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Synthesis of TiO₂ nanoparticles containing Fe, Si, and V using multiple diffusion flames and catalytic oxidation capability of carbon-coated nanoparticles --Manuscript Draft--

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Abstract:	<p>Titanium dioxide (TiO₂) nanoparticles containing iron, silicon, and vanadium are synthesized using multiple diffusion flames. The growth of carbon-coated (C-TiO₂), carbon-coated with iron oxide (Fe/C-TiO₂), silica-coated (Si-TiO₂) and vanadium-doped (V-TiO₂) TiO₂ nanoparticles are demonstrated using a single-step process. Hydrogen, oxygen, and argon are utilized to establish the flames, with titanium tetraisopropoxide (TTIP) as the precursor for TiO₂. For the growth of Fe/C-TiO₂ nanoparticles, TTIP is mixed with xylene and ferrocene. While for the growth of Si-TiO₂ and V-TiO₂, TTIP is mixed with hexamethyldisiloxane (HMDSO) and vanadium (V) oxytriisopropoxide, respectively. The synthesized nanoparticles are characterized using high-resolution transmission electron microscopy (HRTEM) with energy filtered TEM for elemental mapping (of Si, C, O, and Ti), x-ray diffraction (XRD), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), nitrogen adsorption BET surface area analysis, and thermogravimetric analysis. Anatase is the dominant phase for the C-TiO₂, Fe/C-TiO₂, and Si-TiO₂ nanoparticles, whereas rutile is the dominant phase for the V-TiO₂ nanoparticles. For C-TiO₂ and Fe/C-TiO₂, the nanoparticles are coated with about 3-5 nm thickness of carbon. The iron based TiO₂ nanoparticles significantly improve the catalytic oxidation of carbon, where complete oxidation of carbon occurs at a temperature of 470oC (with iron) compared to 610oC (without iron). With regards to Si-TiO₂ nanoparticles, a uniform coating of 3 to 8 nm of silicon dioxide is observed around the TiO₂ particles. This coating mainly occurs due to variance in the chemical reaction rates of the precursors. Finally, with regards to V-TiO₂, vanadium is doped within the TiO₂ nanoparticles as visualized by HRTEM and XPS further confirms the formation of V⁴⁺ and V⁵⁺ oxidation states.</p>
Response to Reviewers:	Reviewer #1:

	<p>Thank you for the comments. Below please find our response.</p> <p>Response to General Comments:</p> <p>All the papers listed have been included within the manuscript as well as any relevant discussion. Please see the highlighted parts within the manuscript.</p> <p>“In my opinion, the study of carbon oxidation kinetics is the novel part of this work” thank you for the comment, we have carried out additional experiments to further validate the carbon oxidation of the Fe-TiO₂ nanoparticles.</p> <p>Individual Comments:</p> <p>1- We have collected 60-80 mg for the silica and vanadia TiO₂ cases and this amount increased to ~120 mg for the carbon containing samples. Precursor was injected to the system using a syringe pump with the flowrate of 20 ml/hr. All gaseous flowrates were controlled using calibrated MKS mass flow controllers with the following flowrates: Fuel: hydrogen: 0.77 SLPM Oxidizer: Oxygen: 2.63 SLPM + Argon: 7.5 SLPM Carrier gas: Argon: 0.22 SLPM or Ethylene: 0.234 SLPM All the above details have been added to the modified manuscript.</p> <p>2- The temperature of the burner has been measured using a K-type thermocouple as done in our previous work (Memon et al. 2013) and the reference has been added.</p> <p>3- We have used the standard BET method and no special changes were made with the doped samples. Since the dopant is 5% it would have a minimal effect on the calculation. This information has been included within the manuscript.</p> <p>4- As mentioned the degree of aggregation discussion has been removed from the manuscript.</p> <p>5- References (Hung and Katz 1992; Xiong and Pratsinis 1993) have been added and highlighted in the text.</p> <p>Reviewer #3: Thank you for the comments. Below please find our response. General Comments:</p> <p>When comparing to FSP, the multiple diffusion flame enables the production of different materials due to the difference in the heat release and residence time. We recently conducted the same experiments using an FSP and were unable to coat the TiO₂ nanoparticles with silica. Additionally the particle morphology and TiO₂ phase were different. Based on your comment we have added more information comparing our work with existing literature.</p> <p>For the Fe-TiO₂ sample additional TGA experiments were conducted with the addition of soot like particles (Printex-U). The results and figure (Figure 11) have been added to the manuscript.</p> <p>For the C 1s peak, since XPS is a surface measurement all samples have similar peaks due to ambient exposure. For that reason it is difficult to quantify the carbon content using the C 1s peak.</p> <p>All the weak points have been corrected as well as the spelling and grammar. For the degree of aggregation, this has been removed based on the comment from Reviewer #1.</p>
Suggested Reviewers:	Wilson E Merchán-Merchán, PhD Associate Professor, The University of Oklahoma wmerchan-merchan@ou.edu

