Applied Catalysis B: Environmental 144 (2014) 333–342

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Visible-light-induced photodegradation of gas phase acetonitrile using aerosol-made transition metal (V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce, and Zr) doped TiO_2

Siva Nagi Reddy Inturi[a], Thirupathi Boningari[a], Makram Suidan[b,*], Panagiotis G. Smirniotis[a,**]

[a] *Chemical Engineering Program, School of Energy, Environmental, Biological and Medicinal Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA*
[b] *Engineering College and Architecture, American University of Beirut, Beirut 1107-2020, Lebanon*

ARTICLE INFO

Article history:
Received 7 April 2013
Received in revised form 20 June 2013
Accepted 12 July 2013
Available online 22 July 2013

Keywords:
Flame spray pyrolysis (FSP)
Titania (TiO_2)
Visible-light-induced
Gas phase
Photodegradation

ABSTRACT

A series of semiconductor photocatalysts based on transition metals (M′ = V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce, and Zr) incorporated TiO_2 (Ti/M′ = 20 atomic ratio) materials have been synthesized by adopting a one-step liquid flame aerosol synthesis technique. The resulting materials were explored for the destruction of acetonitrile in gas phase under visible light irradiation at ambient conditions. Our H_2-TPR studies revealed the formation of Me—O—Ti bonds, which suggest the strong interaction of dopant metal-TiO_2 in all the as-synthesized materials. The reduction peaks in Cr-doped TiO_2 shifted to much lower temperatures, due to the increase in the reduction potential of titania and chromium. The strong interaction (formation of Cr—O—Ti bonds) is the main reason that the Cr/TiO_2 is an active photocatalyst in visible light. Our XPS studies suggest that the relative atomic percentage value of Ti^{3+}/Ti^{4+} characterized by XPS was significantly high for our flame-made Cr/TiO_2 nanoparticles (Ti^{3+}/Ti^{4+} = 0.89, 32.9%), whereas, other samples demonstrated poor atomic percentage value of Ti^{3+}/Ti^{4+} (Ti^{3+}/Ti^{4+} = 0.08–0.32). The existence of Ti^{3+} species with narrow band gap is highly beneficial for the promotion of visible light-induced photocatalytic activity. The position of the Cr 2*p* peaks shifted to lower binding energies in Cr-doped TiO_2 nanoparticles. The electrons migrate from the TiO_2 nanoparticles to chromium species, which reveals a strong interaction between Cr and TiO_2 nanostructure in the interface of flame-made nanoparticles. Conversely, Mn^{3+} species combined with TiO_2 because its surface metal dispersion was kept high after TiO_2 loading. However, Mn^{3+} incorporated catalyst was inactive because of the small energy driving force for electrons to detrap from Mn^{2+}. The UV–vis spectroscopy results of M′-doped TiO_2 (M′ = Fe, Cr, V, Co, Ce, and Ni) materials showed augmentation of light absorption in the visible range. The Cr, V and Fe (Ti:M′ atomic ratio = 20:1) titania aerosol catalysts reduced the bandgap energy of TiO_2 to 2.9 eV under visible light irradiation. Among all of the catalysts we tested, the transition metals (M′ = Cr, Fe, and V) incorporated materials have shown an impressive catalytic performance in visible light. Among all the catalyst tested, Cr-doped titania demonstrated a superior catalytic performance and the rate constant is about 8–19 times higher than the rest of the metal doped catalysts. Their catalytic performances are correlated with the UV–vis spectrum of each synthesized catalyst to reveal the specific role played by each metal ion.

1. Introduction

Photocatalytic treatment of polluted waters and gaseous streams has received enormous attention during recent years, because of the potential application in environmental treatment and the synthesis of fine chemicals. It involves the utilization of ultraviolet or solar light by a semiconductor photocatalyst for abatement conditions [1–4]. Among the available semiconductors, the vast majority of current studies employed TiO_2 as the photocatalyst due to its stability and relatively low price along with its unique properties, such as high refractive index, excellent optical transmittance in the visible and near-infrared regions, high photo-chemical and corrosive resistance, high dielectric constant and photocatalytic activity [4–6]. However, the problem of low

---

* Corresponding author.
** Corresponding author. Tel.: +1 513 556 14 74; fax: +1 513 556 34 73.
E-mail addresses: makram.suidan@uc.edu, msuidan@aub.edu.lb (M. Suidan), panagiotis.smirniotis@uc.edu (P.G. Smirniotis).

