One-step synthesis of noble metal–titanium dioxide nanocomposites in a flame aerosol reactor

Vinay Tiwari a,b,1, Jingkun Jiang a,1, Virendra Sethi b, Pratim Biswas a,*

a Aerosol and Air Quality Research Laboratory, Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, MO 63130, USA
b Center for Environmental Science and Engineering, Indian Institute of Technology, Mumbai 400076, India

1. Introduction

Supported noble metal catalysts are widely used in industrial processes such as chemical synthesis, oil refining and exhaust gas treatment [1]. Nanosized noble metal particles (e.g. Pt, Pd, Rh and Ru) dispersed on high surface area supports (e.g. Al2O3, SiO2 and TiO2) have demonstrated high oxidation activity, good thermal stability and selectivity. Dispersing noble metals on the support surface (e.g. TiO2) can also enhance the catalytic activity of the support by changing its electronic properties [2]. Several researchers have studied the activity and selectivity of metal oxide supported noble metal and bimetallic noble metal (e.g. Pt-Pd) catalysts for environmental applications [2–4]. It was found that nanosized noble metal particles dispersed on the TiO2 support act as electron sinks, and result in a decrease in electron–hole recombination as well as in efficient charge separation during photocatalysis. The noble metal can also prevent the deactivation of the catalyst at high temperatures [5].

A robust synthesis method is critical for the preparation of supported noble metal catalysts with well-controlled properties. Liquid phase methods such as wet impregnation, sol–gel, and precipitation are commonly used for synthesis of catalysts, but these methods require many post treatment steps such as filtration, drying or calcination [6,7]. Compared to liquid phase synthesis routes, gas phase synthesis is a continuous one-step process which can be readily scaled up for high throughput production. It has been used for large-scale synthesis of commodities like carbon black and metal oxides [8]. Gas phase routes have been extensively studied for the synthesis of other nanomaterials including composites, metals, fullerenes and nanotubes [9]. The general principle of gas phase synthesis is to assemble molecules or atoms into desired nanoparticles by controlling the clustering process and aerosol growth dynamics, which depend on the reactant concentration and the reactor temperature–time history [10].
Gas phase synthesis routes such as flame aerosol synthesis [11], flame spray pyrolysis [12,13], high temperature aerosol decomposition (HTAD) [14] and spray reaction (SPR) [15] have been used for synthesis of metal oxide supported noble metal catalysts. Johannessen and Koutsopoulos [11] synthesized Pt/TiO₂ nanomaterials in a flame aerosol reactor (FLAR) where the solid noble metal precursor was delivered using a sublimation unit. Pt and bimetallic Pt-Pd catalysts on alumina support were prepared by Strobel et al. [12] via flame spray pyrolysis of precursors/xylene/acetonitrile mixture. A similar method was used to prepare noble metal catalysts on different supports [8]. These methods can also be used to synthesize nanocomposites which have photocatalytic properties [16]. However, more studies are needed to understand how to control the nanocomposite properties and their resultant photocatalytic activities.

Photocatalytic activities of TiO₂ and noble metal–TiO₂ composites have been studied extensively for various systems [16,17]. Most researchers described the photocatalytic process with a pseudo first order reaction and used a first order reaction rate constant to compare catalyst effectiveness. The role of various rate controlling parameters such as available catalyst surface, catalyst size, and crystal structure were not included [17–20]. The enhancement of photocatalytic activity may be attributed to a higher effective specific surface area due to the deposition of noble metals on the titanium dioxide surface. Therefore, the photocatalytic activity should be compared by a rate constant that incorporates effect of available catalyst surface area or active sites to test the net effect of the noble metals [21].

In this study a flame aerosol reactor was used for one-step synthesis of noble metal–TiO₂ nanocomposites, including Pt/TiO₂, Pd/TiO₂ and bimetallic Pt-Pd/TiO₂. The ability to control the catalyst properties and the resultant photocatalytic activity (photo-oxidation of methyl orange) by varying the nanocomposite synthesis conditions was examined. A model incorporating catalyst surface area was proposed to interpret the results.

