Flame Synthesis and Coating of Nanostructured Particles in One Step

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ABSTRACT

A novel process was developed for direct synthesis and *in situ* coating of flame-made nanostructured particles in one step. Rutile TiO_2 particles made by flame spray pyrolysis (FSP) were coated in a single step with SiO_2 layers in an enclosed flame reactor. This *in situ* particle coating was accomplished by a hollow ring delivering hexamethyldisiloxane (HMDSO) vapor (precursor to SiO_2) through multiple jets in swirl cross-flow to Al-doped nanostructured rutile TiO_2 aerosol freshly made by FSP. The effect of HMDSO injection point, vapor concentration and coating vapor – aerosol mixing intensity on product particle morphology was investigated. The titania particles were uniformly SiO_2-coated with controlled and uniform thickness at a production rate of about 30 g/h and exhibited limited, if any, photoactivity. In contrast, spraying and combusting equivalent mixtures of the above Si/Al/Ti precursors in the above reactor resulted in particles segregated in amorphous (SiO_2) and crystalline (TiO_2) domains which exhibited high photocatalytic activity.

Keywords: Nanoparticle synthesis & applications, coating, flame Synthesis, TiO_2, photocatalysis

1 INTRODUCTION

A range of nanostructured particles (e.g. carbon blacks, silica, alumina and pigmentary titania) are made on an industrial scale at several tons per hour in flame reactors. Recent advances in aerosol and combustion science have contributed to synthesis of a wide spectrum of sophisticated nanostructured particles.[1] These include catalysts, gas sensors, phosphors, fuel cells, batteries, dental and orthopedic materials, and even nutritional supplements. These particles are often coated to condition their surfaces[2] so they can be easily dispersed in liquid suspensions (inks, paints, wafer polishing slurries) or polymers (e.g. dental prosthetics, tires, toothpaste etc.).

For example, in manufacture of pigments, the undesired photo-catalytic activity of TiO_2 is inhibited by applying SiO_2, Al_2O_3, and other oxide coatings in a post-synthesis, wet-phase treatment (Fig. 1: wet coating).[3] Thus, the synthesis and coating of such particles are two distinct processes and, practically, two manufacturing plants. As a result, the cost and complexity of this coating step is quite high.

There is a strong interest to simplify and improve this process by combining both particle synthesis and coating in a one-step gas phase process (Fig. 1: dry coating). Coherent and homogeneous coating on all TiO_2 particles is essential for optimal performance. Furthermore, optimization of coating thickness is desired, as silica decreases the UV absorbance of TiO_2 (e.g. in sunscreens) and increases production costs.
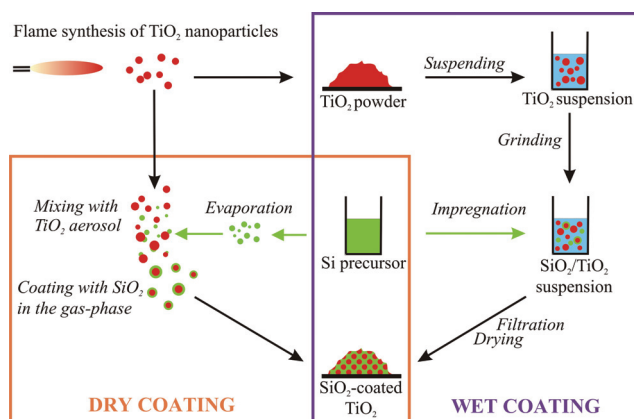

Figure 1: Comparison of conventional wet-phase and *in situ* flame coating methods for the synthesis of SiO_2-coated TiO_2. *In situ* flame-coating allows preparation in one step, whereas the conventional route be impregnation is a multi-step process.

Here a process was developed for *in situ* coating of flame-made particles. The process was applied to the silica (SiO_2) coating of (rutile) TiO_2 nanoparticles. Silica coatings passivate the photocatalytically active TiO_2 surface by hermetic enclosure of the chemically active sites. This improves the photostability of the final application as the particles are incorporated in organic liquid or polymer matrices. Emphasis was placed on hermetically coating particles made in scalable liquid-fed flame reactors, for their capacity to make an array of functional materials.[1]

2 RESULTS

A mostly rutile TiO_2-producing flame spray pyrolysis (FSP) reactor was enclosed (Fig. 2) to enable judicious injection of hexamethyldisiloxane (HMDSO) vapour, the SiO_2 precursor, downstream of the TiO_2 formation zone.[4] The HMDSO vapour was delivered through a hollow ring by multiple jets (typically 16) in swirl cross-flow to the freshly FSP-made TiO_2 aerosol. The effect of the most important process variables (injection location and HMDSO vapour concentration) on product particle

characteristics was investigated. The coating reactor (Fig. 2) was carefully and systematically designed through computer fluid dynamic (CFD) simulations and experiments to develop clear guidelines for design and operation of such reactors.[5] The coating quality was assessed by suspending the particles in isopropanol (IPA) and monitoring its photocatalytic conversion to acetone.
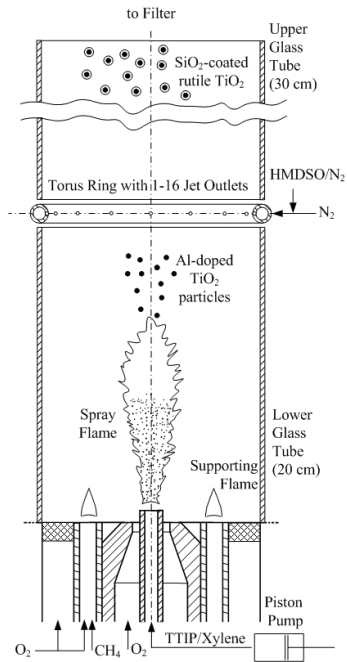

