J Therm Anal Calorim (2010) 101:607–613
DOI 10.1007/s10973-010-0893-7

Thermal behaviour of titanium dioxide nanoparticles prepared by precipitation from aqueous solutions

**P. Pulišová · J. Boháček · J. Šubrt · L. Szatmáry ·
P. Bezdička · E. Večerníková · V. Balek**

CCTA10 Special Issue

Abstract Thermogravimetry-differential thermal analysis, emanation thermal analysis, mass spectrometry detection, Fourier transform infrared and XRD were used to characterize thermal behaviour of titanium dioxide photocatalyst precursors prepared by precipitation at various conditions from peroxotitanic acid sols. The transmission electron microscopy HRTEM technique was used to characterize the surface microstructure. The sols contained TiO_2 anatase particles of approximately 10 nm in diameter. During heating of the air dried samples, their chemical degradation took place giving rise to anatase. On further heating, the crystallization of anatase and formation of rutile phase was observed. To test the photocatalytic activity of the samples, the decomposition of 4-chlorophenol (4-CP) under ultraviolet and visible irradiation was monitored. It was shown that photocatalytic activities of the samples are comparable to the Degussa P25 photocatalyst reference material.

Keywords Thermogravimetry · Differential thermal analysis · Emanation thermal analysis · Titanium dioxide · Anatase · Rutile · Photocatalyst

Introduction

The photocatalysis is one of the most favourable methods to decompose organic contaminants in water or air. Nanoparticulate titanium dioxide (anatase) photocatalyst is considered as the most effective material with respect to its nontoxicity, high photoactivity and low price. To clean contaminated waters, photocatalysis requires sufficient light to initiate chemical reactions leading to the mineralization of organic contaminants. For practical applications of the photocatalysts, it is important to be accessible at acceptable price together with high photoactivity. Another important condition is the environmental acceptability of the process of photocatalyst production.

Moreover, titanium dioxide (TiO_2) is widely applied as a white pigment for paints or cosmetics, a support in catalysis, or is used in gas sensors, in decomposition of dyes in wastewater [1–5]. The uses and performance are strongly influenced by the crystalline structure, the morphology and the particle size. Nanocrystalline TiO_2 particles are of particular interest because of their specifically size-related properties, and therefore many works have focused on the synthesis of nanocrystalline titanium dioxide. As for anatase TiO_2 nanocrystallites, much attention has been paid to hydrothermal methods using amorphous TiO_2 [6], $TiCl_4$ [7–9] or $TiOCl_2$ aqueous solution [10], and sol–gel methods using titanium alkoxides [11–13]. TiO_2 can also be obtained by hydrolysis of titanium compounds, such as titanium tetrachloride ($TiCl_4$) [14, 15] or titanium alkoxides ($Ti(OR)_4$) [16, 17], in solution. However, the use of starting materials containing chlorine or organic ligand usually resulted in the residue of chlorine or carbon in the as-prepared powder, which should increase the environmental impact. Therefore, chlorine- or organic-free route for preparation of high-purity TiO_2 nanoparticle is

---

P. Pulišová (✉) · J. Boháček · J. Šubrt · L. Szatmáry ·
P. Bezdička · E. Večerníková
Institute of Inorganic Chemistry of the AS CR, v.v.i, 250 68
Husinec-Řež, Czech Republic
e-mail: pulisovap@yahoo.com

V. Balek
Nuclear Research Institute Řež plc, 250 68 Husinec-Řež,
Czech Republic

preferable for practical application [1, 4, 6]. Preparation of nanosized TiO_2 is mainly by using a sol–gel method, whose main disadvantage is that costly organic solvents are required. In this study, we developed simple method to synthesize $TiO_2{\cdot}nH_2O$ nanoparticles using precipitation from aqueous solutions containing $TiOSO_4$ by ammonia as a precipitation agent succeeded by addition of hydrogen peroxide. The physical properties of prepared nanosized TiO_2 particles were investigated. We examined the activity of TiO_2 particles as a photocatalyst on the decomposition of 4-chlorophenol (4-CP).

Experimental

Preparation of samples

For preparation of the anatase TiO_2 sol, the following materials were used: titanyl sulphate ($TiOSO_4{\cdot}nH_2O$, containing 29 wt% Ti like TiO_2); hydrogen peroxide (H_2O_2, 30%); ammonia solution ($NH_3.H_2O$, 26%) and distilled water.