2. Experimental methods

2.1. Catalyst synthesis

The experimental setup (Fig. 1) for synthesis of noble metal–TiO₂ nanocomposites has been modified from the design for single component nanoparticle synthesis [10]. It includes a precursor feeding system, a three-port co-flow diffusion burner, a quench/dilution system and a particle collection system. A bubbler was used to feed titanium tetra-isopropoxide (TTIP, 97%, Aldrich) precursor with N₂ carrier gas. The temperature of bubbler was kept constant at 88 °C for all experiments. TTIP precursor vapor carried by N₂ was introduced into the central port of the burner along with additional O₂. Additional O₂ fed in the central port helped to get a soot-free and stable flame. The volumetric flow rate of N₂/TTIP and additional O₂ in central port were 1.0 lpm (liter per minute) and 0.5 lpm, respectively. The acetylacetone salts of platinum and palladium (Pt(acac)₂, 97%, Aldrich; Pd(acac)₂, 99%, Aldrich) dissolved in xylene (96%, Riedel de Haen) and acetonitrile (99.5%, Sigma–Aldrich) mixture (2:1, v/v) were atomized in a stainless steel atomizer. Nanocomposites with different noble metal loading were synthesized by changing the concentrations of platinum and palladium precursors in the xylene/acetonitrile solvent mixture. Methane (CH₄), along with atomized platinum and palladium precursors, was introduced through the next to central port, and oxygen (O₂) was delivered through the outer port of the burner (Fig. 1). The flow rates were precisely controlled by mass flow controllers (MKS Instruments), and were 1 lpm and 5 lpm for CH₄ and O₂, respectively. To control the particle residence time in the high temperature environment [10], a quench ring was placed axially around the flame for selected experimental conditions (see Table 1). The position of the quench ring was varied with respect to the burner outlet (2–4 in., as shown in Fig. 1). Compressed cooling air with a total flow rate of approximately 25 lpm was supplied to the quench ring and entered the flame zone in a radial direction. Nanoparticles were collected downstream on a glass fiber filter assisted by a vacuum pump. For large quantity collection, an electrostatic precipitator can be used [10], whose performance has been studied both experimentally and numerically [22,23]. A water jacket was used before the vacuum pump to cool the gas stream and protect the pump.

2.2. Catalyst characterization

The crystallographic characteristics of synthesized samples were analyzed by a powder X-ray diffractometry (XRD) technique using a Rigaku D-MAX/A9 diffractometer with Cu Kα radiation (λ = 1.5418 Å). BET (Autosorb-1, Quantachrome) isotherm obtained by nitrogen adsorption at 77 K was used to determine

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Fig. 1. Schematic diagram of the system for noble metal–TiO₂ nanocomposite synthesis. Also shown is an illustration of the nanocomposite formation mechanism.
3.1 Synthesis and characterization

Samples and characterization results are presented first, and followed by a discussion. Table 1 summarizes the nanocomposite synthesis conditions. TTIP vapor decomposes at a lower temperature compared to the noble metal precursor acetylacetonate salts. Therefore, TiO$_2$ monomers are formed first and lead to larger TiO$_2$ agglomerates and aggregates through subsequent growth by collision followed by coalescence/sintering.

2.3 Photocatalytic activity evaluation

The photocatalytic activities of synthesized nanocomposites were tested by degrading methyl orange dye solution in a batch reactor (150 mL Pyrex glass beaker with a magnetic stirrer). The volume of methyl orange aqueous solution was 100 mL with an initial concentration of 10 mg/L. The solution was continuously stirred at 500 rpm for all experiments. Oxygen was bubbled through the reactor continuously with a 0.5 lpm volumetric flow rate controlled by a mass flow controller [24,25]. 25 mg of catalyst was used for all experiments. Initially the reactor was kept in the dark for 15 min to establish adsorption equilibrium. Following this, the reactor was irradiated with UV light (365 nm wavelength) by using a 100 W high pressure mercury lamp (Blak-Ray). 8 mL of sample was taken at 15 min intervals for 90 min (total of six samples). Before concentration measurement, all the samples were centrifuged for 20 min and filtered using a 0.2 µm syringe filter to remove the suspended nanoparticles. The concentration of methyl orange in the samples was determined by a UV–vis spectrophotometer (absorption at 460 nm, and standard calibration curve). The time varying concentration of methyl orange in the reactor was then used to establish the degradation kinetics.

