieved for *ca.* 1.7% Cr(VI):Ti(IV) molar ratio. Materials containing higher or lower amounts of $CoCrO_4$ showed a decreased photoreactivity as compared to this material (Table 1). Photocatalytic activity of the materials based on $Cr_2(CrO_4)_3$ was increasing with the growing $Cr^{VI}:Ti^{IV}$ molar ratio, reaching maximum for the composite containing 5% of $Cr^{VI}$ (Table 1).

Calcination temperature revealed as another factor influencing photoreactivity of composites (Table 1). The most active materials were obtained after calcination at 450 °C for 5 h. XRD measurements confirmed formation of the anatase crystal structure of $TiO_2$ under applied conditions. The diffractograms recorded for $TiO_2@CoCrO_4$ and $TiO_2@Cr_2(CrO_4)_3$ materials after such thermal treatment revealed contribution of neither rutile phase of titanium dioxide nor crystal phases characteristic for involved chromates(VI) (Fig. 7). Calcination temperatures lower than 350 °C could not assure good crystallization of the amorphous $TiO_2$ matrix formed during the sol–gel process. On the other hand, too high temperatures may lead to formation of larger crystallites with

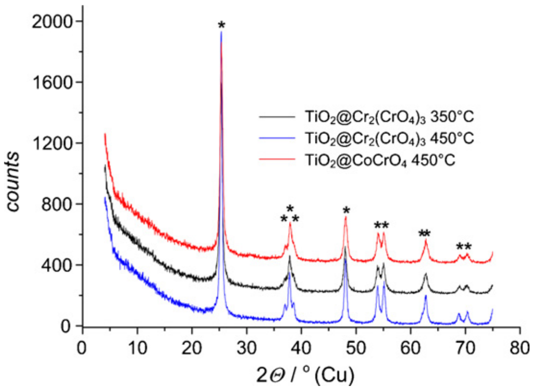

**Fig. 7.** XRD analysis of selected $TiO_2@MCrO_4$ materials annealed at given temperatures. Peaks characteristic for anatase-$TiO_2$ are marked with stars.

lower specific surface area and to some admixtures of the rutile form.

### 3.5. *Stability of photoactive materials*

The material obtained by $TiO_2$ impregnation with fluorochromate(VI), F-$Cr^{VI}@TiO_2$, appeared to be moderately stable. Although the interaction between $TiO_2$ and adsorbed species was relatively strong comparing to $Cr^{VI}@TiO_2$, the bands characteristic for $Cr^{VI}$ species at the absorption spectra of the samples collected during the irradiation and bleaching of the photocatalyst could be observed (data not shown). Since stability of this system was still not satisfactory the quantitative characterization of the $Cr^{VI}$ desorption properties was not undertaken.

The $MCrO_4@TiO_2$ composites showed much higher stability under experimental conditions. No bleaching of the illuminated suspensions was observed. Also the absorption spectra of 4-CP filtrates collected during experiment runs with all prepared composites did not contain the peak at 360 nm, characteristic for dissolved chromates(VI), what proves that neither desorption nor dissolution of $CrO_4{}^{2-}$ species took place.

The synthesis of $TiO_2$ in the presence of water insoluble chromate(VI) salts resulted in formation of the materials characterized by slightly lower, but still a relatively good thermal and photostability. The highest amounts of free chromate(VI) ions (monitored by measuring the solution absorbance at 360 nm) present in tested suspensions were found for samples containing $TiO_2@Cr_2(CrO_4)_3$ (5% $Cr^{VI}$, calcined at 450 °C) and $TiO_2@CoCrO_4$ (2.5% $Cr^{VI}$, calcined at 450 °C), while the lowest concentrations of $CrO_4{}^{2-}$ were observed in the case of $TiO_2@Cr_2(CrO_4)_3$ and $TiO_2@CoCrO_4$ suspensions with the chromium(VI) content below 1%. In the case of $TiO_2@Cr_2(CrO_4)_3$ composites better stability was achieved for materials calcined at higher temperatures.

## 4. Conclusions

The photoreactivity of titanium dioxide modified by chromates(VI) depends on the preparation procedure. The highest activity, accompanied, however, with the unsatisfactory stability, was observed for titanium dioxide impregnated with fluorochromate(VI). Relatively good stability and activity upon visible-light irradiation were found for the composite materials prepared by hydrolysis of $(i\text{-PrO})_4Ti$ in the presence of water insoluble chromate(VI) salts.

The conceivable mechanism of 4-CP degradation involves excitation of the chromate(VI) part of the composite (or surface modified $TiO_2$) within the ligand-to-metal charge transfer transition, $O^{-II} \rightarrow Cr^{VI}$, since the LMCT absorption band of chromate(VI) extends to visible part of light (compare Fig. 1). Some authors postulate excitation of the titania matrix within its vestigial absorption of visible light followed by reduction of $Cr^{VI}$ [38]. Both mechanisms result in chromium(V) formation and 4-CP oxidation. The processes require a good contact between $TiO_2$ and chromate(VI) that should be enabled by $Cr^{VI}$ chemisorption or formation of the $TiO_2@MCrO_4$ composite, as in the case of $TiO_2@CoCrO_4$ material. According to XRD analysis, insoluble chromates ($CoCrO_4$ and $Cr_2(CrO_4)_3$) did not form any crystallites within the titania matrix—a possible explanation of this fact may be based on formation of the $TiO_2$ crystallites around amorphous chromates or *quasi*-homogeneous distribution of the chromate in $TiO_2$ during the sol–gel procedure. In the second case an efficient chromate–titania interaction may be expected. Synthesized and tested composites constitute thus a new class of stable, visible-light active photocatalysts based on titanium dioxide. Further studies, however, are needed to elucidate details of the photosensitization mechanism.

The frequently occurring problem with low stability of modified $TiO_2$ materials can be solved by choice of optimal synthetic parameters. The efficiency of the photocatalytic process depends strongly on the $M^{n+}$ cation, $Cr^{VI}$ content and the calcination temperature. The best photocatalytic activity was observed for 1.7% $TiO_2@CoCrO_4$ and 5% $TiO_2@Cr_2(CrO_4)_3$, calcined at 450 °C, *i.e.* the temperature facilitating anatase formation.

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