Catalysis Communications 24 (2012) 5–10

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

A new method for preparation of rutile phase titania photoactive under visible light

Jakub Orlikowski, Beata Tryba *, Janusz Ziebro, Antoni W. Morawski, Jacek Przepiórski

West Pomeranian University of Technology, Institute of Chemical and Environmental Engineering, Pułaskiego 10, 70-322 Szczecin, Poland

ARTICLE INFO

Article history:
Received 2 January 2012
Received in revised form 28 February 2012
Accepted 29 February 2012
Available online 8 March 2012

Keywords:
TiO_2-rutile
Sol–gel
Phenol photodegradation
Visible light activity

ABSTRACT

New preparation method of rutile phase TiO_2 revealing photocatalytic activity under visible light is described. The photocatalysts were prepared using sol–gel synthesis followed by a flash combustion at 850 °C. As found, addition of glycerol to the titanium isopropoxide during sol–gel synthesis strongly influences size of TiO_2 crystallites. Rutile-type TiO_2 obtained showed ability to degrade photocatalytically phenol under visible light. Effectiveness of the mineralisation of phenol was comparable or insignificantly higher than these of commercial TiO_2 samples: Evonik P25 and R-001.

1. Introduction

In recent years photocatalytic degradation of organic compounds has been widely studied. One of the most important photocatalysts being frequently employed in this process is titania. TiO_2 occurs in three polymorphous states: anatase, rutile, and brookite. Unfortunately, only anatase and to lesser extent rutile TiO_2 exhibit noticeable photoactivity under UV light [1–3]. Anatase titania is usually considered to be more active than rutile. Even so, the latter is thermodynamically stable phase and reveals a lower band gap than anatase. As a consequence, photo-absorption properties of rutile in visible light region are superior, however, compared to those of anatase, still low [4]. Either modifications of TiO_2 or new preparation routes can be considered as potential ways to improve photocatalytic activity of titania in visible light region. The latter approach has been a key point of recent investigations. The rutile TiO_2 can be directly prepared through several methods, including sol–gel process, combustion synthesis or hydrothermal treatment of TiO_2 precursor [5–7]. The sol–gel process has several advantages over other production methods. Apart from a simple processing and high purity and homogeneity of the obtained products, this technique is suitable for production of TiO_2 with controlled particle size [8,9]. It has been found that properties of the final product are influenced by both a TiO_2 precursor (e.g. titanium isopropoxide, titanium tetrachloride, etc.) and a solvent employed in a sol–gel process. As confirmed elsewhere [10–12], organic solvents used for preparations have a strong impact on gelation time, particle morphology, porosity, and on some other parameters [10–12]. Normally, a product obtained in the conventional sol–gel process is amorphous phase TiO_2. Hence, in order to transform the product to the crystalline TiO_2, an appropriate heat treatment has to be carried out [13–15]. Nano-sized rutile particles are usually obtained through calcination of either amorphous titania or anatase at suitable temperature, usually from ca. 600 °C [16–18]. For example, 2 h long calcination of anatase at 1150 °C in air atmosphere was reported to produce pure rutile [19]. On the other hand, annealing of amorphous TiO_2 in oxygen atmosphere at 600 °C for 6 h resulted in only partial transformation of the substrate to rutile [20].

Due to the fact that the calcinations are costly and time – consuming processes, much attention has been paid to develop new methods for the thermal synthesis of rutile TiO_2. Combustion synthesis or hydrothermal process described by others [21–23] may act as examples. Nevertheless, both alternatives reveal certain shortcomings. For instance, the combustion synthesis requires combustible compounds or the redox mixture (oxidizer-fuel) in optimal amounts [24]. On the other hand the hydrothermal route requires long time autoclaving which can be considered as a disadvantage [25].

In this study, we report a new, easy method for preparation of rutile phases titania revealing photoactivity under visible light irradiation. The two-step preparation procedure consists of (1) preparation of an amorphous TiO_2 followed by (2) a thermal treatment. Amorphous TiO_2 has been obtained at room temperature through a sol–gel process using glycerol as a new solvent for this purpose. Obtained product was subjected to non-conventional flash burning in air for different periods of time.

2. Experimental

2.1. Materials

Titanium isopropoxide (TTiP, 97.0% purity) purchased from Sigma-Aldrich Chemie GmbH (Germany) served as TiO_2 precursor. Solvents used during preparations were glycerol (99.5% purity) and 2-propnaol

---

* Corresponding author. Tel.: +48 91 4494326; fax: +48 91 449 4686.
E-mail address: beata.tryba@zut.edu.pl (B. Tryba).

1566-7367/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2012.02.027

(99.7% purity), both purchased from Chempur (Poland). Phenol of analytical grade used as a model organic pollutant was purchased from Reactivul Bucaresti (Romania). All the intermediate reagents were used as received, without any extra purification. P25 titanium dioxide (Evonik, Germany) and Tytanpol R-001 rutile TiO_2 (Police SA, Poland) were used as a commercial reference materials.

2.2. Catalysts preparation

2.2.1. Sol–gel process

Six samples of amorphous TiO_2 were obtained by the sol–gel process at ambient conditions. In order to minimize hydrolysis of titania precursor (TTiP) with water vapour naturally included in the air, 29.7 mL of the first was diluted with equivalent volume of 2-propanol. Obtained solution was dropped into a beaker containing glycerol. During dropping (ca. 30 min.), mixture was magnetically stirred. Two TTiP/glycerol molar ratios, i.e. 1:1 and 1:4, were used. In both cases obtained gels revealed white – yellow colour. An intensity of the colour was noticeably higher for samples obtained using larger volumes of the glycerol for preparation. The products were divided into portions. Parts of the obtained sols were left for seven days in the dark and then combusted. The other parts were kept for 1 h under ambient condition. After that, the sols without any drying were subjected to the flash combustion process as described below.

