Catalytic Oxidation of Carbon using TiO_2 based Nanoparticles prepared using Flame Synthesis

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ABSTRACT

Titanium dioxide (TiO_2) nanoparticles are used in numerous applications involving catalysis, photo-catalysis, water purification, electrode for Li-ion batteries, polymer fillers, and pigments. Multiple-diffusion flames are used to coat/dope the TiO_2 nanoparticles with various elements such as carbon, vanadium, silicon, and iron. The use of multiple diffusion flames offers several key advantages, such as uniform temperature and chemical species profiles and many of the limitations related to premixed flames such as flashback and flame speed are avoided. Crystal phase and size of the TiO_2 nanoparticles are determined using x-ray diffraction (XRD). The nanoparticles are further characterized using Raman spectroscopy, thermal gravimetric analysis (TGA), and Brunauer–Emmett–Teller (BET). The morphology and crystal structure of the samples are characterized using high-resolution transmission electron microscopy (HRTEM), with elemental mapping. With silicon precursors, the TiO_2 nanoparticles are coated in a layer of silica, while for vanadium, the nanoparticles are doped with vanadium oxide. An iron based precursor results in the formation of iron-oxide alongside the TiO_2 nanoparticles. Finally the iron based TiO_2 nanoparticles significantly improve the catalytic oxidation of carbon, where complete oxidation of carbon occurs at a temperature of 470^{o}C (with iron) compared to 610^{o}C (without iron).

Keywords: flame synthesis, multiple diffusion flames, titanium dioxide, carbon oxidation

1 INTRODUCTION

Titanium dioxide (TiO_2) is widely used in a number of advanced applications, especially with regards to energy and water. Such applications of TiO_2 include next-generation of solar cells [1], photocatalytic water splitting [2], and waste-water treatment [3]. Flame synthesis is currently the leading method for large-scale production of TiO_2 nanoparticles [4]. Thus, it is important to investigate the use of advanced TiO_2 nanoparticles using flames.

Fe-doped TiO_2 is of interest in applications related to magnetism [5] and photocatalysis. The presence of magnetic ions can enable potential applications in spintronic applications and magneto-optic devices [6]. Doped anatase TiO_2 has been studied as a photocatalyst [7]. Tryba et al. [8] noticed the photocatalytic effect of doping TiO_2 with iron on phenol decomposition under UV irradiation. A higher formation of OH* radicals results in the enhance photocatalytic activity. Also, iron and iron-oxide based nanoparticles are an encouraging material for catalytic oxidation of carbon. Such materials can be used for reducing of diesel engine exhaust [9].

TiO_2 composite materials with silica or vanadia have been used for a number of applications such as catalysts and photocatalysts. Strobel et al. [10] published a detail review on the potential of flame made catalysts involving TiO_2/silica and TiO_2/vanadia.

Previously, we synthesized carbon-coated TiO_2 using multiple diffusion flames [11]. It was noticed that coating TiO_2 with carbon maintains the anatase phase and improved its optical properties [12]. The present work involves the production of TiO_2 nanoparticles containing C, Fe, Si, and V. Multiple diffusion flames were operated at atmospheric pressure condition. For carbon-containing samples the oxidation characteristics were investigated.

2 EXPERIMENT

TiO_2 synthesis is performed using multiple diffusion flames at atmospheric pressure, Fig. 1. Titanium tetraisopropoxide (TTIP) is used as the main precursor for TiO_2 NPs. Hexamethyldisiloxane (HMDSO) is mixed with TTIP for the silica-coated titania (Si-TiO2) and vanadium (v) oxytriisopropoxide is used for vanadium-doped titania NPs (V-TiO2). To synthesize carbon-coated titania (C-TiO_2), ethylene (99.95% purity) is mixed with TTIP, while ferrocene dissolved in xylene is used to synthesize carbon-coated iron-doped titania (Fe/C-TiO2). The precursor carrier gas flows through a center tube (Fig. 1). The evaporator and precursor lines are heated to prevent any precursor condensation. H_2 is used as the fuel and oxygen (O_2) (with Ar) is used as the oxidizer. The global equivalence ratio is kept at ~0.5, thus providing a highly oxidizing environment. The titania nanoparticles are collected on an aluminum plate downstream from the burner.