3. Results and discussion

The experimental conditions and nanocomposite characterization results are summarized in Table 1. Nanocomposite synthesis and characterization results are presented first, and followed by a discussion of photocatalytic activity evaluation of the synthesized nanomaterials.

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2.3. Photocatalytic activity evaluation

The proposed formation mechanism of noble metal–TiO$_2$ nanocomposite is illustrated in Fig. 1. TTIP vapor decomposes at a lower temperature compared to the noble metal precursor acetylacetonate salts. Therefore, TiO$_2$ monomers are formed first and lead to larger TiO$_2$ agglomerates and aggregates through subsequent growth by collision followed by coalescence/sintering.

At regions of higher temperature in the flame, acetylacetonate salts of platinum and palladium decompose to form platinum and palladium vapor molecules. As the temperature decreases downstream, the noble metal vapors are saturated, and they can either condense on the TiO$_2$ agglomerate surface or homogeneously nucleate in the gas phase followed by subsequent deposition via collision mechanisms with the TiO$_2$ particles [8]. Noble metal particles on the TiO$_2$ nanoparticle can undergo further growth through condensation and coalescence/sintering mechanisms. TTIP was introduced through the central port of the burner and acetylacetonate salts of Pt and Pd were delivered through the next port to promote enhanced interaction of noble metal with the already formed TiO$_2$ nanoparticles.

TEM micrographs of Pt/TiO$_2$ nanocomposites with different loadings are shown in the Fig. 2. Pt metal particles of size approximately 2–4 nm were uniformly dispersed on the TiO$_2$ nanoparticles (30–40 nm). As the Pt metal loading was increased from 0.5% to 3% (weight percentage with respect to TiO$_2$), the surface coverage increased. The electron diffraction patterns of the pristine TiO$_2$, Pt/TiO$_2$ and Pt-Pd/TiO$_2$ are shown in Fig. 3. By comparing to theoretical d-spacing of each crystal plane for TiO$_2$, Pt and Pd, one can determine the composition of the nanocomposite. For pristine TiO$_2$, all the TiO$_2$ diffraction planes were identified (Fig. 3a). For conditions with Pt and Pd (or both) on TiO$_2$, platinum and/or palladium diffraction planes were observed respectively, in addition to TiO$_2$ diffraction planes (Fig. 3c and d). Some diffraction planes of Pt and Pd were missing due to the diffraction rings overlapping with those of the TiO$_2$. Other techniques such as X-ray photoelectron spectroscopy (XPS) can also be used to provide additional information about nanocomposites surface properties.

Incorporation of noble metals affected the crystal phases of the TiO$_2$ nanoparticles. XRD patterns of the TiO$_2$ with 0.5% total loading of noble metals (Pt, Pd and Pt-Pd) and pristine TiO$_2$ synthesized with identical flame reactor conditions are shown in Fig. 4. No peaks for Pt or Pd could be detected due to the low concentrations of the noble metals, similar to that reported by previous researchers [26]. For pristine TiO$_2$, a mixture of anatase and rutile phases were obtained due to the specific flame conditions selected in this work. On addition of the noble metals (Pt and Pd) the formation of the rutile phase of TiO$_2$ was suppressed. Incorporation of the noble metal on the TiO$_2$ surface stabilized the anatase phase, and inhibited anatase to rutile transformation probably due to an enhancement in phase transformation temperature as a result of a surface modification [25]. Similar phenomena were also observed when introducing dopants into titanium dioxide using flame
synthesis [27, 28] and employing surfactants during titanium dioxide liquid phase synthesis [29].

