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Thermal analysis methods in the characterization of photocatalytic titania precursors

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Abstract A new method for the preparation of titania photocatalyst was proposed. Precursors of the photoactive titania were prepared from $TiOSO_4 \cdot nH_2O$ solution by precipitation with ammonia and addition of H_2O_2 or HNO_3, respectively. Methods of TG, DTA, ETA, EGA/MS detection and FTIR were used to characterize the thermal degradation of the titania precursor and to determine the optimal temperature to obtain the photoactive titania. ETA made it possible to characterize the microstructure development of the samples in the heating conditions.

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

Introduction

Methods for preparation of photoactive titania and the characterization of its photocatalytic properties have been described in several publications [1–14]. In this study, a new modified procedure for the preparation of titania photoactive samples is proposed using precipitation of $TiOSO_4 \cdot nH_2O$ solution by ammonia as a precipitation agent and the subsequent addition of H_2O_2 or HNO_3, respectively.

Experimental

Preparation of samples

For the preparation of titania sol, the titanyl sulphate $TiOSO_4 \cdot nH_2O$ was used.

The $TiO_2 \cdot nH_2O$ suspensions were prepared in the two ways:

(i) Titanyl sulphate was dissolved in the demineralised water at 35 °C and precipitated by adding ammonia solution to reach pH $\approx$ 8. The white precipitate was filtered and washed with a demineralised water to remove NH_4^+ and SO_4^{2-} ions formed, subsequently a demineralised water was added. The pH value of the precipitate was decreased to pH $\approx$ 2.5 by addition of H_2O_2; a continual magnetic stirring for 1 h was used to avoid immediate dense gel formation during dissolution.

(ii) Titanyl sulphate was dissolved at 35 °C in the demineralised water and precipitated by adding ammonia solution to reach pH $\approx$ 8. The precipitate was filtered and washed with demineralised water. The pH value of the precipitate was reduced to pH $\approx$ 1.5 by addition of HNO_3; a continual magnetic stirring for 24 h at 70 °C was used.

Methods of samples characterization

The thermogravimetry (TG), differential thermal analysis (DTA), evolved gas analysis/mass spectrometry (EGA/MS) measurements were carried out by heating in argon using the equipment NETZSCH STA 409 MS. The measurements were carried out by heating rate 10 °C min^{-1} in the argon flow (75 mL min^{-1}). The dried fine powders of the

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titania were used for the TG, DTA and EGA/MS measurements. The samples mass was 0.05 g. Gaseous products were analysed in the MID mode as intensity (A) of individual selected fragments.

The emanation thermal analysis (ETA) was used to characterize the microstructure development of the prepared titania precursors. ETA measurements were carried out in argon using the NETZSCH DTA-ETA Type 404 equipment. Details concerning the ETA measurements are described in publications [15, 16]. The samples for the ETA measurements were labelled by traces of ^{228}Th as a source of radon, the release of which was measured. Atoms of radon, ^{220}Rn were formed by a spontaneous α-decay of ^{228}Th and ^{224}Ra and incorporated into the sample using the recoil energy of 85 keV atom^{-1}. The maximum depth of ^{220}Rn penetration is 80 nm as calculated with Monte Carlo method using TRIM code [17].

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 4,000–400 cm^{-1}.

A scanning electron microscope (SEM, Type CP XL 30, Philips) equipped with EDS analyzer was used to characterize the particle size and morphology of the titania samples.