	<p>Expert on the flame synthesis of nanomaterials and combustion oxidation reactions.</p> <p>Margaret Wooldridge, PhD Professor, University of Michigan mswool@umich.edu Expert on the use of multiple diffusion flames for synthesis and and combustion oxidation reactions.</p>
Additional Information:	
Question	Response
Scientific Justification (Available to Reviewers)	<p>In this publication, we performed a one-step flame based process for the synthesis of advanced TiO₂ particles containing Fe, Si, and V. Such techniques can be used for large-scale production of TiO₂ based materials. With silicon precursors, the TiO₂ 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 TiO₂ nanoparticles.</p> <p>The iron based TiO₂ nanoparticles significantly improve the catalytic oxidation of carbon, where complete oxidation of carbon occurs at a temperature of 450oC (with iron) compared to 600oC (without iron).</p>

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Synthesis of TiO₂ nanoparticles containing Fe, Si, and V using multiple diffusion flames and catalytic oxidation capability of carbon-coated nanoparticles

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Keywords: Flame synthesis; Multiple Diffusion Flames; Titanium dioxide; Carbon Oxidation

ABSTRACT

Titanium dioxide (TiO_2) nanoparticles containing iron, silicon, and vanadium are synthesized using multiple diffusion flames. The growth of carbon-coated (C-TiO_2), carbon-coated with iron oxide (Fe/C-TiO_2), silica-coated (Si-TiO_2) and vanadium-doped (V-TiO_2) TiO_2 nanoparticles are demonstrated using a single-step process. Hydrogen, oxygen, and argon are utilized to establish the flames, with titanium tetraisopropoxide (TTIP) as the precursor for TiO_2 . For the growth of Fe/C-TiO_2 nanoparticles, TTIP is mixed with xylene and ferrocene. While for the growth of Si-TiO_2 and V-TiO_2 , TTIP is mixed with hexamethyldisiloxane (HMDSO) and vanadium (V) oxytriisopropoxide, respectively. The synthesized nanoparticles are characterized using high-resolution transmission electron microscopy (HRTEM) with energy filtered TEM for elemental mapping (of Si, C, O, and Ti), x-ray diffraction (XRD), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), nitrogen adsorption BET surface area analysis, and thermogravimetric analysis. Anatase is the dominant phase for the C-TiO_2 , Fe/C-TiO_2 , and Si-TiO_2 nanoparticles, whereas rutile is the dominant phase for the V-TiO_2 nanoparticles. For C-TiO_2 and Fe/C-TiO_2 , the nanoparticles are coated with about 3-5 nm thickness of carbon. The iron based TiO_2 nanoparticles significantly improve the catalytic oxidation of carbon, where complete oxidation of carbon occurs at a temperature of 470°C (with iron) compared to 610°C (without iron). With regards to Si-TiO_2 nanoparticles, a uniform coating of 3 to 8 nm of silicon dioxide is observed around the TiO_2 particles. This coating mainly occurs due to variance in the chemical reaction rates of the precursors. Finally, with regards to V-TiO_2 , vanadium is doped within the TiO_2 nanoparticles as visualized by HRTEM and XPS further confirms the formation of V^{4+} and V^{5+} oxidation states.

1. Introduction

Titanium dioxide (TiO_2) is an important nanoparticle as it is used in a number of advanced applications, especially in relation to energy and water (Chen et al. 2012; Grabowska et al. 2012). Such applications of TiO_2 based nanoparticles (NPs) include next-generation of perovskite solar cells (Grätzel 2001), photocatalytic water splitting (Lindan et al. 1996; Linsebigler et al. 1995), and waste-water treatment (Xu 2012). Flame synthesis is currently the dominant method for mass production of TiO_2 nanoparticles in industrial processes (Teoh et al. 2010). Thus, it is important to investigate the production of advanced TiO_2 nanoparticles using flames, as it can be readily applicable for commercial applications.

Iron based nanoparticles are a promising material for catalytic oxidation of carbon, as they can be used for reducing of diesel engine exhaust and regeneration in diesel particulate filters (Song et al. 2006). Additionally, iron oxide has been used for soot oxidation (Legutko et al. 2013) and Fe-based perovskite-type oxides can be used for the simultaneous elimination of soot and NO_x , from the exhaust of diesel engines (Wang et al. 2012; Xu et al. 2010). Fe-doped TiO_2 is of significant interest in magnetism (Rodriguez-Torres et al. 2008). The presence of magnetic ions in non-magnetic matrices has a great potential in spintronic applications and magneto-optic devices (Matsumoto et al. 2001). Doped anatase TiO_2 has also been widely studied as a photocatalyst (Belver et al. 2006; Thompson and Yates 2006). Tryba et al. (Tryba et al. 2006; Tryba et al. 2005) investigated the photocatalytic effect of doping TiO_2 with iron on phenol decomposition under UV irradiation. A higher formation of OH^* radicals on the Fe- TiO_2 surface was observed under UV irradiation in comparison with TiO_2 . The increase in OH^* radical formation was probably due to the reduction of Fe^{3+} to Fe^{2+} under UV irradiation. Deng et al. (Deng et al. 2009) synthesized Fe-doped TiO_2 nanotubes using a sol-gel process. The photocatalytic activity of Fe/ TiO_2 NTs was evaluated through photodegradation of aqueous methyl orange. Doping TiO_2 with iron (III) was demonstrated to enhance its photocatalytic efficiency (Deng et al. 2009).

