Available online at www.sciencedirect.com

ScienceDirect

Applied Catalysis B: Environmental 79 (2008) 53–62

APPLIED CATALYSIS B: ENVIRONMENTAL

www.elsevier.com/locate/apcatb

Flame-made WO_3/TiO_2 nanoparticles: Relation between surface acidity, structure and photocatalytic activity

Kranthi K. Akurati [a], Andri Vital [a], Jean-Philippe Dellemann [a], Katarzyna Michalow [a], Thomas Graule [a,*], Davide Ferri [b], Alfons Baiker [b]

[a] *EMPA, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for High Performance Ceramics, Uberlandstrasse 129, 8600 Dubendorf, Switzerland*

[b] *Institute for Chemical and Bioengineering, ETH Zurich, Honggerberg, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland*

Received 27 April 2007; received in revised form 26 September 2007; accepted 28 September 2007
Available online 2 October 2007

Abstract

WO_3/TiO_2 composite nanoparticles have been synthesized by dissolving W and Ti precursors in a suitable solvent and spraying into a high temperature acetylene-oxygen flame using a reactive atomizing gas. Particles with controlled W:Ti ratios were produced at various flow rates of precursor solution and the resulting powders were characterized by Brunauer–Emmett–Teller (BET) surface area analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman and attenuated total reflection infrared (ATR-IR) spectroscopy. Two-dimensional coordinatively unsaturated wolframyl species were well dispersed on the TiO_2 surface for the samples with equal to or less than 3.6 mol% WO_3 and contributed to an increase of the surface acidity. Crystalline WO_3 was formed for samples with >3.6 mol% WO_3. Formation of crystalline WO_3 is attributed to the enhanced rate of condensation of W species with increasing loading of tungsten. Variation of λ (defined as the ratio of the actual oxygen-to-fuel ratio of the reactants to the stoichiometric oxygen-to-fuel ratio) influences the residence time of the particles in the high temperature flame and affects the type of surface species and thereby the resultant acidity. The photocatalytic activity of the composite particles was tested for the degradation of methylene blue (MB) and was compared with that of commercial Degussa P25-TiO_2. The improved photocatalytic activity of the composite particles is attributed to the increased surface acidity and better charge separation due to the coupling of WO_x species and TiO_2 within the composite nanoparticles.

Keywords: Lewis acids; Acidity; Raman spectroscopy; Photocatalysis; Nanoparticles; Flame spray synthesis; Adsorption; WO_3; TiO_2

1. Introduction

Among the various nanocrystalline photocatalytic materials that have been studied over the last 30 years, research has mainly focused on titanium dioxide (titania, TiO_2) as photocatalyst in diverse areas ranging from water and air treatment to self cleaning surfaces. In the past years TiO_2 has been modified to suit various applications. WO_3/TiO_2 has been successfully tested for selective catalytic reduction (SCR) of NO_x in lean exhaust gases of automobiles to meet the stringent emission standards for both NO_x and particulate matter [1–3]. SiO_2/TiO_2 exhibits super hydrophilic properties which makes it an ideal material for antifogging and self cleaning surfaces such as for window glasses, automobile mirror wind shields, etc. [4]. Numerous papers have appeared on the fundamentals of pure titania systems; the mechanisms of oxidation and the ways to improve its photocatalytic activity (PCA) have been investigated in detail [5–9]. The improvement of the PCA of TiO_2 has been achieved by coating with noble metals such as Ag [10], Au [11], Pt [12], Pd [13] which can trap the electrons facilitating an effective charge separation. Complementary to metal/TiO_2 photocatalysts, TiO_2 has been coupled with other semiconductors such as SnO_2 [14–17] which can induce effective charge separation by trapping photogenerated electrons. The PCA of metal/metal oxide modified TiO_2 photocatalysts can be further improved if the metal/metal oxide adsorbs more pollutant along with the function

---

Abbreviations: FSS, flame spray synthesis; PCA, photocatalytic activity; TTIP, titanium tetraisopropoxide; AMT, ammonium metatungstate; DMF, dimethyl formamide; CED, combustion enthalpy density; SSA, specific surface area; MCT, mercury–cadmium–telluride; MB, methylene blue; FWHM, full width at half maximum; HyCOM, hydrothermal crystallization in organic media.

* Corresponding author. Tel.: +41 44 823 4123; fax: +41 44 823 4150.
E-mail address: thomas.graule@empa.ch (T. Graule).