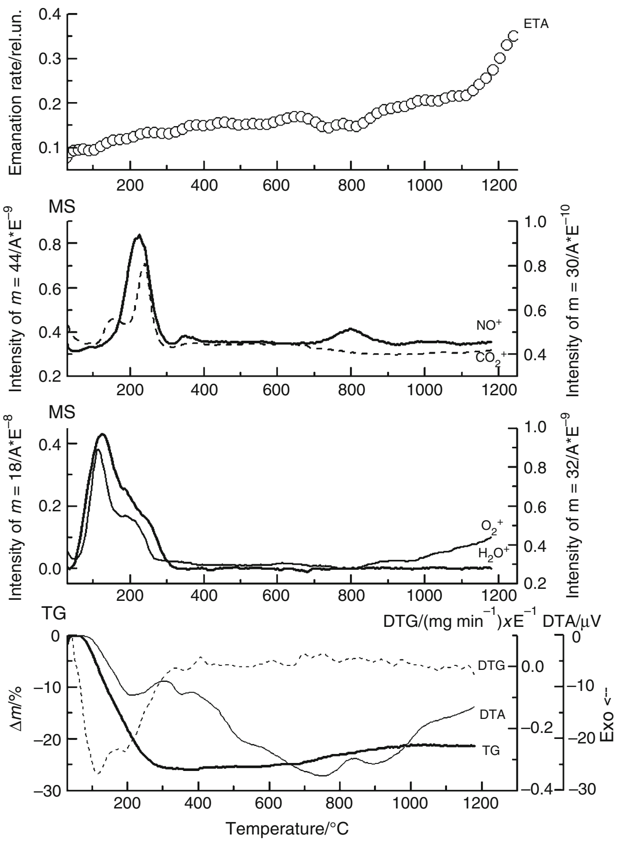

Fig. 1 Results of ETA, EGA/MS, TG and DTA characterizing thermal behaviour of the titania precursor prepared by addition of H_2O_2

Results and discussion

Figures 1 and 2 depict the results of TG, DTA, ETA and results of EGA/MS of the samples during heating in argon. The TG and DTA effects observed on heating to 300 °C are due to the release of water as confirmed by the results of EGA/MS. Moreover, the EGA/MS indicated the release of water, ammonia, NO_x and CO_2, making it possible to determine the temperature intervals of the gases evolution during the thermal degradation of the precursors.

Results of emanation thermal analysis (ETA), presented as temperature dependencies of radon release rate (emanation rate E), characterize the microstructure development due to thermal degradation of the prepared samples and the formation of photoactive titania. In the titania precursor prepared by using H_2O_2, the decrease of the emanation rate in the range from 650 to 750 °C (Fig. 1) characterize the microstructure arrangement of the sample after titania precursor degradation. From the ETA results in Fig. 2 it followed that the microstructure arrangements of the titania precursor prepared by addition of HNO_3 take place in the temperature range from 250 to 750 °C associated with the titania precursor degradation. The effect on the ETA curve (Fig. 2) in the range from 920 to 1,000 °C corresponds to the crystallization of rutile phase. The thermal analysis results were used to determine temperature intervals of the degradation and microstructure development during heating of the samples. The optimal conditions for the heat treatment of the titania precursors to prepare the photoactive titania were recommended from these data.

The FTIR spectra (Figs. 3 and 4) of the both titania precursors studied contain the bands at 3,400 cm^{-1} and approx. at 1,600 cm^{-1} assigned to the stretching vibration of hydrogen bonded OH groups of the adsorbed water molecules. The adsorption bands observed at 3,200 cm^{-1} and 1,400 cm^{-1} correspond to the vibration of the NH_4^+ cation on the surface of the sample. This vibration band is characteristic for the NH_4^+ containing salts. The vibrations characterized by the peak at 1,400 cm^{-1} can be assigned to the ions of CO_3^{2-} or NO_3^-. Broad bands found below 1,000 cm^{-1} are characteristic for the Ti–O bonds in TiO_2 lattice.

A sharp effect at 914 cm^{-1} observed in Figs. 3 and 5 is not typical for the titania system. There is a possibility that the chemical reaction between titanium cations with H_2O_2 take part, giving rise to a poorly soluble peroxo-titania complexes $(NH_4)_x(TiO_y)(OOH)_z$ or $(TiO_y)(OOH)_z(OH)_w$, respectively. No similar effect was observed in the FTIR spectra of the titania sample prepared by using HNO_3 (Fig. 4).