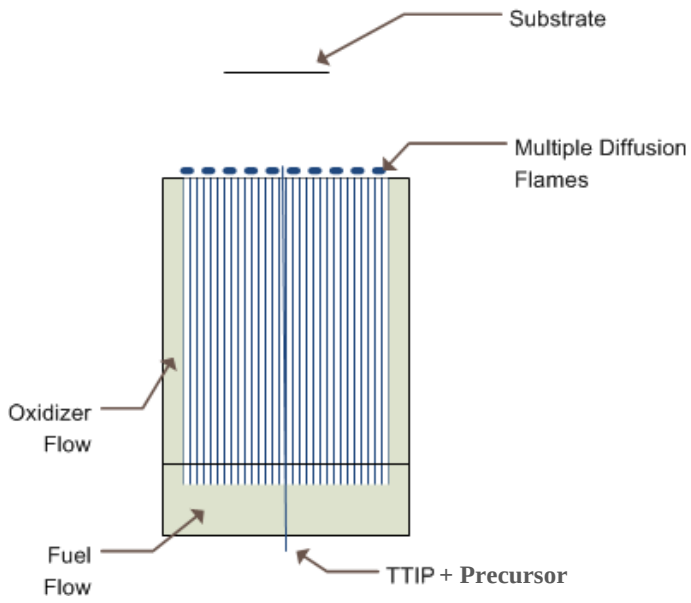

Figure 1: Experimental setup of the multiple diffusion flames

Crystal structure of the titania nanoparticles are determined using X-Ray diffraction (XRD), Bruker D8 Advance diffractometer, which operates using Cu(Kα) radiation. The nanoparticles are further characterized using a Raman microspectrometer, Horiba LabRAM HR Visible. Thermogravimetric analysis (TGA), Mettler Toledo TGA/DSC 1, is performed to determine the carbon weight percentage and oxidation temperature of the samples. Finally the samples are analyzed using transmission electron microscopy (TEM) and high resolution TEM (HRTEM). Both TEM and HRTEM images are obtained using FEI Company's Titan G2 80–300 electron microscope equipped with an EDS detector from EDAX and a GIF energy filter Gatan, Inc. Images are recorded on a 2k by 2k pixel CCD camera of model US1000 from Gatan, Inc.

3 RESULTS

3.1 TiO_2 with Carbon and Iron Oxide

XRD is first used to determine the crystal structure of the carbon-coated titania (C-TiO_2) and carbon-coated titania with iron (Fe/C-TiO_2). From the XRD pattern in Fig. 2, the growth of majority anatase titania nanoparticles is confirmed. A TEM image of the Fe/C-TiO_2 nanoparticles are shown in Fig. 3. A carbon coating of 5-8 nm can be seen around the nanoparticles. The growth of carbon on TiO_2 has been attributed to a diffusion process, where carbon enters the TiO_2 lattice structure and then carbon precipitates onto the surface [12].

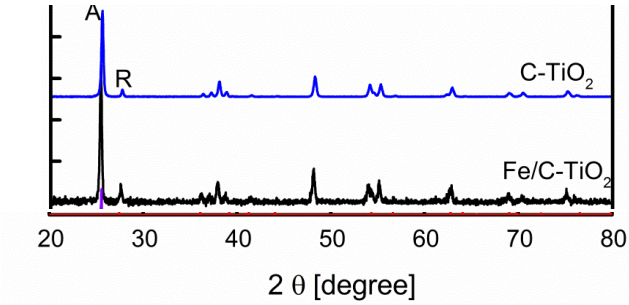

Figure 2: XRD of C-TiO_2 and Fe/C-TiO_2

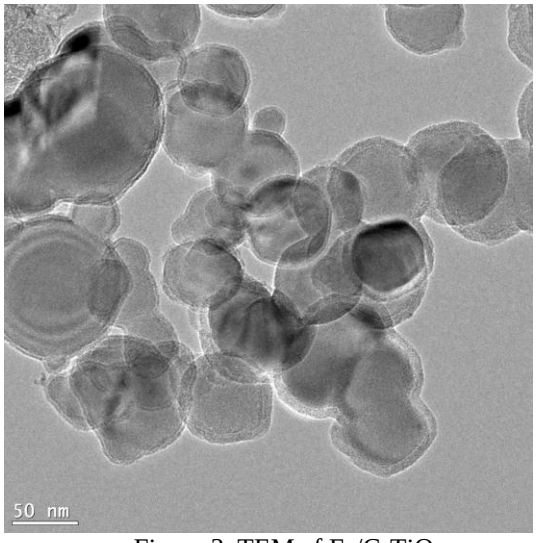

Figure 3: TEM of Fe/C-TiO_2

For the growth of Fe/C-TiO_2, TTIP is mixed with ferrocene (dissolved in xylene) and H_2 is used as the precursor carrier gas. Hence the source of carbon is the precursor liquid. The pyrolysis of ferrocene has been used in for the synthesis of iron-oxide [13]. The BET of the Fe/C-TiO2 nanoparticles is 55.3 m^2/g, which is around double the area as compared with that of the C-TiO_2 nanoparticles having a BET surface area of 27.6 m^2/g.

TiO_2 is a useful catalyst for carbon oxidation due to its reactivity and thermal stability [14]. Numerous metal oxides containing Ce, Fe, V, and other metals have been examined for the reduction of soot [15]. Based on this, non-isothermal oxidation experiments with different heating rates is performed on C-TiO_2 and Fe/C-TiO_2 in an air environment using TGA. Table 1 shows the weight loss of the samples, where the C-TiO_2 sample contains 6.13% carbon while the Fe/C-TiO_2 sample contains 17.37% carbon. The Fe/C-TiO_2 catalytically improves the oxidation of carbon. The start and end oxidation temperatures for C-TiO_2 are 440°C and 610°C, respectively, and for Fe/C-TiO2 are 300°C and 470°C, respectively. For both samples, the carbon is totally removed after the oxidation process.