TiO_2 and SiO_2 based composites have been used for a number of applications such as gas sensors (Tiefenthaler and Lukosz 1989), catalysts and photocatalysts (Fujishima 1972; Grätzel 1981; Mills and

Le Hunte 1997). Yoshida and Prasad (Yoshida and Prasad 1996) prepared SiO₂-TiO₂ nanoparticles using sol-gel method as a composite materials for optical waveguides. TiO₂ can also be used in a number of applications related to coatings, UV filters, and lenses, where the photocatalytic effects of TiO₂ are harmful (Nie et al. 2009). To overcome this challenge, TiO₂ can be coated with SiO₂ to limit the photocatalytic activity of the nanoparticles (Teleki 2009). Teleki et al., (Teleki et al. 2005) synthesized silica-titania composites and studied the evolution of composite particle morphology from ramified agglomerates to spot- or fully coated particles. When the silica ratio in the mixture was below 20%, a silica coating layer was observed on the surface of the titania particles. If the silica ratio was increased to above 20%, segregated regions of silica and titania were observed. V-doped TiO₂ has proven to be an effective photocatalyst (Tian et al. 2009). Vanadia-titania prepared by flame spray pyrolysis (Stark et al. 2001) has been used for selective catalytic reduction of NO by NH₃. Ren et al. (Ren et al. 2014) studied the mechanism of vanadia/titania doping by in situ diagnostic of phase selective laser-induced break-down spectroscopy (LIBS). They proposed that the doping of V significantly reduced the band gap of TiO₂, while Ti doping did not affect the band gap of V₂O₅. Finally, Strobel et al. (Strobel et al. 2006) prepared a detailed review on flame-made catalysts involving TiO₂/SiO₂ and TiO₂/vanadia.

Diffusion flame aerosol reactor has been used to prepare carbon-coated titania using TTIP and acetylene as precursors (Kammler and Pratsinis 2003), where the particle surface area ranged from 29 to 62 m²/g and the rutile-phase content ranged from 17 to 68 wt.%. Recently, we synthesized carbon-coated TiO₂ using multiple diffusion flames (Memon et al. 2013). It was found that coating TiO₂ with carbon maintains the anatase phase and enhances its optical properties (Anjum et al. 2013). The present study focuses on the production of TiO₂ nanoparticles containing C, Fe, Si, and V, considering the potential application of such nanoparticles as explained. Multiple diffusion flames were utilized under atmospheric pressure condition. The setup offers a high degree of flexibility in controlling precursor delivery when compared with premixed flames. For carbon-coated samples, the oxidation characteristics of carbon were also investigated.

2. Experiment

Multiple diffusion flames are used to synthesize titanium dioxide TiO_2 nanoparticles doped and coated with different elements. The burner, as schematically shown in Fig. 1a, was composed of a square array of small tubes, a honeycomb, and a center tube. Detailed dimensional information can be found in our previous paper (Memon et al. 2013). Hydrogen (H_2 ; purity 99.9999%) is used as the fuel (0.77 SLPM) and 2.63 SLPM of oxygen (O_2 ; purity 99.9995%) mixed with 7.5 SLPM of Argon (Ar; purity 99.9999) was used as the oxidizer for the multiple diffusion flames. The global equivalence ratio was maintained at 0.5 (without the precursor), thus providing a highly oxygen-rich environment. Figure 1b shows an image of the multiple diffusion flames that provide a homogeneous gas-phase temperature of $\sim 600^\circ\text{C}$, at 3.5 cm above the burner (Memon et al. 2013).

Titanium tetraisopropoxide (TTIP; Sigma-Aldrich, 97% purity) was used as the main precursor for TiO_2 NPs. Hexamethyldisiloxane (HMDSO; Sigma-Aldrich, $\geq 98\%$ purity) was mixed with TTIP for the silica-coated titania (Si-TiO_2) and vanadium (v) oxytriisopropoxide (Sigma-Aldrich) was used for vanadium-doped titania NPs (V-TiO_2). To synthesize carbon-coated titania (C-TiO_2), 0.234 SLPM of ethylene (99.95% purity) was used as the carrier gas, while ferrocene dissolved in xylene (Sigma-Aldrich) was mixed with TTIP to synthesize carbon-coated iron-doped titania (Fe/C-TiO_2). Elemental ratio of Si/Ti, V/Ti, and Fe/Ti was kept constant at 5% and the appropriate amounts of precursors were calculated according to this ratio. All precursors were injected using a syringe pump into a vaporizer with a flowrate of 20 ml/hr (Fig. 1a). Argon (Ar) with flowrate of 0.22 SLPM was used as the carrier gas for silica and vanadia-doped samples. The carrier gas was supplied through the center tube at a flow rate of 0.4 SLPM (Fig. 1). The vaporizer and precursor lines were heated to 180°C to prevent any precursor condensation. The synthesized nanoparticles were collected on an aluminum plate downstream from the burner. Around 60-80 mg samples were collected for the silica and vanadia cases and this amount increased to ~ 120 mg for the carbon containing samples. All experiments were conducted at atmospheric pressure.

