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ScienceDirect

Applied Catalysis B: Environmental 77 (2007) 35–45

APPLIED CATALYSIS B: ENVIRONMENTAL

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Influence of mesoporous and platinum-modified titanium dioxide preparation methods on photocatalytic activity in liquid and gas phase

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Received 31 May 2007; received in revised form 29 June 2007; accepted 2 July 2007
Available online 7 July 2007

Abstract

Mesoporous titanium dioxide photocatalysts have been synthesized by template method using widely used precursors and templates with the purpose of choosing the best method for liquid and gas phase photocatalytic oxidation. Titanyl sulphate (TS) and tetrabutyl titanate (TBT) were precursors and cetyl trimethylammonium bromide (CTAB) and dodecylamine (DDA) were templates. Hydrothermal treatment temperature was optimized for the best obtained photocatalyst. The catalysts were characterized by N_2 adsorption–desorption measurements, XRD and UV–vis diffuse reflectance spectroscopy. Samples obtained from TBT contained significant amounts of brookite. Activity was measured in liquid phase for dimethyl methylphosphonate (DMMP) and in gas phase for acetone complete oxidation. The highest activity in liquid phase was observed for catalyst prepared from TS and DDA and aged at 160 °C. Activity was higher than that of TiO_2 Degussa P25 in the low concentration range. The highest activity in gas phase was observed for catalyst prepared from TBT and CTAB. Activity of mesoporous catalysts correlates with their surface area and pore volume for gas phase reaction, whereas in the case of liquid phase DMMP oxidation, there is no sufficient correlation. The effect of DMMP initial concentration on initial oxidation rate is well fitted by Langmuir–Hinshelwood competitive adsorption model. Mesoporous catalysts possess higher adsorption constant but lower reaction rate constant than TiO_2 P25. Platinum was deposited by impregnation and soft chemical reduction (SCR) or photodeposition methods (PD). Catalysts obtained by PD were 50% more active than by SCR and 4.5-fold more active than TiO_2 P25 in aqueous phase. The reasons for extraordinarily high activity of this mesoporous catalyst are discussed.

Keywords: Photocatalysis; Oxidation; Template synthesis; Pt; TiO_2; Phosphonate; Chemical warfare agent; Decontamination; Sarin; Soman

1. Introduction

Mesoporous and nanosized TiO_2 has been a long-time subject of research on materials because of their wide applications [1,2]. Photocatalytic oxidation over titanium dioxide is an effective method for degradation of hazardous organic pollutants of many classes. It usually works in a wide range of pH and air humidity. In addition, solar radiation can be used to carry out the reaction. Thus, photocatalysis over titanium dioxide is considered as a promising method for water and air purification.

Numerous publications are available on various synthetic methods for preparation of nanostructured photocatalysts with controlled shape, e.g. papers [3,4]. According to IUPAC classification, mesopores are pores with effective size from 2 to 50 nm [5]. Mesoporous TiO_2 with large surface area is considered to provide higher activity than conventional TiO_2 [6]. To date, several preparative approaches utilizing supramolecular templating mechanism have been reported for the preparation of mesoporous titanium dioxide [7]. Mesoporous titanium dioxide was first prepared using phosphate surfactant through a modified sol–gel process [8,9]. The main problem of the preparation procedure is that a significant amount of surfactant remains in these materials, and specific surface area falls during calcination that is used for template removal [7]. Not only surfactants, but also triblock copolymers [10] and many non-surfactant organic compounds are used as structure-directing and pore-forming agents to prepare mesoporous TiO_2. Yang et al. prepared mesoporous TiO_2 using amphiphilic poly(alkylene oxide) block copolymers as structure-directing

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doi:10.1016/j.apcatb.2007.07.001

agent, titanium inorganic salts as precursor in a non-aqueous solution [7,10–12]. The preparation of non-phosphated mesoporous TiO_2 using dodecylamine as directing agent, titanium isopropoxide as organic precursor and emptying the pores by extraction has been reported by Antonelli [13]. Yan et al. [14] reported nitric acid addition during TiO_2 sol–gel preparation. Nitric acid prolongs gelation time, thereby controlling hydrolysis and polymerization rate. They managed to obtain material with specific surface area above 280 m^2/g. Peng et al. [2] proposed to remove ionic surfactants by ion-exchange treatment, which allows one to remove most of the surfactant before calcination. Despite the variety of techniques used, it still remains unclear which method is preferable for obtaining photocatalysts for gas and for liquid phase.