0926-3373/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.apcatb.2013.07.032

energy efficiency of the photocatalytic process in solar light is what has hindered its practical application. It has become indispensable to bring the photocatalytic activity of TiO_2 into visible spectrum and control the particle size of titania nanoparticles. During solar-light-induced photodegradation, the radiation from sun has minimal conversion efficiency for excitation of valence bond electrons. If at all excitation occurs, there is high electron–hole recombination. In addition, these drastic disadvantages involved with the conventional TiO_2 catalysts prevent these photo-catalytic processes from being commercially applied. Both these concerns could be addressed synthetically with appropriate design of an anchoring functionality that could covalently bind the TiO_2 surfaces very efficiently [7–11]. The doping of metal/metal oxides has enabled the formation of hybrid O 2*p* conduction band with lower band gap energy, favoring absorption over the whole visible spectrum [12–16].

On the other hand, conventional synthesis procedures suffer from the low yield in addition to the long processing time, especially for very fine and pristine nanoparticles. All these, necessitate the needs for large tanks and high energy equipment which in turn limits its flexibility in direct scaling-up. Additionally, they also incur additional costs in terms of production time, high energy consumption, floor space and waste disposal, which are subsequently reflected in the price of the final products. An increasingly popular alternative process is to synthesize fine nanoparticles in a single-step and without further processing. Examples of such technique include the flame aerosols [17,18], spray pyrolysis [17,19], furnace and plasma processing [20], laser ablation [21] and chemical vapor deposition [22]. In particular, the flame aerosol technique (FSP) is an established and elegant synthesis technique capable of producing inexpensive nanoparticles at industrial scale. At present, large scale production of simple nanoparticles is routinely achieved in a single step technique using a compact flame reactor design for (in descending order of production mass) carbon blacks, pigmentary titania, zinc oxide, fumed silica and optical fibers with an estimated annual production in the order of million metric tons [23]. An added benefit of FSP technique is being able to utilize a broader spectrum of liquid precursors so that even noble metal deposited TiO_2 can be made in one step [17].

Acetonitrile is an extremely stable, volatile and toxic molecule present in various civil and industrial wastewaters. Acetonitrile is also detected as an in-door air component emitted by commercial fibrous polymeric materials, resins and smoking tobacco [24]. Acetonitrile is an interesting model molecule for photo-oxidation studies because it possesses an alkyl and a cyanide group that may undergo different oxidation routes.

In the present work we report, the synthesis of different transition metal modified TiO_2 photocatalysts for the visible light photodegradation of acetonitrile using a flame spray pyrolysis (FSP) technique. All of the materials were characterized by various physicochemical techniques. Photocatalytic activity of different M'/Ti aerosol nanoparticles is evaluated for the degradation of acetonitrile in visible light. The doping of TiO_2 nanoparticles with Cr, Fe and V exhibited better conversions in the visible region whereas, the incorporation of the other transition metals (Mn, Mo, Ce, Co, Cu, Ni, Y and Zr) showed an inhibition effect on the photocatalytic activity. Among all the M'/TiO_2, Cr modified TiO_2 demonstrated a superior photocatalytic activity and the rate constant is about 8–19 times higher than the rest of the metal doped catalysts. Our XPS results suggested that the doping of TiO_2 with chromium cations using flame spray pyrolysis technique leads to the production of Ti^{3+} species. The energy level of Ti^{3+} lies between the valence band and the conduction band of TiO_2, which could effectively promote the electrons in the new valence band (VB) to be excited to the conduction band of TiO_2. Therefore, the existence of Ti^{3+} species on the surface that makes TiO_2 excited under visible illumination. The chromium nanoparticles could serve as trapping centers for electrons photo-induced in the conduction band of TiO_2, meanwhile leaving the holes in the valence band of TiO_2. These results imply that the migration of charges is prompted on the interface of metal-doped TiO_2 flame-made nanoparticles and the recombination of photo-induced e^-/h^+ pairs is suppressed by the well-known Schottky barrier effect, which will contribute to the enhancement of photocatalytic activity in the visible region.