The collected nanoparticles were characterized using X-ray diffraction (XRD) by an X-ray powder diffractometer (Bruker, D8 Advance) with Cu K α ($\lambda=1.5406$ Å) radiation. Raman spectroscopy measurements were performed on a Raman spectrometer (Aramis, LabRAM HR Visible) using 473 nm excitation from a diode-pumped solid-state (DPSS) laser (7 mW with a 1.1 cm⁻¹ spectral resolution). Particle crystallinity and morphology were examined by transmission electron microscope (TEM) (FEI, Titan G² 80-300 CT). The TEM was operated at electron beam energy of 300 keV. The bright-field TEM (BFTEM) micrographs were acquired at a magnification of 30-80 kX for particle size distribution analysis. Similarly, high-resolution TEM (HRTEM) micrographs were acquired by setting the magnification in the range of 250-400 kX to investigate the crystal structure of the TiO₂ particles. Electron micrographs were recorded on a 4k $\times$ 4k pixel charged couple devices (CCD) camera (Gatan, Inc., US4000). Energy-filtered TEM (EFTEM) analysis was carried out in this microscope by using a post-column energy filter (Gatan, Inc., GIF Tridiem). The so called 3-window method was adopted (Egerton 2011) in generating an elemental mapping of titanium, oxygen, and silicon elements during the EFTEM analysis of the samples. It should be noted that the ionization edges of Ti-L₂₃ (455 eV), O-K (532 eV), and Si-L₂₃ (99 eV) were selected for generating the Ti, O, and Si elemental maps, respectively. A specific surface area (SSA) was calculated based on multi-point Brunauer–Emmett–Teller (BET) nitrogen adsorption (Micromeritics, ASAP 2420). Samples were degassed for 16 h at 150 °C and the standard BET isotherms, based on 46 points, were used to calculate SSA.

Chemical composition at the surface of powdered samples was analyzed using high resolution X-ray photoelectron spectroscopy (XPS). XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α x-ray source ($h\nu=1486.6$ eV) operating at 150 W, which also has a multichannel plate and delay line detector under a vacuum of 1~10⁻⁹ mbar. Measurements were performed in hybrid mode using electrostatic and magnetic lenses, and the take-off angle (angle between the sample surface normal and the electron optical axis of the spectrometer) was 0°.

All spectra were recorded using an aperture slot of 300 μm $\times$ 700 μm . The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. Samples were mounted in a floating mode in order to avoid differential charging. The data was analyzed with commercially available software program CASAXPS.

Non-isothermal thermogravimetric analysis (TGA; TA Instruments, Q5000) was performed to determine the percentage of carbon and its activation energy for the carbon-coated samples. About 7.0 mg of TiO_2 was loaded in an alumina crucible and heated in ultra-high purity air (flow rate of 100 ml/min) from 25 to 800°C at different heating rates of 2, 4, 6 and 8 °C/min.

3. Results and discussion

3.1 Characterization of TiO_2 nanoparticles

Various TiO_2 nanoparticles were investigated with the addition of precursors containing iron, silicon, and vanadium, as summarized in Table 1. TiO_2 nanoparticles were coated with carbon using a one-step process (C- TiO_2). The nanoparticles were prepared without having any metal precursor, ethylene (C_2H_4) was used as the precursor carrier gas for carbon-coating. In the case of iron, the TiO_2 samples were coated with carbon, Fe/C- TiO_2 , and doped with iron. While for Si- TiO_2 , the samples were coated with silica and finally for V- TiO_2 the samples were doped with vanadium.

XRD is commonly used to identify the crystalline structure of TiO_2 nanoparticles. Figure 2 shows the XRD patterns of the various synthesized materials. For the case of C- TiO_2 , anatase phase was dominant when adding small amounts of carbon, which differs from the results by (Kammler and Pratsinis 2003), in which they found that adding large amounts of carbon (up to 52%) can decrease the anatase percentage. Similar to C- TiO_2 , Fe/C- TiO_2 and Si- TiO_2 , have anatase as the dominant phase, while for V- TiO_2 it is rutile. The anatase to rutile ratio in the samples was calculated by integrating the respective XRD

peak intensities (anatase (101) peak at $2\theta = 25.4^\circ$ and rutile (110) peak at $2\theta = 27.5^\circ$) using the following equation (Li et al. 2004)

$$W_R = \frac{A_R}{0.884A_A + A_R} \quad (1)$$

where W_R is the weight fraction of rutile in the TiO_2 sample and A_A and A_R are the integrated areas under the anatase and rutile peaks, respectively. The values of anatase percentage ($1 - W_R$) in the mixtures are listed in Table 1.

Table 1. Summary of the results for the synthesized nanoparticles.

Particles	Precursor	Anatase %	d_{XRD} [nm]	BET [m ² /g]	d_{BET} [nm]	Degree of aggregation
C-TiO ₂	TTIP + C ₂ H ₄	90.8	33.6	27.6	54.1	4.18
Fe/C-TiO ₂	TTIP + Ferrocene/Xylene	90.4	36.2	55.3	27.0	0.42
Si-TiO ₂	TTIP + HMDSO	80.0	42.8	23.14	64.1	3.36
V-TiO ₂	TTIP + V-oxytriisopropoxide	28.9	30.7	22.1	64.9	9.44

The crystallite size d_{XRD} of TiO_2 NPs can be obtained from the position of the (101) and (110) peaks using the Scherrer formula (Chen and Dobbins 2000)

$$L = \frac{K * \lambda}{\beta * \cos \theta} = d_{\text{XRD}} \quad (2)$$

where L is the crystallite size, K is 0.89, θ is the Bragg's angle, β is the full width at half-maximum of the corresponding peaks, and λ is the wavelength of X-ray radiation (Cu K α 1.5418 Å).