The differences in FTIR spectra (see Fig. 5) of the titania samples prepared by using H_2O_2 before heat

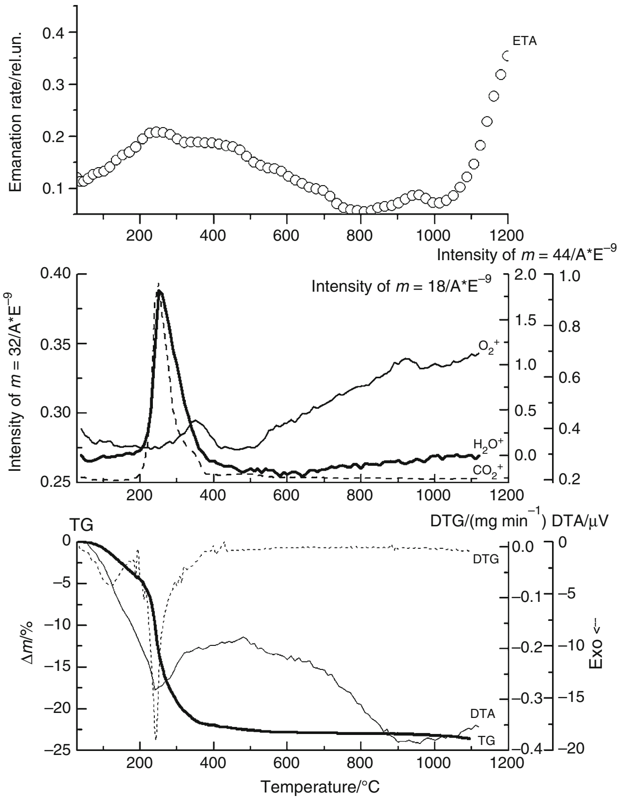

Fig. 2 Results of ETA, EGA/MS, TG and DTA characterizing thermal behaviour of the titania precursor prepared by addition of HNO_3