Figure 2: Experimental set-up for *in situ* SiO₂ coating of TiO₂ made in a FSP reactor enclosed by sequential glass tubes and in between them the torus pipe ring with 1 – 16 outlets for injection of HMDSO-laden N₂.[4]

Early injection of HMDSO at low burner-ring-distance (BRD) resulted in some coated particles and separate SiO_2 and TiO_2 regions or particles by precursor vapour co-oxidation. Similarly, FSP of HMDSO-containing Ti precursor solutions led to segregated morphologies (Fig. 3b) that exhibit high photocatalytic activity. In contrast, all particles appeared homogeneously coated with 2 – 4 nm thick SiO_2 films (Fig. 3a) and no separate domains or particles were visible when HMDSO was injected further downstream from the TiO_2 formation zone.

The coating thickness was controlled by the silica content. At less than 10 wt% SiO_2, no coating films were visible by TEM as the theoretical coating thickness was < 1 nm. The effect of coating thickness was also studied photocatalytically. Uncoated TiO_2 particles form 225 μg of acetone per mL of IPA. For silica-coated titania, the released acetone is reduced drastically to 149 and 26 μg acetone/mL IPA by coating with 5 and 10 wt% SiO_2, respectively. The reduction in released acetone (photocatalytic activity) with increasing silica content comes from the passivation of the TiO_2 surface by the coatings (Fig. 3a). At 2.5 wt% SiO_2, the coating should be very thin (< 0.5 nm) or rather partial (patchy) and thus

insufficient to hinder the photocatalytic activity of TiO_2. The coating coverage and thickness increases with increasing silica content, and at 10 wt% unambiguously visible SiO_2 coatings have been formed. Further increasing the silica content to 30 wt % has rather little effect on the acetone released. This indicates that coating with 10 wt % SiO_2 is sufficient to inhibit the photocatalytic activity of TiO_2.
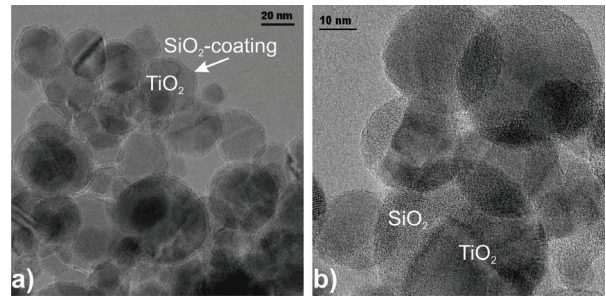

Figure 3: TEM images of 10 wt% SiO_2-coated TiO_2 (a) and co-oxidized 20 wt% SiO_2/TiO_2 (b).

The effect of jet intensity or power of mixing on gas composition in the mixing area between jets and aerosols was studied.[5] The exit velocity or the number of jet outlets for HMDSO-laden N₂ gas was varied. CFD showed that low flowrates or few jet outlets resulted in incomplete mixing across the radius of the reactor. At such conditions the coating efficiency decreased: separate SiO_2 and poorly coated TiO_2 particles were observed in transmission electron microscopy (TEM) images. In contrast, SiO_2-encapsulated TiO_2 particles were obtained at high mixing intensity or with multiple coating vapor jets which exhibited low photoactivity in UV-irradiated IPA suspensions.

Certainly, the coating of individual particles can be visualized by transmission electron microscopy (TEM) as was shown here in Fig. 3a,b. However, in order to gather statistically reliable data, more than 1000 representative particles must be analyzed, which makes TEM very time-consuming. Thus, simple and fast characterization methods were investigated to assess the coating quality and efficiency of partially and hermetically SiO_2-coated TiO_2 particles.[6] So, the flame-made Al-doped, mostly rutile, TiO_2 nanoparticles mixed or *in situ* coated with SiO_2 were characterized optically, electrophoretically, chemically and spectroscopically. Silica shifted the isoelectric point of aqueous supensions of externally mixed SiO_2 and TiO_2, co-oxidized or partially SiO_2-coated TiO_2 nanoparticles to lower pH compared to pure TiO_2 approaching that of pure SiO_2. Uncoated or partially coated TiO_2 particles could chemisorb isopropanol and partially convert it to propene. Coating titania, however, with more than 10 wt% SiO_2 completely inhibited isopropanol chemisorption and resulted in negative ζ potentials at all pH values. Particles containing segregated SiO_2 and TiO_2 domains present in co-oxidized SiO_2/TiO_2 exhibited stronger IR intensities of Si–O–Ti bonds than hermetically-coated TiO_2. Furthermore,

the intensity of the IR band or peak at 1225 cm^{-1} attributed to Si–O–Si asymmetric vibrations indicated a certain strain in these bonds for thin hermetic SiO$_2$-coatings in contrast to pure or separate domains of SiO$_2$. So electrophoretic behaviour and isopropanol chemisorption of these silica-coated TiO$_2$ particles could distinguish between partial (patchy) and complete (hermetic) coatings of TiO$_2$ and when combined with FT-IR it might be possible to identify separate SiO$_2$ domains (rough coatings) or particles.

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