Raman spectroscopy was performed to further characterize the TiO_2 nanoparticles. It is known (Zhang et al. 1998) that anatase TiO_2 has 15 optical modes and 6 of these are Raman active (irreducible representation of A_{1g} (515 cm^{-1}), $2B_{1g}$ (399 and 519 cm^{-1}), and $3E_g$ (144, 197 and 639 cm^{-1})), whereas rutile TiO_2 has 11 optical modes, among which 4 are Raman active (irreducible representation of A_{1g} (612 cm^{-1}), B_{1g} (143 cm^{-1}), B_{2g} (826 cm^{-1}), and E_g (447 cm^{-1})). The Raman spectra in the visible region (Fig. 3) also show that the anatase phase is dominant for the C-, Fe/C- and Si-TiO₂ samples, while the rutile phase is dominant for the V-TiO₂ sample, which are consistent with previous XRD data. Raman spectroscopy is a unique method in characterizing the order-disorder effect in carbonaceous materials, which typically have

two major bands (Memon et al. 2011; Williams et al. 2006), with the graphitic G-band around 1580 cm^{-1} and the disordered or amorphous D-band around 1340 cm^{-1} . These two carbonaceous bands appear in the carbon-coated samples, which indicate the existence of both crystalline and amorphous carbon in these two samples. Fe/C-TiO₂ sample shows higher intensity of D- and G-bands than C-TiO₂ sample.

The specific surface area (SSA) of the nanoparticles is measured using BET nitrogen adsorption technique and the results are shown in Table 1. The SSAs for the titania NPs were in the range of 22.1-27.6 m²/g when doping with vanadium, silicon or carbon. This SSA was almost doubled (55.3 m²/g) when the NPs are doped with iron and coated with carbon (Fe/C-TiO₂). Based on the surface area obtained from BET analysis and assuming spherical particles, the average primary particle size d_{BET} is calculated by

$$d_{\text{BET}} = \frac{6}{[V_A * \rho_A + V_R * \rho_R] * \text{SSA}} \quad (3)$$

where V_A and V_R are the volume fractions of anatase and rutile phase, respectively, ρ_A is the density of anatase (3.99 g/cm³) and ρ_R is the density of rutile (4.26 g/cm³) (Akurati et al. 2006). The dopant material was not factored into the calculation. For Si-, V-, and C-coated/doped TiO₂ NPs, the average particle sizes, d_{BET} , are larger than the average primary particle diameter calculated from XRD analysis (Table 1), which can be attributed to particle aggregation (Reddy et al. 2004).

3. 2 Carbon-coated TiO₂ nanoparticles with iron-oxide

TEM and HRTEM images of the carbon-coated TiO₂ nanoparticles are shown in Fig. 4. A coating thickness of 5 nm can be seen around the nanoparticles. The growth of carbon on TiO₂ has been investigated previously (Anjum et al. 2013) and this has been attributed to a potential diffusion process, where carbon initially enters the TiO₂ structure and then upon saturation, carbon precipitates onto the surface.

Chemical composition of the samples was analyzed using the high resolution XPS. High resolution XPS spectra of C 1s and Ti 2p core levels are obtained as shown in Fig. 5. The Ti 2p_{3/2} core level is fitted

using two components. The dominant peak centered at 458.6 eV is associated to Ti ions with a formal valence 4+ (Ti^{4+}), while the peak at the lower binding energy ~ 456.6 eV is associated to Ti ions with a reduced charge state (Ti^{3+}) (Biesinger et al. 2010). Ti^{3+} species represent 2% of the total Ti ions present on the surface of the C-TiO₂ powder and is typical of commercially available TiO₂ samples (Pan et al. 1992). The O 1s core level is centered at 529.8 eV, which corresponds to the metal oxide (TiO₂) (Biesinger et al. 2010) and the C 1s core level is centered at 284.4 eV. These C 1s, Ti 2p, O 1s peaks are also observed for all the TiO₂ samples (C-TiO₂, Fe/C-TiO₂, Si-TiO₂, and V-TiO₂).

For the growth of carbon-coated TiO₂ nanoparticles containing iron (Fe/C-TiO₂), TTIP was mixed with ferrocene (dissolved in xylene) and H₂ was used as the precursor carrier gas. Thus, the source of carbon is the precursor liquid. Note that the pyrolysis of ferrocene has been used in a number of experiments for the synthesis of iron-oxide (Inamdar and Haram 2006; Zhang et al. 2001) and carbon-nanotubes (Andrews et al. 1999; Schnitzler et al. 2003). XRD and Raman spectroscopy (Figs. 2 and 3) confirm that the Fe/C-TiO₂ nanoparticles are predominately in the anatase phase. The TEM image shown in Fig. 6a shows the formation of isolated iron-oxide nanoparticles together with TiO₂ particles. Additionally, HRTEM image confirms the coating of the TiO₂ nanoparticles with carbon (Fig. 6b).