The $TiO_2{\cdot}nH_2O$ suspensions were prepared in the two ways.

(a) The titanyl sulphate solution in the distilled water at 35 °C was precipitated by adding the ammonia at approx. 0 °C at three various pH values (pH values were 3, 6 and 8). The white precipitate was filtered and sufficiently washed with distilled water, then treated by hydrogen peroxide to reduce pH value of the precipitate and subsequently treated by isopropanol. Finally, the sample was dried at 35 °C.

(b) Titanyl sulphate was dissolved in the distilled water at 35 °C, then precipitated by adding ammonia solution to reach the pH ≈ 8 and white precipitate $[Ti(OH)_4]$ resulted. The white precipitate was filtered and sufficiently washed with distilled water to remove the NH_4^+ and SO_4^{2-} formed in the reaction, and then added 400 mL distilled water to disperse the precipitate homogeneously. The pH value of the precipitate was reduced by hydrogen peroxide; continual magnetic stirring was required to avoid the immediate dense gel formation during dissolution and to keep the reactant mixed uniformly. The obtained yellow transparent sol was kept in closed bottle and part of it was dried in air at room temperature.

Methods of samples characterization

The thermogravimetry (TG) and differential thermal analysis (DTA) and mass spectrometry (MS) measurements were carried out heating in air and argon, respectively, by using the equipments SETARAM SETSYS Evolution-16-MS and NETZSCH STA 409 MS. The dried fine powders of synthesized samples TiO_2 were used for measurements. The mass of each sample measured was 50.41 mg, and heating rate was 10 °C min^{-1} (from 20 to 1,200 °C).

The emanation thermal analysis (ETA) has been used to characterize the thermal behaviour, transport properties and annealing of microstructure irregularities of the prepared samples on heating in argon. ETA measurements were carried out by using the updated NETZSCH DTA-ETA Type 404 equipment. Details of the less common ETA measurements have been described elsewhere [18, 19]. The ETA involves measurements of radon release rate from samples. The samples were labelled by traces of ^{228}Th as nitrate from the acetone solution. Atoms of radon, ^{220}Rn, were formed by a spontaneous α-decay of ^{228}Th and ^{224}Ra and were incorporated into the sample using the recoil energy of 85 keV $atom^{-1}$. The maximum depth of ^{220}Rn penetration was 80 nm as calculated with Monte Carlo method using TRIM code [20].

The Fourier transform infrared (FTIR) spectra of the samples were measured by Nicolet Nexus 670 FTIR spectrometer in form of KBr pellet in the region 4,000–500 cm^{-1}.

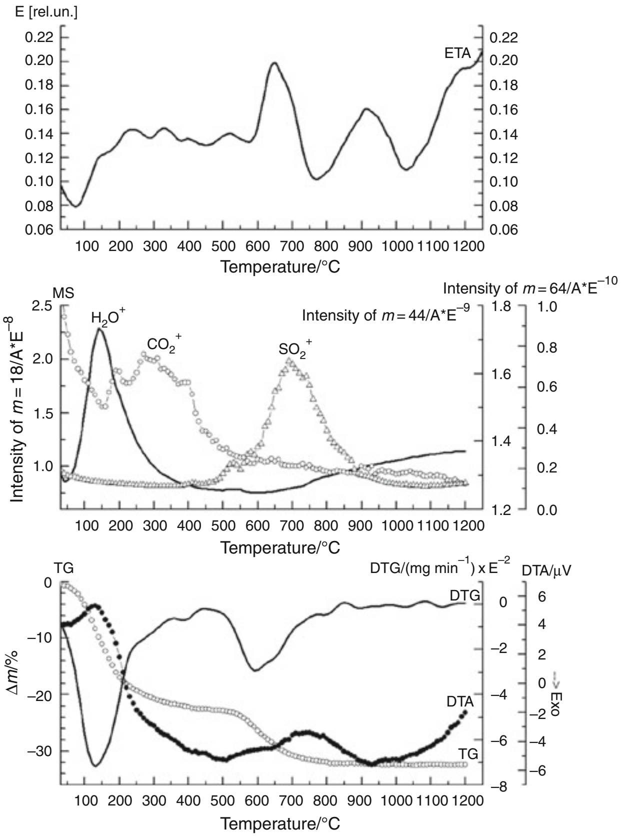

Fig. 1 Results of ETA, MS detection of evolved gases and TG-DTA during heating in air—sample *type a* (pH ≈ 3)