2. Experimental

2.1. Catalysts preparation

The synthesis procedure for the flame-made nanoparticles is explained in detail in our previous studies [25–29]. Briefly, a mixture of O-xylene (Sigma–Aldrich Reagent, 99%)/acetonitrile (Sigma–Aldrich Reagent) in the volume ratio of 3/1 is used as the solvent. For pure FSP made titanium-tetra-isopropoxide (TTIP, Sigma–Aldrich, purity N 97%) was used as precursor and diluted with the solvent to a 0.5 M solution metal oxide nanoparticles were synthesized by a one-step FSP synthesis technique. Precursor solutions resulting in powders of transition metal incorporated TiO_2 were prepared by dissolving predetermined amounts of TTIP and metal precursor (chromium(III) 2-ethylhexanoate (Strem, 70% Cr in mineral spirits), vanadium(V) tri-*i*-propoxy oxide (Strem, ~98% V), iron(III) naphthenate (Strem, 80% Fe in mineral spirits), manganese(III) naphthenate (Strem, 56% Mn in mineral spirits), nickel(III) naphthenate (Strem, 60% Ni in toluene), copper(II) 2-ethylhexanoate (Strem, 16–19% Cu solvent free), cobalt 2-ethylhexanoate (Strem, 65% Co in mineral spirits), molybdenum 2-ethylhexanoate (Strem, 15% Mo), zirconyl 2-ethylhexanoate (Strem, 6% Zr in mineral spirit) and yttrium(III) naphthenate (Strem, 60% Y in toluene) such that the atomic ratios of Ti/M' is 20. The total molar concentration of Ti + M (transition metal) in the liquid precursor was set at 0.5 M. During FSP, the liquid precursor was fed through a spray nozzle at a flow rate of 3 $mL\,min^{-1}$ using a syringe pump (Cole Parmer, 74900 series), where it was dispersed by a surrounding 5 $L\,min^{-1}$ flow of O_2 (1.5 bar, Wright Brothers, 99.98%). Combustion of the dispersed droplets was ignited by a surrounding supporting flame (premixed 1.0 $L\,min^{-1}$ O_2/1.0 $L\,min^{-1}$ CH_4). Additional 3 $L\,min^{-1}$ sheath O_2 (BOC Gases) was issued through the outer most sintered metal ring. Fine aerosol nanoparticles leaving the flame were collected on a flat glass fiber filter (Whatman GF/A, 150 mm in diameter) aided by a vacuum pump (Grainger Inc.). The aerosol nanoparticles were scraped from the filter for direct use as catalyst without any further treatment. The metal components of the catalysts are denoted Ti/M.

2.2. BET surface area and pore volume measurements

The BET specific surface area of the as-prepared nanoparticles was determined from nitrogen adsorption equilibrium isotherms at liquid nitrogen temperature (77 K) using an automated gas sorption system (Micromeretics ASAP 2010) operating in continuous mode. Prior to the analysis, 0.050 ± 0.005 g of catalyst were evacuated under helium atmosphere for 3 h at 250 °C in the degassing port of the instrument. The adsorption isotherms of nitrogen were collected at 77 K using approximately six values or relative pressure ranging from 0.05 to 0.99 and by taking 0.162 nm^2 as the molecular area of the nitrogen molecule. The BET-equivalent diameter was calculated as $d_{BET} = 6/(\rho \times SSA)$ where ρ is the mass-weighted density of the powder ($\rho_{anatase} = 3.84\,g/cm^3$ and $\rho_{rutile} = 4.26\,g/cm^3$).