Addition of noble metals to titanium dioxide is known to significantly increase its photocatalytic activity. Titanium dioxide with supported platinum was first synthesized for water decomposition because pure TiO_2 does not decompose water [15]. Supporting platinum is thought to enhance charge separation in semiconductor and decrease electron–hole pair recombination. Earlier platinum was deposited on TiO_2 P25 by H_2PtCl_6 impregnation with further soft chemical reduction by $NaBH_4$. It leads to the increase of organics oxidation rate [16]. Platinum was also previously deposited on mesoporous template-synthesized TiO_2 [17,18], but these materials were used for hydrogen production.

We aimed at screening template synthesis of mesoporous TiO_2 by using different precursors, including cheap and easily available titanyl sulphate, which is commonly used for synthesis of titania by thermohydrolysis without any template [18]. Two structure-directing agents were investigated. Deposition of platinum on the best obtained mesoporous catalysts was carried out by two quite different techniques. Photocatalytic activities of all catalysts were measured for destruction of model hazardous organophosphorous compound dimethyl methylphosphonate (DMMP) and oxidation of gas phase pollutant acetone. The work resulted in catalysts of greatly increased activity.

2. Experimental

2.1. Chemicals

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and were used without further purification and treatment. Tetrabutyl titanate (TBT), dodecylamine (DDA) and dimethyl methylphosphonate (DMMP) were purchased from Aldrich. Their purity was not less than 98%. Cetyl trimethylammonium bromide (CTAB, 99%) was received from Sigma, sodium chloride (99%) was purchased from Laverna, titanyl sulphate (TS, 99%) obtained from "Vekton", sodium borohydride (98%) received from ACROS. Acetone (99%), chloroplatinic acid hexahydrate (98%) and nitric acid were received from Reakhim. Weight content of HNO_3 was not less than 65%. Distilled deionized water and absolute ethanol were used in all experiments. Commercial TiO_2 Degussa P25 (80% anatase и 20% rutile, SSA 57 m^2/g, DegussaAG) and Hombifine N (100% anatase, SSA 336 m^2/g, Sachtleben Chemie, GmbH) were used as references.

2.2. Mesoporous titanium dioxide preparation

Samples of prepared titanium dioxide are designated by letters A–E. The preparation procedure for each of them follows below. The precursor, template and media are highlighted in the title of each synthesis.

2.2.1. $TiOSO_4$ + dodecylamine (H_2O)

TS was used as a precursor for titanium dioxide synthesis. Synthesis ran according to the following method: 2 g of DDA was dissolved in 5 ml of distilled water during strong agitation. After that, 100 ml of 10 wt.% TS solution was added to this solution dropwise. The obtained suspension was agitated for 1 h; then aging of titania was carried out at 80, 100, 120, 140, 160 or 180 °C for 48 h in a Teflon-lined autoclave. These catalysts are called A-80, A-100, etc. The obtained slurry was placed in C_2H_5OH/H_2O (1:1) solution with 0.1 wt.% NaCl content and was agitated for 4 h at 40 °C. Thereafter, the catalysts were washed by distilled water and dried at 350 °C for 1 day.

2.2.2. $TiOSO_4$ + CTAB (H_2O)

Synthesis was accomplished according to the procedure for samples A with the following modifications. DDA template was replaced by CTAB, and calcination lasted 2 days.

2.2.3. $Ti(OBu)_4$ + dodecylamine (EtOH)

Catalyst preparation was carried out according to paper [7]. Mixture of 2 g DDA and 4 g TBT was stirred for 10 min. Then dry ethanol (20 ml) was added and the mixture was stirred until a homogeneous solution was obtained. Distilled deionized water (20 ml) was then added and the mixture was stirred for 2 h. Thereafter, the reaction mixture was aged at room temperature for 48 h followed by 80 °C for 48 h in an autoclave. Catalyst was washed, dried and calcinated according to the procedure for specimens A and B.

2.2.4. $Ti(OBu)_4$ + dodecylamine (EtOH+HNO_3)

Synthesis was carried out according to paper [14]. 3.2 g of DDA and 8.2 g of TBT were dissolved in 10 ml of absolute ethanol, and then nitric acid was added dropwise. After stirring for 40 min, 11 ml of dry ethanol and 1 ml of distilled water was added into the obtained solution. Mixture was stirred during 1 h, aging of the gel lasted 24 h; then the gel formed was washed by distilled water twice and dried at 80 °C. Template was extracted by the mixture of ethanol and nitric acid (5:1) at 70 °C. The obtained slurry was washed by ethanol and dried at 80 °C followed by calcination for 20 min at 350 °C.

2.2.5. $Ti(OBu)_4$ + CTAB (H_2O)

Catalyst was synthesized according to the following method: 10 ml of TBT was dropwise added to 2 g of CTAB water solution. Obtained mixture was stirred for 1 h; then the slurry was aging for 24 h at ambient temperature. Thermal treatment