In situ high-temperature powder diffraction were collected with a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (CoKα radiation, 40 kV, 30 mA, line focus) and a multichannel detector X'Celerator with an anti-scatter shield and with the high-temperature chamber HTK 16 (Anton Paar, Graz, Austria). X-ray patterns were measured in the range of 19° to 93° 2Θ with step of 0.0167° and 30 s per step, which resulted a total scan-time of approx. 17 min. Subsequent heating steps were programmed for 25 °C, 100–500 °C for every 100 °C and from 550 to 1,100 °C for every 25 °C with the ramp of 60 °C/min. Qualitative analysis was performed with the HighScore software package (PANalytical, The Netherlands, version 1.0d), Diffrac-Plus software package (Bruker AXS, Germany, version 8.0) and JCPDS PDF-2 database, release 2004. To characterize the particle size and external morphology of the prepared samples, a high-resolution transmission electron microscopy (HRTEM, Type JEOL) at 300 kV accelerating voltage, equipped with EDS was used.

The photocatalytic activities of the prepared samples were characterized from the results of the photodegradation of 4-chlorophenol (4-CP) in an aqueous solution under UV illumination. The source of UV illumination was high pressure mercury lamp with the power of 125 W. The concentration of 4-CP was 0.1 mM and concentration of the photocatalyst was 1 g L^{-1}. The changes in concentrations of 4-CP were estimated by liquid chromatography.

Results and discussion

Figures 1, 2, 3 depict the results of TG-DTA, ETA and MS detection of the gases evolved during air heating of the samples prepared at three pH values (samples of the *type a*). The DTA curves of the each sample show on heating in air endothermic peaks in range from 110 to 300 °C due to the release of chemical and physical absorbed water. In case of sample prepared at pH $\approx$ 8, the endothermic peak around 300 °C may be due to the decomposition of NH_4^+ that remained in the sols. The broad exothermic peak can be seen in the range of 800–1,000 °C due to the slow phase conversion from anatase to rutile phase in each sample.

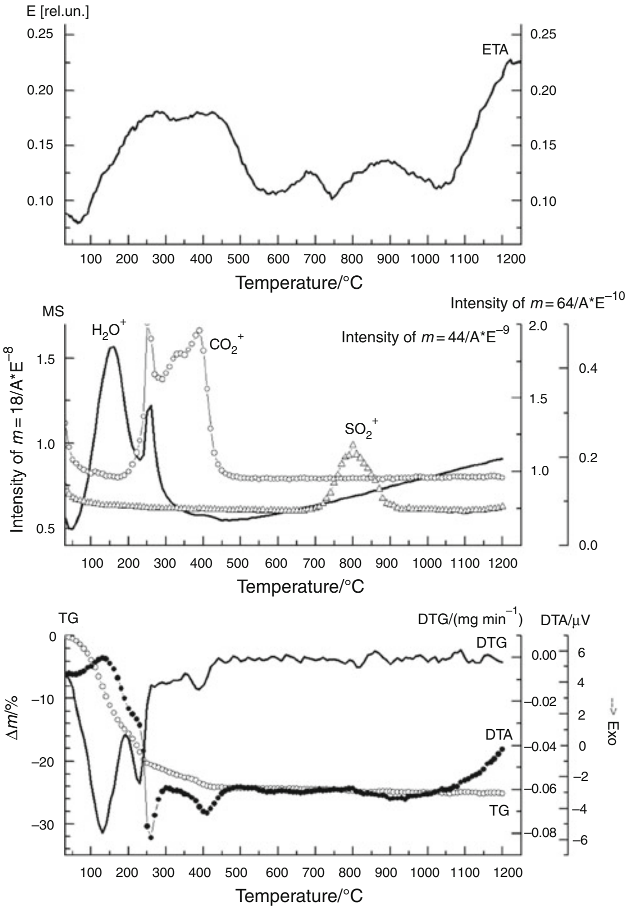

Fig. 2 Results of ETA, MS detection of evolved gases and TG-DTA during heating in air—sample *type a* (pH $\approx$ 6)