The specific surface area of the synthesized nanocomposite is a function of noble metal loading, and can also be controlled by adjusting the quench ring position. The catalyst specific surface area increased with increasing platinum loading on the TiO$_2$ surface (Fig. 5), due to the smaller sized platinum particles present on the surface of the TiO$_2$ particle. The surface area increase with increasing noble metal loading was consistent with the observed increased surface coverage (Fig. 2). The specific surface area can also be controlled by adjusting the nanomaterial residence time in the high temperature zone with the aid of the quench ring [10]. The specific surface areas of Pt/TiO$_2$ nanocomposites with 1% loading collected with the quench ring at different distances from burner outlet are shown in Fig. 5. When the quench ring was close to the burner outlet, nanocomposites with higher specific surface area were obtained, while those with smaller specific surface area were collected at higher quench ring positions. At the higher quench ring position, particle growth resulted in a decrease in the specific surface area.

3.2. Photocatalytic activity

The effective nanocomposite surface area should be taken into account when examining the overall photocatalytic activity. Most studies in the literature evaluated the catalyst activity based on a pseudo first order rate constant, without considering the modified catalyst surface area [17–19]. Using a model independent of surface area, the rate expression for methyl orange dye degradation by TiO$_2$ catalyst can be written as

$$\ln\left(\frac{C}{C_0}\right) = -kt$$

where $C_0$ is the initial methyl orange dye concentration (mol/L), $C$ is the methyl orange dye concentration at time $t$ (min), and $k$ is the reaction rate constant (min$^{-1}$). Experiments were done to examine the photocatalytic activity of commercial Degussa TiO$_2$ (P25, specific surface area of 57 m$^2$/g) of different total surface areas and with initial methyl orange dye concentration 10 mg/L: (1) 25.0 mg P25 mass loading and 100 mL methyl orange solution; and (2) 12.5 mg P25 mass loading and 100 mL methyl orange solution. Using Eq. (1), the rate constants were found to be 0.076 and 0.039 min$^{-1}$, respectively. Different rate constants were obtained as the model did not account for the catalyst surface area. These two experiments had different catalyst surface area per unit volume of solution, and hence different rate constants. To incorporate the effect of the surface area, the rate expression

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**Fig. 2.** TEM micrographs of platinum–TiO$_2$ nanocomposites with different Pt loadings: (a) 0.5% (no. 2), (b) 2% (no. 11), and (c) 3% (no. 13).

**Fig. 3.** Electron diffraction patterns of different samples: (a) pristine TiO$_2$ (no. 1), (b) Pt/TiO$_2$ (no. 2), (c) Pd/TiO$_2$ (no. 3), and (d) Pt-Pd/TiO$_2$ (no. 4).
was modified as

$$\ln \left( \frac{C}{C_0} \right) = -k'At \tag{2}$$

where $A$ is the photocatalyst surface area concentration (m$^2$/L of solution); and $k'$ is the modified rate constant (min$^{-1}$ m$^{-2}$ L). Using Eq. (2), the modified rate constants ($k'$) for the two experiments were found to be identical at 0.0053 min$^{-1}$ m$^{-2}$ L, as expected. Clearly, more detailed kinetic models have been developed and account for several other factors [24,25,30,31]. However, in this work, the overall approach used in Eq. (2) was found to be sufficient for comparing reactivities of pristine and composite titanium dioxide.