Figure 7 shows an additional HRTEM image, demonstrating that iron-oxide nanoparticles are encapsulated within carbon. Note that d_{XRD} are comparable between C-TiO₂ and Fe/C-TiO₂ (Table 1), which is reasonable based on the sizes from TEM images. While the BET surface area of the Fe/C-TiO₂ nanoparticles was 55.3 m²/g ($d_{\text{BET}} = 27.0$ nm), which is almost the double as compared with that of the C-TiO₂ nanoparticles having value of 27.6 m²/g ($d_{\text{BET}} = 54.1$ nm). The difference in surface areas was due to the degree of aggregation (4.18 for C-TiO₂ and 0.42 for Fe/C-TiO₂). Such increase in BET surface area can be partially attributed to the formation of small iron-oxide nanoparticles (diameter ~ 5 nm) encapsulated within carbon. Note that iron-oxide nanoparticles are typically acting as seeds for the growth of carbon, where similar growth mechanism is used for carbon nanotubes (Schnitzler et al. 2003). Raman

spectroscopy further confirmed the growth of carbon, as D and G peaks are clearly visible within the spectrum in Fig. 3.

High resolution XPS spectrum of the Fe 2p core level is shown in Fig. 8. The Fe 2p core level in red color is fitted (thick black line) using four components located at 710.9 eV (Fe 2p_{3/2}) and 719.5 eV (corresponding satellite peak), together with 724.4 eV (Fe 2p_{1/2}), and 733.0 eV (corresponding satellite peak). The area ratio of Fe 2p_{3/2} / Fe 2p_{1/2} is equal to 2:1 and the doublet separation is equal to 13.5 eV. The same values are used for their corresponding satellites. The binding energies of the components of the Fe 2p doublet and their corresponding satellites are a characteristic of the Fe³⁺ oxidation state of iron (Aronniemi et al. 2005; Barreca et al. 2001; Fujii et al. 1999). The other core levels are similar to the C-TiO₂ sample (Fig. 5), where Ti³⁺ species represent 1-2% of the total Ti ions present on the surface of the Fe/C-TiO₂ powder.

3.3 Carbon oxidation kinetics

TiO₂ is an effective catalyst for carbon oxidation due to its mobility, reactivity, and thermal stability (Lee and Choi 2002; Neeft et al. 1997; Oi-Uchisawa et al. 2003). Several metal oxides consisting of Pt, Ce, Fe, V, and other metals have been investigated for the simultaneous reduction of soot and NO_x (Shangguan et al. 1997; Teraoka et al. 1996). In this regard, non-isothermal oxidation experiments with different heating rates were performed with the carbon-coated samples in air environment using TGA. Figure 9 shows the weight loss of these samples as a function of temperature, at a heating rate of $\beta = 2$ K/min. The C-TiO₂ sample contains 6.13% carbon while the Fe/C TiO₂ sample contains 17.37% carbon, which contains substantial amounts of amorphous carbon, as observed from HRTEM (Fig. 7). Even with the addition carbon, Fe/C-TiO₂ catalytically enhances the oxidation of carbon. The start and end oxidation temperatures for Fe/C-TiO₂ are 300°C and 470°C, respectively, which are much lower when compared to C-TiO₂, 440°C (start temperature) and 610°C (end temperature). For both samples, the carbon is believed to be totally removed after the oxidation process, which can be visualized in Fig. 10, where the initial

black samples becomes white for the C-TiO₂ samples and turns yellow for the Fe/C-TiO₂ sample. The yellow color is due to Fe doping.

The kinetics of carbon oxidation can be considered using heterogeneous condensed phase reactions (Vyazovkin 2000) and can be described by an Arrhenius reaction:

$$d\alpha/dt = Ae^{-E/RT}f(\alpha) \quad (5) \quad ($$

where α is the degree of conversion (the extent at which carbon is burned), t is the time, A is the pre-exponential factor, E is the activation energy, R is the gas constant, T is the temperature, and $f(\alpha)$ is the differential conversion function. For non-isothermal reaction with constant heating rate of $\beta = \Delta T/\Delta t = \text{const.}$, Eq. (5) becomes

$$d\alpha/dt = (A/\beta) e^{-E/RT(t)}f(\alpha) \quad (6) \quad ($$

Here, a simplified algebraic expression proposed by Pérez-Maqueda et al. (Perez-Maqueda et al. 2006) is adopted with $f(\alpha) = c \times \alpha^m (1-\alpha)^n$, where c , m , and n are fitting constants, which has the advantage of fitting all kinetic ideal models proposed for solid-state reactions and also fits for any deviation from these ideal kinetic models. By substituting $f(\alpha)$ into Eq. (6), the logarithmic form becomes

$$\ln(d\alpha/dt) - \ln[\alpha^m(1-\alpha)^n] = \ln cA - E/RT \quad (7)$$

A linear regression analysis has been performed using the TGA data to determine the kinetic parameters, which are summarized in Table 2. The difference in m between the two samples indicates a different oxidation mechanism due to the catalytic effect of iron. Fe/C-TiO₂ sample also shows smaller activation energy (123.1 kJ/mol as compared with 132.1 kJ/mol for C-TiO₂). The pre-exponential factor for Fe/C-TiO₂ of 1.17E+08 1/min is much larger than that for C-TiO₂ of 5.89E+6 1/min. The combination of lower activation energy and higher pre-exponential factor results in a large increase in the oxidation of carbon for the Fe/C-TiO₂ samples. Based on the results obtained, the iron-based TiO₂ samples can be regarded as a promising material for soot oxidation reactions. The Fe/TiO₂ sample (Fe/C-TiO₂ after

oxidation) has the same oxidation state of iron (Fe^{3+}) as the original sample (before oxidation) which is a good indication of using this sample multiple times for oxidation without losing its catalytic properties.