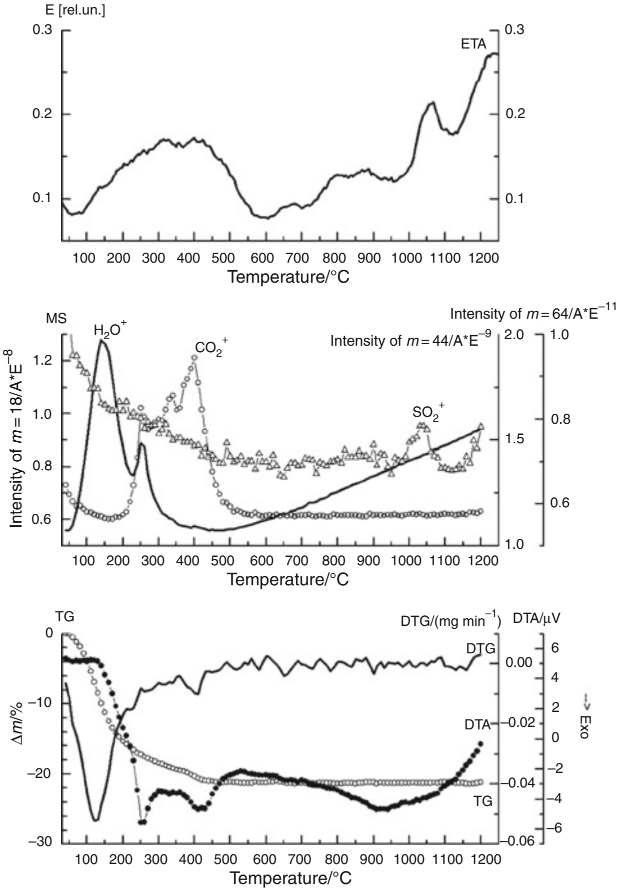

Fig. 3 Results of ETA, MS detection of evolved gases and TG-DTA during heating in air—sample *type a* (pH $\approx$ 8)

The weight loss in the TG curves is from approx. 31.7% for pH ≈ 3 to 20.3% for pH ≈ 8, which is caused by the release of absorbed water and decomposition of NH_4^+ and SO_4^{2-}. From these results, we decided to start use pH ≈ 8 at precipitation step.

Results of emanation thermal analysis, presented as temperature dependencies of emanating power *E*, characterize of the microstructure changes due to the release of gaseous products as the result of thermal degradation and formation of titania. For example in the precursor prepared at pH ≈ 3, the release of SO_2^+ was indicated by the effect on the ETA curve in the range 600 to 800 °C, whereas the effect in the range 900 to 1,050 °C can be ascribed to the crystallization of rutile phase. In the precursor sample prepared at pH ≈ 8, the crystallization of rutile phase was indicated by the effect on the ETA curve in the range 950 to 1,080 °C.

Moreover, another type of the samples was prepared from the $TiO_2 \cdot nH_2O$ suspensions, which were filtered and then few times washed by distilled to remove the NH_4^+ and SO_4^{2-} formed in the reaction. The pH value was reduced from 3 to 4 by adding the H_2O_2 (yellow transparent sol).

The sample kept in closed bottle changed over period of 6 months (transformation from yellow to white colour), no coagulation and precipitate appeared. It was the result of decomposition of peroxotitanic acid (PTA) molecules and increasing content of anatase crystals. When the sample was stored at open air, the yellow transparent sol transforms to yellow gel and then next stage was yellow and orange glassy product, which contains reactants of PTA.

Figures 4 and 5 depict the results of TG-DTA and MS detection of the gases evolved during heating in argon of the samples *type b*.

The results of MS detection are in a good agreement with results of TG-DTA of the sample stored in closed bottle (white colour, Fig. 4) and sample dried in open air (yellow and orange glassy product, Fig. 5). The DTA curves of the each sample measured on heating in argon show endothermic peaks in range from 100 to 400 °C due to the release of chemical and physical absorbed water. The amorphous phase is resulting and the crystallization of anatase phase takes place on further heating. The endothermic peak around 300 °C (Fig. 5) may probably be due to the decomposition of NH_4^+ that remained in the sols. The broad exothermic peak (Fig. 4) can be seen in the range of 550–750 °C due to the slow phase conversion from anatase to rutile phase.