Sample	**Carbon %**	**Start of Oxidation (°C)**	**Complete Oxidation (°C)**
C-TiO_2	6.13	440	610
Fe/C-TiO_2	17.37	330	470

Table 1: TGA Results of C-TiO_2 and Fe/C-TiO_2

3.2 TiO_2 with Silica and Vanadia

The formation of TiO_2 containing silica (Si-TiO_2) and vanadia (V-TiO_2) is investigated by adding HMDSO and V-oxytriisopropoxide, respectively, to the TTIP precursor. H_2 is used as the precursor carrier gas. The XRD data in Fig 4 confirms that the Si-TiO_2 nanoparticles are primarily in the anatase phase and for V-TiO_2 are in the rutile phase.

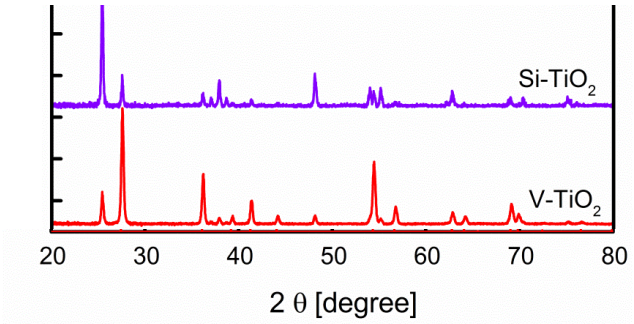

Figure 4: XRD of Si-TiO_2 and V-TiO_2

Figure 5 shows the TEM images of Si-TiO_2, indicating that TiO_2 nanoparticles are coated by SiO_2, with thickness ranging from 3 to 8 nm. Such coating happens due to a difference in the chemical reaction rates of the precursors. In our case, the oxidation of TTIP resulting in the formation of TiO_2 is faster than the oxidation of HMDSO resulting in formation of SiO_2.

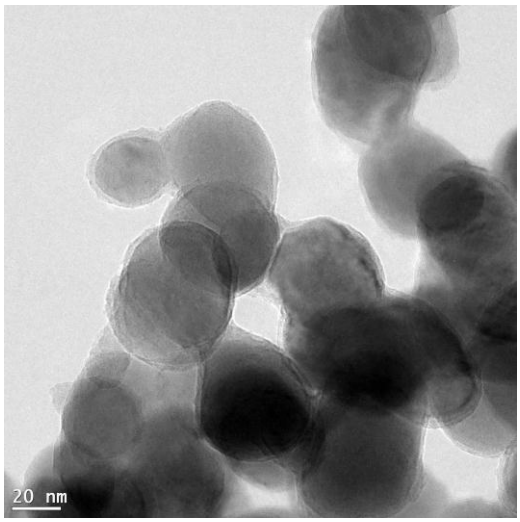

Figure 5: TEM of Si-TiO_2

The V-TiO_2 nanoparticles are predominately in the rutile phase, where vanadia is doped within TiO_2. The addition of dopants is known to change the antase to rutile precentage [16]. The TEM image in Fig. 6 showns the TiO_2 nanoparticles containing vanadia.

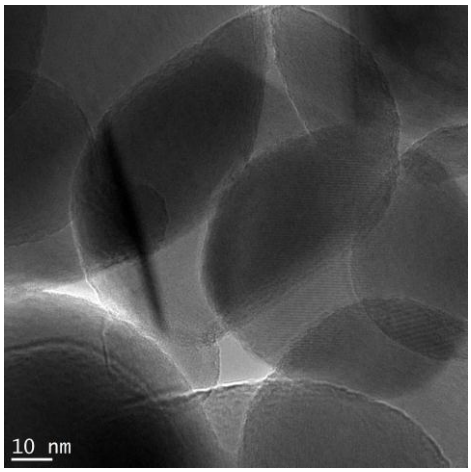

Figure 6: TEM of V-TiO_2

4 CONCLUSION

Multiple diffusion flames are used to synthesize TiO_2 nanoparticles containing C, Fe, Si, and V in a single-step process. The growth of carbon-coated (C-TiO_2), carbon-coated with iron oxide (Fe/C-TiO_2), silica-coated (Si-TiO_2) and vanadia-doped (V-TiO_2) TiO_2 nanoparticles is shown. XRD confirms that all samples are predominantly anatase, except for V-TiO_2, which is mostly rutile. For Fe/C-TiO_2, the nanoparticles are coated with 5 to 8 nm of carbon. Iron based TiO_2 nanoparticles significantly improve the catalytic oxidation of carbon, where complete oxidation of carbon occurs at a temperature of 470^{o}C (with iron) compared to 610^{o}C (without iron). For Si-TiO_2 nanoparticles, a coating of 3 to 8 nm of SiO_2 is observed around the TiO_2 particles. Finally, for V-TiO_2, vanadia is doped within TiO_2.

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