Table 2. Kinetic parameters (Eq. 7) for carbon oxidation in carbon-coated TiO_2 samples.

	C- TiO_2	Fe/C- TiO_2
m	-0.74	-1.0
n	0.13	0.13
E [kJ/mol]	132.1	123.1
A [1/min]	5.89E+06	1.17E+08

To emphasize the catalytic effect of the generated samples, the iron-containing sample is used as a catalyst for soot oxidation. A model soot (Printex-U) was mixed with the iron-doped sample with a ratio of 1:4. The mixture was dissolved in ethanol and sonicated for 60 min to have good contact between the soot particles and the Fe- TiO_2 particles. After sonication the sample was left to dry for 12 hours then the mixture was tested using TGA and compared to the raw soot material. In TGA, both samples are heated first to 100 °C with nitrogen gas for one hour to remove any moisture content and then cooled down to 60 °C. Afterwards the gas is changed to air before raising the temperature by 8 °C/min up to 800 °C.

The weight loss of the soot samples with temperature changes are shown in Fig. 11. The soot sample starts oxidation at a temperature of 230 °C and ends oxidation at 659 °C. Mixing the soot sample with the catalyst (Fe- TiO_2) enables the oxidation temperature to start at 155.5 °C with complete oxidation at 604 °C. The reduction in oxidation temperatures indicates that mixing the soot samples with iron-doped titania enhances the oxidation characteristics of the soot sample which is indicative of the catalytic effect of the Fe- TiO_2 sample.

3.4 Silica coated TiO_2 nanoparticles

The formation of TiO_2 containing silica is investigated by adding HMDSO to the TTIP precursor. H_2 was used as the precursor carrier gas to avoid any additional growth of carbon. The XRD data in Fig 2 confirmed that the TiO_2 nanoparticles were primarily in the anatase phase (~80 wt%), while a slight

increase in rutile fraction was observed, as compared with carbon coated nanoparticles. Raman spectroscopy further substantiated the formation of anatase TiO_2 nanoparticles (Fig. 3). The surface area measured using BET was $23.14 \text{ m}^2/\text{g}$, which is similar to the C- TiO_2 nanoparticles. Figure 12 shows the TEM and HRTEM images, indicating that TiO_2 nanoparticles are covered by a layer of SiO_2 , with thickness ranging from 3 to 8 nm. Silica coating on titania nanoparticles is well known from previous literature. Such coating could occur due to differences in chemical reaction rates of the precursors (Hung and Katz 1992). At small HMDSO concentrations, few and small SiO_2 particles or aggregates can also deposit on the surface of titania particles (Powell et al. 1997). Also, the oxidation of TTIP along with the formation of TiO_2 is faster as compared with the oxidation of HMDSO for the formation of SiO_2 (Hung and Katz 1992; Xiong and Pratsinis 1993). Hence, SiO_2 ends up coating the TiO_2 nanoparticles. Figure 13 shows the elemental mapping using electron energy loss spectroscopy (EELS). The result confirms that SiO_2 is formed around the TiO_2 sample and is not doped inside the particle. This is consistent with previous result (Teleki et al. 2005), however when the concentration of SiO_2 is increased significantly (> 40 wt%), the growth of segregated regions of TiO_2 and SiO_2 occurs.

A high resolution XPS spectrum of the Si 2p core level is shown in Fig. 14. The Si 2p core level (red line) is fitted with single peak centered at 103.5 eV (thick black line), corresponding to 4+ oxidation state (Si^{4+}) (Ingo et al. 1993; Jensen et al. 2013). This confirms the existence of SiO_2 on the surface of the TiO_2 NPs. The other core levels are similar to the C- TiO_2 sample where Ti^{3+} species represent 2% of the total Ti ions present on the surface of the Si- TiO_2 powder.

3.5 Vanadium doped TiO_2 nanoparticles

For the addition of vanadium, V-oxytriisopropoxide, was added to the TTIP precursor. The nanoparticles were predominately in the rutile phase based on XRD, where the anatase percentage is 28.9 % (Table 1). The addition of dopants is known to cause a shift in the anatase to rutile percentage of TiO_2 nanoparticles (Nie et al. 2009). Doping TiO_2 with some metal ions (including V^{4+}) increases the rutile content and changes the visible-light photoreactivity of TiO_2 nanoparticles (Choi et al. 2009). Raman

spectroscopy (Fig 3) further confirmed the increase in the rutile ratio. Additionally, a broad peak from 700 to 900 cm^{-1} as shown in Fig. 3 suggests the growth of polymeric vanadate (Kryukova et al. 2003; Stark et al. 2001), while the formation of V_2O_5 , which has a peak at $\sim 990\text{cm}^{-1}$ is not observed. This indicates that vanadium is most probably doped within the TiO_2 structure. The TEM images of V- TiO_2 are shown in Fig 15. The HRTEM image Fig. 15b shows spotted patterns, an indication of vanadium doping inside the TiO_2 nanoparticle.