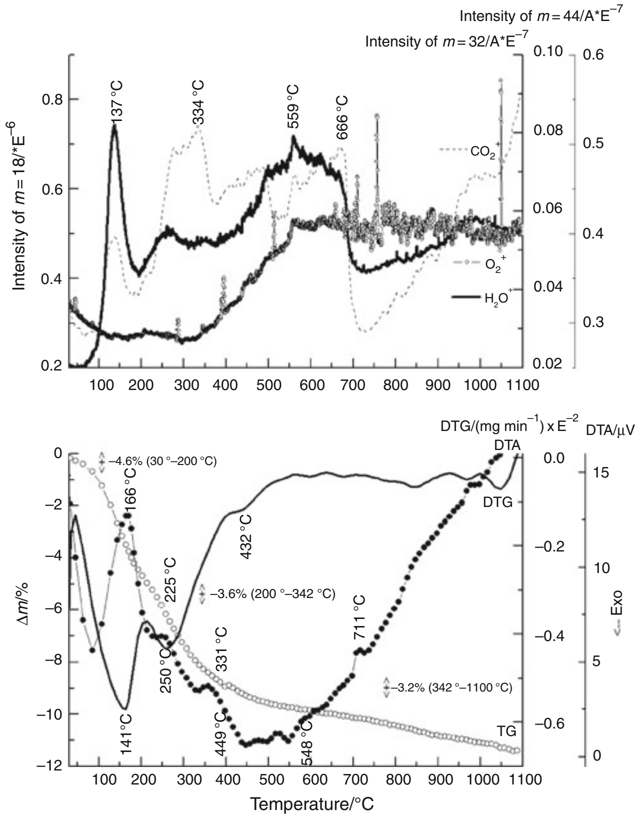

Fig. 4 Results of TG-DTA and MS detection of evolved gases measured in argon—sample *type b* (*white colour*)

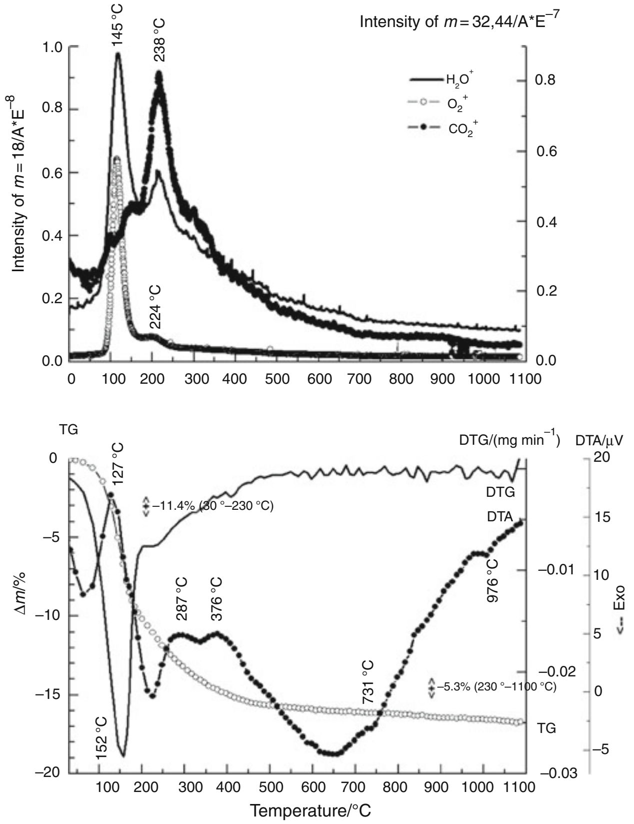

Fig. 5 Results of TG-DTA and MS detection of evolved gases measured in argon—sample *type b* (*yellow glassy product*)