The normalized residual methyl orange dye concentration as a function of time is shown in Fig. 6 for pristine TiO$_2$ and TiO$_2$ with 0.5% noble metal (Pt, Pd and bimetallic Pt-Pd) loading. Without UV illumination, no degradation of methyl orange dye was observed. Compared to pristine TiO$_2$, 0.5% platinum loading enhanced the photocatalytic activity dramatically, whereas 0.5% palladium loading showed a detrimental effect on the photocatalytic activity. 0.5% Pt-Pd/TiO$_2$ nanocomposites showed an intermediate photocatalytic activity that was better than pristine TiO$_2$ and Pd/TiO$_2$, but lower than Pt/TiO$_2$. Since 0.5% noble metal loading does not result in a significant increase in the nanocomposite surface area compared to pristine TiO$_2$, the trends for the modified rate constants for different catalysts were consistent with the above observations.

The effect of noble metal loading on the photocatalytic activities for Pt/TiO$_2$, Pd/TiO$_2$ and bimetallic Pt-Pd/TiO$_2$ is shown in Fig. 7. The photocatalytic activity of Pt/TiO$_2$ started to decrease when the platinum loading was higher than 1.0%. An optimum loading of platinum around 0.5–1.0% was observed for the photocatalytic oxidation of methyl orange dye. The photocatalytic activity of Pd/TiO$_2$ decreased with increasing palladium loading (the minimum palladium loading tested here was 0.5%). When both Pt-Pd are used, a possible combination effect of the two noble metals was observed.

The presence of noble metal particles on the TiO$_2$ surface can lead to efficient charge separation by trapping or removing electrons from the TiO$_2$. As a consequence of the improved separation of electrons and holes, they are readily available to participate in the chemistry (transferring holes to create OH radicals, and electrons to the dissolved oxygen), thus enhancing the photocatalytic activity [2]. Platinum has the highest potential to remove/trap electrons from the TiO$_2$ surface [32], and therefore results in the highest activity enhancement, as also confirmed by
our experiments. The observed optimum platinum loading is consistent with results in the literature [2]. On further increasing Pt loading beyond the optimum levels, results in excessive coverage of the TiO₂ surface resulting in a shielding effect that potentially reduces electron–hole pair generation by incident UV light; and hence the effective photoactivity [33]. Increasing the platinum loading can also decrease the average distance between trap sites such that metal particles can now attract holes and promote electron–hole recombination [2]. The reason why palladium shows detrimental effects is not clear, although it is commonly believed that the deposition of noble metals can be either beneficial or detrimental in enhancing photoactivity, depending on the chemical nature of the pollutants [34]. For instance, it was previously reported that Pd, Pt and Ag addition onto TiO₂ can reduce the chlorinated hydrocarbon degradation efficiency, but lead to an increase of alcohol photodegradation [30,31,35]. Another possible explanation is that the lowest palladium loading used in our experiments, 0.5%, is already higher than the optimum palladium loading for methyl orange dye degradation. Low optimum palladium loading have been observed before in other systems, e.g. 0.05% Pd for photocatalytic oxidation of acid green 16 dye [36] and 0.15% Pd for photodegradation of 1,4-dichlorobenzene [17]. More studies such as detailed surface characterization and the interaction of Pd-TiO₂ need to be conducted to elucidate the reasons for a decrease in the photoactivity.

The nanocomposite surface area effect on the photocatalytic activity was also examined. The pseudo first order rate constant and the modified rate constant (k’. min⁻¹ m⁻² L) for 1% Pt/TiO₂ nanocomposites synthesized at different quench ring positions (resulting in different specific surface areas).

4. Conclusions

One-step synthesis of noble metal (Pt, Pd, and bimetallic Pt-Pd)–TiO₂ nanocomposites was demonstrated in a flame aerosol reactor. Strict control of effective surface area, crystal structure and noble metal loading was accomplished by adjusting the temperature–time history and the precursor feed rate. A range of samples were synthesized to evaluate the effects on the resultant photocactivity. Using a surface area based kinetic model, a comparison of photocatalytic activities of the different samples was performed. The influence of Pt and Pd, their loadings and surface area on photocatalytic activity was examined. Compared to conventional liquid phase synthesis methods that are multistep processes, flame synthesis provides better control on resultant nanocomposite properties; and can produce such materials in a single step.

References