High resolution XPS spectrum of O 1s/V 2p region is shown in Fig. 16. The V 2p core level is decomposed into 2 doublets V $2p_{3/2}$ – V $2p_{1/2}$ with a fixed area ratio equal to 2:1 and a doublet separation of 7.3 eV. The binding energies of V $2p_{3/2}$ for the two components are 515.8 eV, and 516.7 eV which is attributed to V^{4+} and V^{5+} oxidation states, respectively (Lars and Andersson 1990; Mendialdua et al. 1995). A mixture of V^{4+} and V^{5+} is commonly observed when vanadium is doped within TiO_2 lattice (Bhattacharyya et al. 2008).

4. Concluding remarks

Multiple diffusion flames were utilized to synthesize TiO_2 nanoparticles containing C, Fe, Si, and V in a single-step flame synthesis process. The growth of carbon-coated (C- TiO_2), carbon-coated with iron oxide (Fe/C- TiO_2), silica-coated (Si- TiO_2) and vanadium-doped (V- TiO_2) TiO_2 nanoparticles was demonstrated. XRD and Raman data confirmed that coating TiO_2 NP with carbon and the addition of iron does not have a significant effect on the anatase content ($\sim 90\%$ anatase), whereas adding Si decreases the anatase content by $\sim 10\%$. The addition of vanadium substantially changes the anatase phase to rutile ($\sim 29\%$ anatase). A graphitic carbon layer with thickness of 3 to 5 nm was coated on TiO_2 nanoparticles for C- TiO_2 . Adding iron to the sample (Fe/C- TiO_2) increases the carbon layer and small iron oxide nanoparticles were observed. TGA result showed that complete oxidation of carbon occurs at a temperature of 470°C (iron based sample) compared to 610°C (without iron) indicating the catalytic effect of iron based sample. XPS confirms the formation of Fe^{3+} oxidation state of iron. With regards to Si- TiO_2 nanoparticles, a uniform

coating of 3 to 8 nm of SiO₂ was observed around the TiO₂ particles. This coating can be attributed to the differences in the chemical reaction rates of the precursors. Finally, with regards to V-TiO₂, vanadium is doped within the TiO₂ nanoparticles, as observed from HRTEM, and XPS further confirms the formation of V⁴⁺ and V⁵⁺ oxidation states of vanadium.

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Figure 1: (a) Schematic diagram for the multiple diffusion flame burner, and (b) actual image of multiple diffusion flames without precursor loading.

Figure 2: XRD patterns for TiO₂ nanoparticles with the lower part representing the XRD-database for anatase and rutile phases.

Figure 3: Raman spectra for TiO₂ nanoparticles; A(anatase), R(rutile), D(carbon disorder) and G(carbon sp²).

Figure 4: TEM (a) and HRTEM (b) of C-TiO₂ nanoparticles.

Figure 5: High resolution XPS spectra of C 1s peak (a) and Ti 2p core level (b) for C-TiO₂ samples.

Figure 6: TEM (a) and HRTEM (b) of Fe/C-TiO₂ nanoparticles.

Figure 7: HRTEM of iron-oxide nanoparticles encapsulated within carbon.

Figure 8: High resolution XPS spectra of Fe 2p core level.

Figure 9: TGA results indicating the weight loss vs. temperature for C-TiO₂ and Fe-TiO₂ nanoparticles at constant heating rate of 2 K/min.

Figure 10: Images of carbon-coated samples (upper) before oxidation

Figure 11: TGA results indicating the weight loss vs. temperature for Printex-U and Printex-U mixed with Fe-TiO₂ nanoparticles at a constant heating rate of 8 K/min.

Figure 12: TEM (a) and HRTEM (b) of Si-TiO₂ nanoparticles.

Figure 13: Elemental mapping of the Si-TiO₂ nanoparticles; indicating (a) raw HRTEM image and elemental maps for (b) oxygen, (c) titanium, and (d) silicon.

Figure 14: High resolution XPS spectra of Si 2p core level.

Figure 15: TEM (a) and HRTEM (b) of Vi-TiO₂ nanoparticles.

Figure 16: High resolution XPS spectra of O 1s/V 2p core levels.

Table 1: Summary of the results for the synthesized nanoparticles.

Doped-particles	Precursor	Anatase %	d_{XRD} [nm]	BET [m ² /g]	d_{BET} [nm]
C-TiO ₂	TTIP + C ₂ H ₄	90.8	33.6	27.6	54.1
Fe/C-TiO ₂	TTIP + Ferrocene/Xylene	90.4	36.2	55.3	27.0
Si-TiO ₂	TTIP + HMDSO	80.0	42.8	23.14	64.1
V-TiO ₂	TTIP + V-oxytriisopropoxide	28.9	30.7	22.1	64.9

Table 2: Kinetic parameters (Eq. 7) for carbon content in the carbon-coated TiO₂ samples.

	C-TiO ₂	Fe/C-TiO ₂
m	-0.74	-1.0
n	0.13	0.13
E [KJ/mol]	132.1	123.1
A [1/min]	5.89E+06	1.17E+08