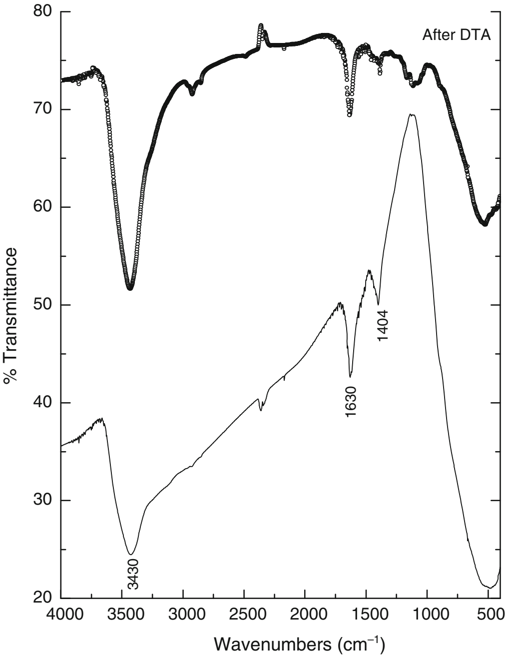

Fig. 6 FTIR spectra of the dried—sample *type b*

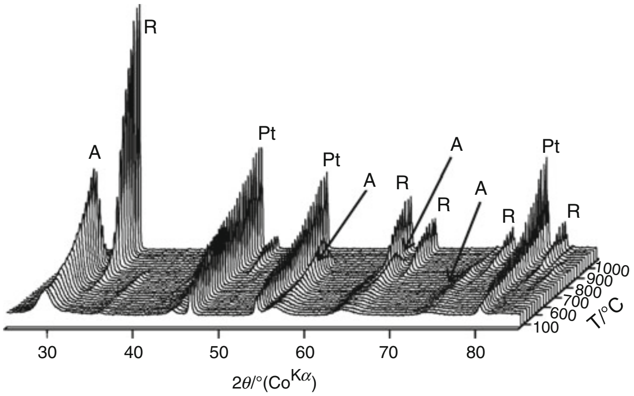

Fig. 7 In situ HT-XRD results of the sample *type b* heated up to 1,100 °C, A—anatase, R—rutile, Pt—platinum sample holder

The FTIR spectra of the sample prepared by the synthesis method *type b* are shown in Fig. 6. The as-dried gels exhibited peaks at 500, 1,404 and 1,630 cm^{-1}, as well as a broad band at 3,200–3,600 cm^{-1}. The absorption from 3,200 to 3,600 cm^{-1} with maximum at 3,400 cm^{-1} can be assigned to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water and the titanium hydroxide. The adsorption around 1,630 cm^{-1} is due to the bending vibration of adsorbed H_2O molecules. The adsorption at 500 cm^{-1} can be, respectively, assigned to the stretching vibrations of the Ti–O bonds and Ti–O–O bonds. The peaks around 1,404 cm^{-1} are due to the stretching vibration of the N–H bonds in the NH_4^+ and CO_3^{2-}, respectively, that remained.