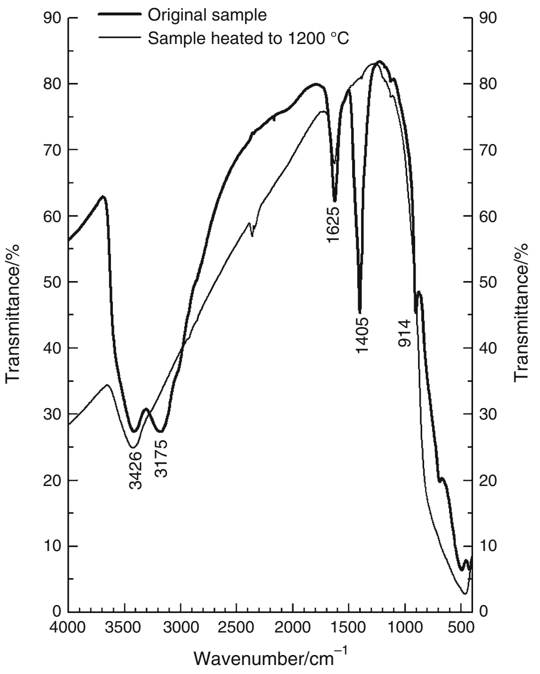

Fig. 3 FTIR spectra of the titania precursor prepared by using H_2O_2

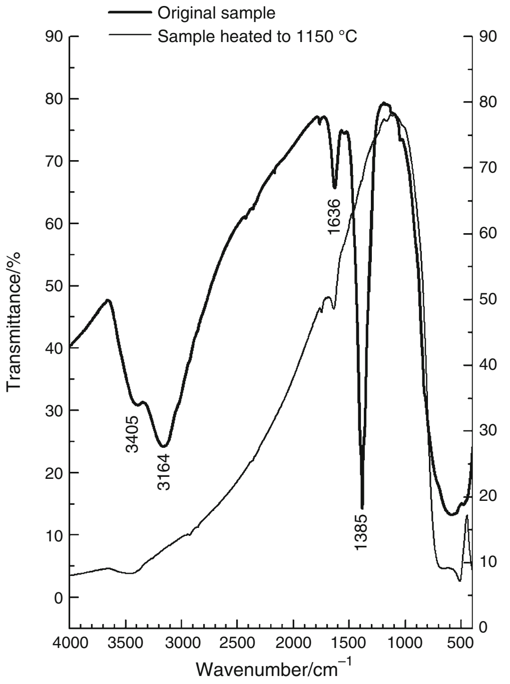

Fig. 4 FTIR spectra of the titania precursor prepared by using HNO_3

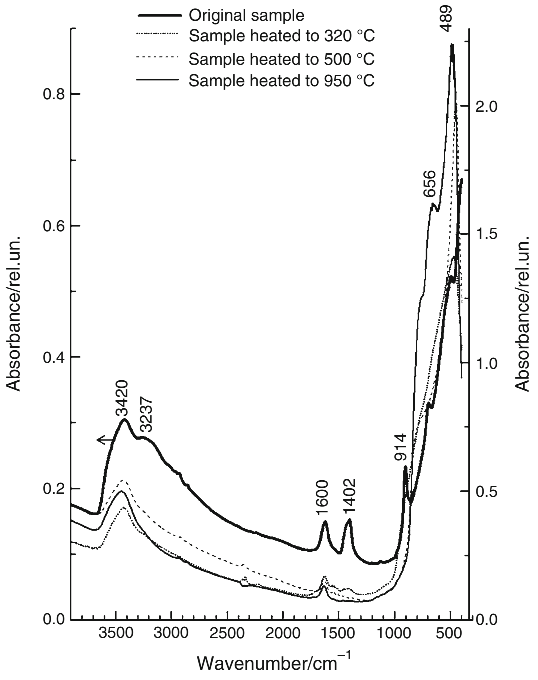

Fig. 5 FTIR spectra of the titania samples prepared from the precursor using H_2O_2 and heated to 320, 500 and 950 °C, respectively

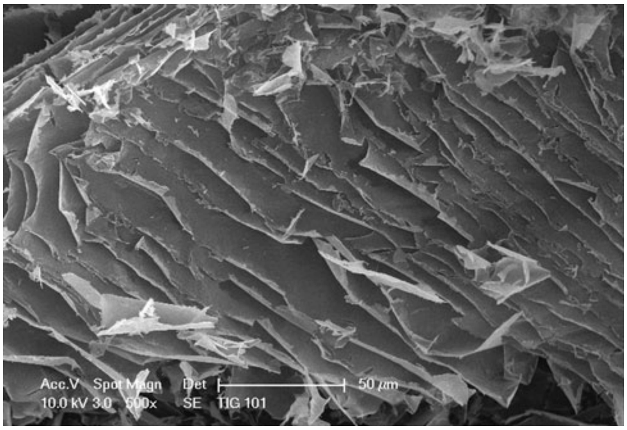

Fig. 6 SEM micrograph of titania precursor prepared by using H_2O_2

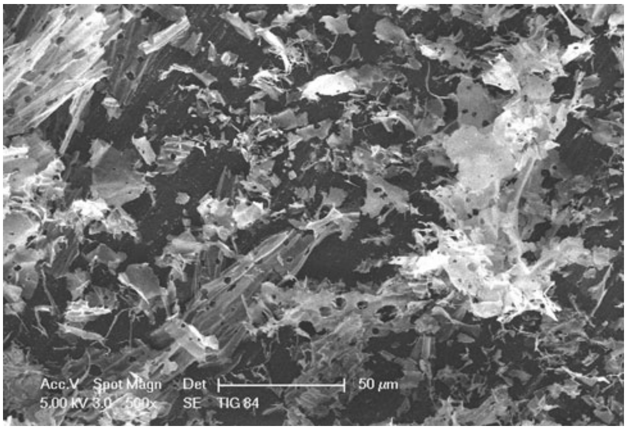

Fig. 7 SEM micrograph of titania precursor prepared by using HNO_3

treatment and after heating to 320, 500 and 950 °C confirmed that the ions of CO_3^{2-} or NO_3^- were eliminated from the sample by heating.

From the SEM micrographs of the titania samples prepared at various conditions (Figs. 6 and 7) it can be seen that the thin foils shaped samples have a layered structure.

Conclusions

A new method for the preparation of titania photocatalyst was developed. Methods of TG, DTA, ETA, EGA/MS and FTIR made it possible to characterize the thermal behaviour of titania precursors prepared by using H_2O_2 and HNO_3, respectively and to recommend optimum temperature for the preparation of the photoactive titania.

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