0926-3373/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2007.09.036

of electron trapping. Unfortunately, deposited metal particles only serve as electron trapping agent and are not effective to enhance the adsorption of the pollutants. TiO_2 coupled with other semiconductors has been reported to perform both the above-mentioned functions. This has been realized by coupling the WO_3 semiconductor with TiO_2. As a basic function, WO_3 has a suitable conduction band potential to allow the transfer of photogenerated electrons from TiO_2 facilitating effective charge separation. Additionally, formation of a monolayer of WO_x species on TiO_2 can significantly increase the surface acidity as WO_3 is 15 times more acidic than TiO_2 [18]. Because of this increased acidity WO_3/TiO_2 can adsorb more hydroxyl groups and simultaneously more organic reactants on its surface. Thus, significant improvement of the PCA has been achieved in comparison to the standard commercial photocatalysts. To date, WO_3/TiO_2 has been synthesized by sol–gel [19,20], ball milling [21], incipient wetness impregnation [22,23] and multiple grafting [24]. Thin films of WO_3/TiO_2 have also been produced by dip coating [25] and spin coating [26]. Kwon et al. [18] produced WO_3/TiO_2 by wetness impregnation method which includes the suspension of pure TiO_2 powder in a dilute ammonia solution mixed with the required amount of H_2WO_4 to adjust the concentration of WO_3. The resultant powder was then calcined at 400 °C for 2 h. Acidity increased with increasing amount of WO_3 and reached a maximum value for a WO_3 concentration of 3.2 mol%. A further increase in WO_3 concentration did not have any influence on the acidity of WO_3/TiO_2 composite particles. Interestingly, the PCA also followed the same hysteresis as the acidity dependence. Song et al. [23] reported similar results and in addition showed that the stability of the colloidal suspensions of WO_3/TiO_2 was enhanced compared to that of TiO_2 owing to the increased surface acidity. Li et al. [19] synthesized the WO_3/TiO_2 by sol–gel process using ethanol solutions of $Ti(O–Bu)_4$ and aqueous solutions of ammonium metatungstate. The resultant amorphous $WO_x–TiO_2$ gel was calcined at 973 K for 2 h to produce crystalline WO_3/TiO_2 nanocomposites. The isoelectric point of the resulting 3 mol% WO_3/TiO_2 composite was found to be at pH 5.0 compared to pH 6.40 for TiO_2. This difference in the isoelectric point can greatly enhance the absorption of organic components on the WO_x/TiO_2 photocatalysts.

All the mentioned synthesis routes involve several process in order to improve the crystallinity of the as-synthesized amorphous particles. In this study, the WO_3/TiO_2 particles have been synthesized in a single step using the flame spray synthesis (FSS). The concentration of tungsten oxide has been varied in order to produce particles with improved surface acidity and acid strength. As the particle formation takes place at high temperatures in the flame, the resultant powder has a high crystallinity and does not need any further post treatment.

2. Experimental procedure

2.1. Apparatus

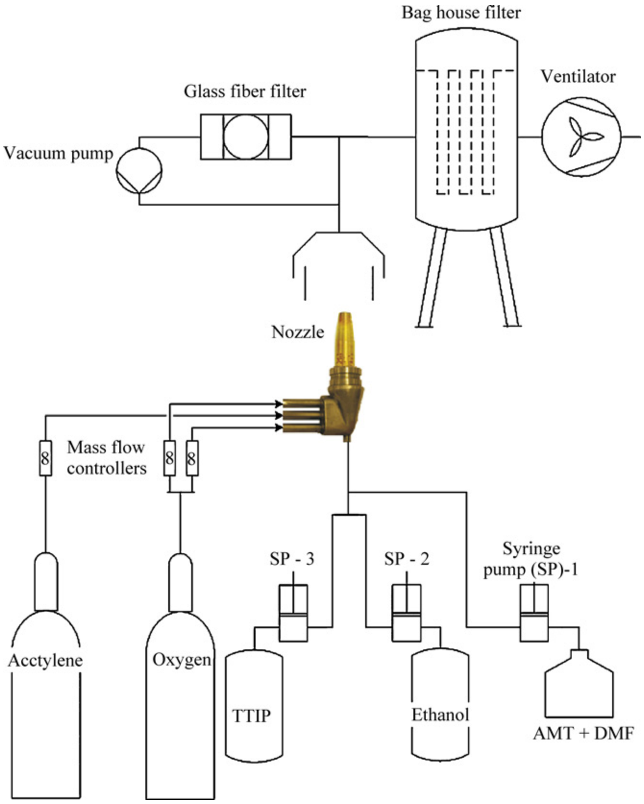

Fig. 1. Experimental set-up for the synthesis of WO_3/TiO_2 nanocomposites by flame spray synthesis (FSS) [titanium tetraisopropoxide (TTIP), ammonium metatungstate (AMT), dimethyl formamide (DMF)].

Fig. 1 shows the schematic of the experimental set-up of the FSS. It consists of three syringe pumps to feed the precursor and solvent mixtures, an external mixing gas-assisted nozzle and the powder collection unit. Liquid precursor and solvent are stored in separate vessels and both are mixed externally in controlled amounts by adjusting their flow rates with the syringe pumps. The nozzle consists of a central opening (2.8 mm), where a capillary tube (1.05 and 1.59 mm internal and external diameter, respectively) is incorporated and through which the precursor mixture is fed to the flame. The spacing between the capillary tube and central opening is used to feed the atomizing gas (oxygen) that forms a fine spray of the liquid precursor mixture. The spray is ignited by six supporting premixed flamelets produced by C_2H_2 (13 l/min) and O_2 (17 l/min). The openings (1.3 mm) of the supporting flames are located at 3.25 mm from the centre of the nozzle. All gas flow rates are controlled by the mass flow controllers (Bronkhorst HI-TEC). Due to the high exit velocities of the process gases, particles are collected in a bag house filter (Friedli, Switzerland) and representative samples of about 1 g are collected on a glass fiber filter (Type GF50, Schleicher and Schuell, Germany), via a by-pass, using vacuum pumps.

As a precursor source of TiO_2, titanium tetraisopropoxide (TTIP, $Ti(C_3H_7O)_4$, purity $> 99\%$, VWR International) dissolved in ethanol (99.9% absolute, Fluka AG) was used. Ammonium metatungstate (AMT, $(NH_4)_6H_2W_{12}O_{40}(H_2O)_x$, 99.9%, ABCR) was used as the precursor source for WO_3 and was dissolved in dimethyl formamide (DMF, C_3H_7NO, 99%, ABCR). A 2 M solution of TTIP was prepared and AMT dissolved in different amounts of DMF (0.02 M) was added at a