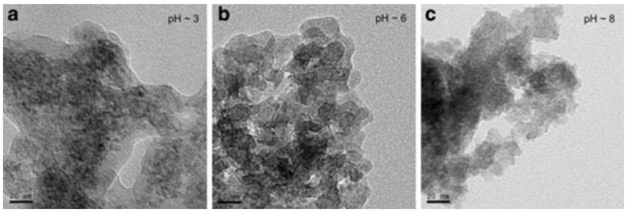

Fig. 8 HRTEM micrographs of prepared samples at various pH values

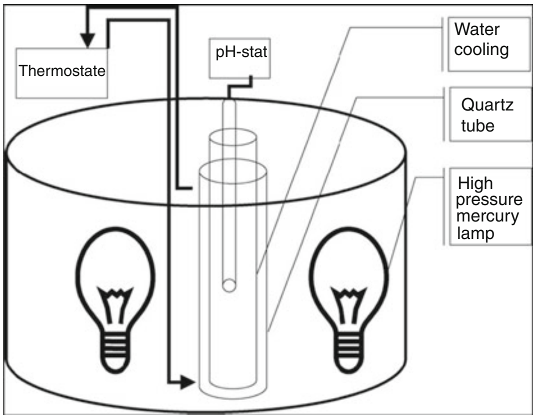

Fig. 9 Water-jacketed laboratory photoreactor

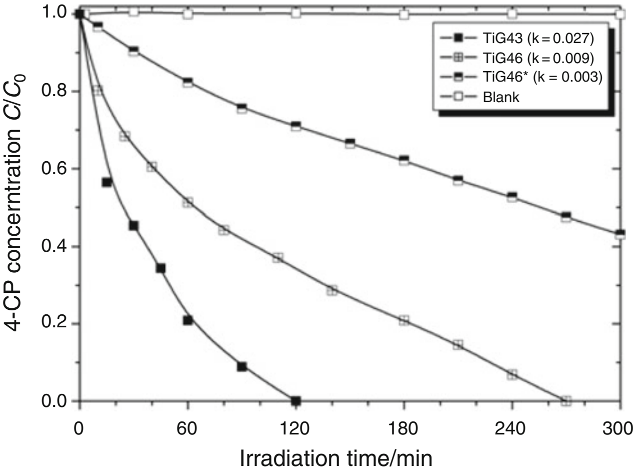

Fig. 10 Results of the kinetics of 4-CP photodegradation to characterize the photoactivity—samples *type b* ("Blank" experiment)

Results of the in situ high-temperature XRD analysis of the sample *type b* are presented in Fig. 7. The XRD patterns of the sample heated from the room temperature to 1,100 °C give four distinctive TiO_2 diffraction lines corresponding to anatase and seven lines corresponding to rutile for temperatures above 700 °C. Broad diffraction lines at lower temperatures indicated nano-crystalline character of the starting anatase phase contrarily to rutile formed at higher temperatures with better crystallinity.

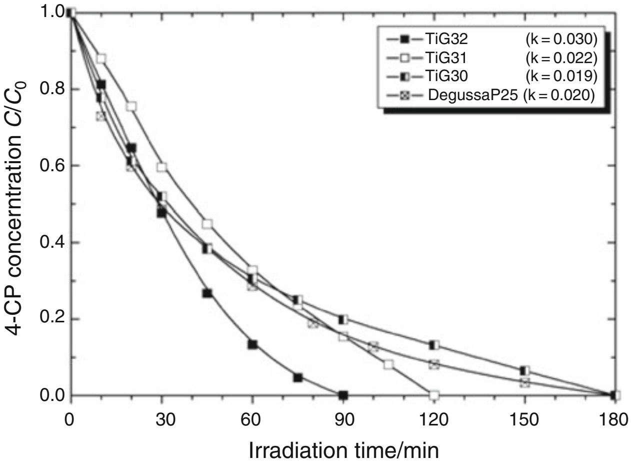

Fig. 11 Results of the kinetics of 4-CP photodegradation—samples *type b* (comparison with reference material Degussa P25)

The HRTEM micrographs of the samples *type a* prepared at various pH values are shown in Fig. 8a, b, c. From the micrographs, we can see that the morphology of the particles is changing with increasing pH value. The borders between particles occur with increasing pH and the amount of SO_2^+ is reduced (see TG-DTA curves, Figs. 1, 2, 3). Owing to these processes, the particle volume is reduced and particles are approx. 10 nm in diameter.

Figure 9 depicts the scheme of the water-jacketed magnetically stirred laboratory photoreactor. Figures 10 and 11 show the results of the decreasing concentration of 4-CP during the photodegradation test by using the prepared sample *type b*.

It is obvious from Figs. 10 and 11 that the sol samples prepared in this study exhibited the photocatalytic activity comparable to the reference titania sample Degussa P25. To exclude the possibility of decomposition of 4-CP by oxidation of hydrogen peroxide the “BLANK” experiment performed without presence of light source. Lower photodegradation of the 4-CP was affected by lower volume of the sample because of previous “BLANK” experiment (Fig. 10).

Conclusions

The TG-DTA, ETA, MS detection, FTIR and XRD were used for characterization of thermal behaviour of titania photocatalyst prepared at various conditions from titania sols. The yellow transparent samples were synthesized by precipitation from PTA sol in various conditions (in various pH and storage conditions). During heating the chemical composition of the samples in air, the amorphous anatase was formed. On further heating of the samples, the crystallization of anatase and formation of rutile phase took place. The photocatalytic activity of the initial samples were tested by the photodegradation of 4-CP. It was shown that the photocatalytic activities of the prepared samples are comparable to the Degussa P25 photocatalyst reference material. By this way, a new inexpensive method for the preparation of titania photocatlayst was suggested.

Acknowledgements This work was supported by Ministry of Education, Youth and Sports of the Czech Republic (Project NANOPIN 1 M4531477201 and Project INGO LA-292).

