Distinguishing between aggregates and agglomerates of flame-made TiO$_2$ by high pressure dispersion

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Non-agglomerated TiO$_2$ particles are desired for pigments or composites, while agglomerated ones are desired when making catalyst pellets to facilitate reactant/product flow. The interparticle bond-energies can range from weak van-der Waals forces (agglomerates) to stronger solid-state necks (aggregates). In post-synthesis processes, high stresses are needed to break even physical bonds in nanoparticle agglomerates, e.g. by ball-milling or high shear mixing in rotor-stator systems. High-pressure dispersion (HPD) has been used for impurity-free fragmentation of flame-made SiO$_2$ nanoparticle agglomerates (Wengeler et al., 2006).

Here the capacity of HPD and dynamic light scattering (DLS) for quantitative assessment of the extent of particle aggregation and agglomeration is investigated by examining the effect of applied pressure drop on the entire particle size distribution (Teleki et al., 2007). Titania particles made by flame spray pyrolysis (FSP; Madler et al., 2002) as well as commercially available (Degussa P25) ones are investigated. Upon fragmentation of their suspension by HPD, the resulting fragment size distributions are analyzed by DLS and compared to primary particle diameter measured by nitrogen adsorption (BET) and crystallite size by X-ray diffraction (XRD). Furthermore, the degree of particle aggregation is increased progressively by sintering FSP-made TiO$_2$ particles at 200 – 800 °C for four hours.

The cumulative volume distributions of Degussa’s P25 TiO$_2$ after dispersion are shown in Figure 1. Initially (0 bar, circles) the distribution is unimodal, as the P25 suspension is dispersed, bimodal distributions are obtained at all applied pressure drops. The small mode is shifted to smaller sizes as the pressure drop increases, most likely by erosion from larger agglomerates as the mass of fines is increasing. As the fine mode of P25 is larger than its BET and XRD diameters even at 1400 bar, it can be concluded it has few, if any, non-aggregated particles. In contrast, after dispersion at 1400 bar FSP-TiO$_2$ agglomerates were broken up into their constituent primary particles (peak around 25 nm) and aggregates (peak around 70 nm). The peak of the FSP-made fine particle mode (45 % of total mass) was comparable to its primary particle diameter (BET) and crystallite size (XRD). Increasing the post-synthesis sintering temperature of FSP TiO$_2$ resulted in larger fine particles even at the lowest temperatures (e.g. 200 °C) and enhanced the formation of aggregates by anatase to rutile phase transformation at the highest temperatures (e.g. 800 °C).

In conclusion, the dispersion of TiO$_2$ agglomerates suspensions through a nozzle at 200 to 1400 bar reduced the size of agglomerates (particles bonded by weak physical forces) resulting in bimodal size distributions composed of their constituent primary particles and aggregates (particles bonded by strong chemical or sinter forces).

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