2.2.2. Combustion process

A flash combustion of the prepared sols was carried out in a static air atmosphere, using muffle furnace (chamber volume 14 dm^3) preheated to 850 °C. Flat-bottomed crucibles containing portions (ca. 10 g) of a sol were placed directly into the furnace that was immediately closed after sample insertion. As confirmed by separate blind experiments carried out with open-door chamber, each sample immediately caught on fire and was burning faintly for ca. 3 min without observable bumping. After a specified period of time, 10 or 60 min, treated materials were removed from the furnace and left to cool down to the room temperature. Six samples could be prepared according to the manner described above. All of them were white-yellow-greyish powders. Nomenclature of the products obtained, a chemical composition of gels used for preparation, and durations of heat treatment and ageing in the dark, are listed in the Table 1.

2.3. Catalysts characterization

Several methods, including X-ray diffraction (XRD), transmission electron microscopy (TEM), UV–vis/DR and IR spectroscopies were used to characterize obtained catalysts. The X-ray diffraction patterns were measured with X'Pert PRO diffractometer (Philips), using CuKα lamp (λ = 1.54439 Å, 35 kW, 30 mA). Contents of both anatase and rutile were determined on the basis of the obtained diffractograms, according to following formulas:

$$R_A = \frac{I_A \cdot 100}{I_A + I_R \cdot 1.242}(\%) \qquad (1)$$

Table 1
Amounts of components used for preparations of sols and heat treatment times applied during combustion process.

Sample	Molar ratio, TTiP:glycerol	TTiP [ml]	Glycerol [ml]	Aging time [days]	Time of violent burning [min]
P25	–	–	–	–	–
R-001	–	–	–	–	–
1-1	1:1	29.738	7.487	–	60
1-2	1:1	29.738	7.487	–	10
1-3	1:1	29.738	7.487	7	10
2-1	1:3.98	29.738	29.738	–	60
2-2	1:3.98	29.738	29.738	–	10
2-3	1:3.98	29.738	29.738	7	10

$$R_R = \frac{1.242 \cdot I_R \cdot 100}{(I_A + I_R \cdot 1.242)}(\%) \qquad (2)$$

where RA and RR are the molar contents of anatase and rutile, respectively, and IA and IR are the intensities of the peak of anatase and rutile, respectively.

The microstructures of the powder and crystallite size were observed using a Philips CM30 transmission electron microscope (TEM).

UV–vis/DR spectra were recorded using UV–vis diffuse reflectance spectrophotometer (Jasco V-650, Japan), equipped with an integrating sphere. The bang gap energies were evaluated from the diffuse reflectance data, by plotting of the Kubelka-Munk function, $(F(R)h\upsilon)^{1/2}$ versus hυ, where R- reflectance, h- Planck constant, υ- frequency and $F(R) = (1-R)^2/2R$ [26–29].

FT-IR/DRS spectra presented in this work were recorded in the air atmosphere using FT/IR 4200 spectrophotometer (Jasco, Japan).

2.4. Photodegradation studies

Photoactivities of the prepared samples as well as of Tytanpol R-001 and Evonik P25 (used as the reference TiO_2) were examined under VIS region. Phenol was selected for this purpose as a model organic compound. As first, 500 mL of phenol aqueous solution (20 ppm) and 0.1 g of a photocatalyst powder were loaded into a glass beaker. In order to ensure an achievement of an adsorption/desorption equilibrium, the suspensions obtained were agitated with a magnetic stirrer (200 rpm) for 1 h in a dark. Afterwards, the mixtures were irradiated using OSRAM light bulb (60 W) for 24 h. The measured intensity of the reflux light was around 223.5 W/m^2 in the vis region and 0.18 W/m^2 in UV.

After every 30 min. of irradiation, 10 mL of each suspension was taken for analysis. After filtration through 0.45 μm membrane filter, total organic carbon (TOC) contents and phenol concentrations were measured in the obtained filtrates. The measurements were performed using TOC analyser (Analitic Jena Analyzer multi N/C 3100, Germany).

3. Results and discussion

3.1. XRD and TEM analysis

XRD patterns collected for all the prepared materials as well as for commercial R-001 and P25 are shown in Fig. 1. The molar fractions of anatase and rutile phases, calculated according to formula (1) and (2), are listed in Table 2.

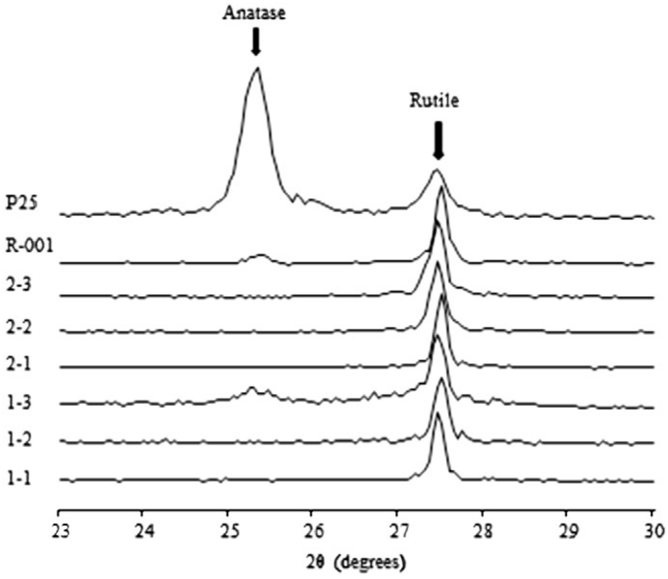

Fig. 1. XRD patterns measured for prepared samples and for P25 and R-001.