References

1. Gao Y, Masuda Y, Seo W-S, Ohta H, Koumoto K. TiO_2 nanoparticles prepared using an aqueous peroxotitanate solution. Ceram Int. 2004;30:1365–8.
2. Thompson DW, Kelly CA, Farzad F, Meyer GJ. Sensitization of nanocrystalline TiO_2 initiated by reductive quenching of molecular excited states. Langmuir. 1999;15:650–5.
3. Crepaldi EL, Soler-Illia GJAA, Grosso D, Ribot F, Cagnol F, Sanchez C. Controlled formation of highly organized mesoporous titania thin films: from mesostructured hybrids to mesoporous nano-anatase TiO_2. J Am Chem Soc. 2003;125: 9770–8.
4. Ryu YB, Jung WY, Lee MS, Jeong ED, Kim HG, Yang JS, Lee G-D, Park SS, Hong S-S. Hydrothermal synthesis of titanium dioxides from peroxotitanate solution using basic additive and their photocatalytic activity on the decomposition of orange II. J Phys Chem Solids. 2008;69:1457–60.
5. Ge L, Xu M, Sun M, Fang H. Fabrication and characterization of nano TiO_2 thin films at low temperature. Mater Res Bull. 2006;41:1596–603.
6. Yanagisawa K, Ovenstone J. Crystallization of anatase from amorphous titania using the hydrothermal technique: effects of starting material and temperature. J Phys Chem B. 1999;103: 7781.
7. Cheng H, Ma J, Zhao Z, Qi L. Hydrothermal preparation of uniform nanosize rutile and anatase particles. Chem Mater. 1995;7:663–71.
8. Moser J, Grätzel M. Light-induced electron transfer in colloid semiconductor dispersions: single versus dielectronic reduction of acceptors by conduction-band electrons. J Am Chem Soc. 1983;105:6547–55.
9. Anpo M, Shima T, Kodama S, Kubokawa Y. Photocatalytic hydrogenation of CH_3CCH with H_2O on small-particle TiO_2: size quantization effects and reaction intermediates. J Phys Chem. 1987;91:4305.
10. Kim S-J, Park S-D, Jeong YH, Park S. Homogeneous precipitation of TiO_2 ultrafine powders from aqueous $TiOCl_2$ solution. J Am Ceram Soc. 1999;82:927.
11. Zhang Z, Wang C-C, Zakaria R, Ying JY. Role of nanoparticle size in nanocrystalline TiO_2-based photocatalysts. J Phys Chem B. 1998;102:10871.
12. Uchida H, Hirao S, Torimoto T, Kuwabata S, Sakata T, Mori H, Yoneyama H. Preparation and properties of size-quantized TiO_2-particles immobilized in poly(vinyl pyrrolidinone) gel films. Langmuir. 1995;11:3725–9.
13. Crisan M, Braileanu A, Crisan D, Raileanu M, Dragan N, Mardare D, Teoderescu V, Ianculescu A, Birjega R, Dumitru M. Thermal behaviour study of some sol-gel TiO_2 based materials. J Therm Anal Calorim. 2008;92(1):7–13.

14. Santacesaria E, Tonello M, Storti G, Pace RC, Carra SJ. Kinetics of titanium dioxide precipitation by thermal hydrolysis. J Colloid Interface Sci. 1986;111:44–53.
15. Matijevic E, Budnick M, Meites L. Preparation and mechanism of formation of titanium dioxide hydrosols of narrow size distribution. J Colloid Interface Sci. 1977;61:302–11.
16. Chemseddine A, Moritz T. Nanostructuring titania: control over nanocrystal structure, size, shape and organization. Eur J Inorg Chem. 1999;2:235–45.
17. Bischoff BL, Anderson MA. Peptization process in the sol-gel preparation of porous anatase (TiO_2). Chem. Mater. 1995;7:1772.
18. Balek V, Tölgyessy J. Emanation thermal analysis and other radiometric emanation methods, In: Svehla G, editor. Wilson and Wilson's comprehensive analytical chemistry, Part XIIC. Amsterdam: Elsevier Science Publishers; 1984. 304 pp.
19. Balek V, Brown ME. Less common techniques. In: Brown ME, editor. Handbook on thermal analysis and calorimetry, vol. 1, chap. 9. Amsterdam: ELSEVIER SCIENCE B.V.; 1998. p. 445.
20. Ziegler JF, Biersack JP, Littmark U. The stopping and range of ions in solids. New York: Pergamon Press; 1985.