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Mechanical stability measurements of surface modified nanoparticle agglomerates

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ABSTRACT

A low pressure impactor is used to measure the mechanical stability of nanoparticle agglomerates. The stability at different impaction velocities is quantified as changes in the projection area of agglomerate fragments deposited on TEM grids mounted on the impaction plate. Platinum particles produced in a spark discharge generator are used as model particles. The mechanical stability of unmodified Pt-agglomerates is compared with the ones of thermally pretreated and coated agglomerates. The coatings are produced in a plasma assisted chemical vapor deposition process using the post-discharge environment of a dielectric barrier discharge. The coating process allows the coating of particles with silica at ambient temperature and so minimizes structural changes of the agglomerates before impaction. The precursors utilized are tetraethyl orthosilicate for silica and hexamethyldisiloxane for silica-organic coatings. Both coatings improve the stability of the agglomerates as indicated by reduced structural changes during impaction. The silica-organic coating, which is applied at 200 °C, seems to prevent sinter-related changes to the particles, which is observed for the uncoated particles at this temperature. This is further corroborated by the deposition behavior of these coated particles, which resembles more that of the original particles at 24 °C. Furthermore, the rebound behavior of coated agglomerates impacting on the TEM grid is shown. It is found that a minority of the particles rebound back from the TEM grid into the gas, which occurs in parallel to the structural changes.

1. Introduction

The mechanical stability of agglomerates is determined by the adhesion forces acting at the contact areas between individual primary particles. Particles can adhere to each other due to solid contacts, such as sintering necks, capillary forces of adsorbed liquids, electrostatic forces and van-der-Waals forces. If counteracting external forces exceed the adhesion forces, the agglomerate may restructure or fragment. Such external forces can include thermal (Weber & Friedlander, 1997), ultrasonic (Kusters, Pratsinis, Thoma, & Smith, 1993), electrostatic (Svestka, Cermak, & Grün, 1993) or shear forces (Eggersdorfer, Kadau, Herrmann, & Pratsinis, 2010). The resulting deagglomeration is of interest when smaller particles are desired, e.g. in medical (Voss & Finlay, 2002) or food (Guraya & James, 2002) applications. However, many other applications rely on stable bonds between primary particles, e.g. particulate coatings on substrates (Stepien et al., 2013).

The mechanical stability of nanoparticle agglomerates in the gas-phase was extensively studied in impactors. Due to the small mass of nanoparticles, high velocities are required to impact them onto a surface with sufficient energy to overcome the adhesion

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forces. This can be achieved in a low pressure impactor (LPI), where the impaction is accomplished at pressures of a few mbar. Froeschke, Kohler, Weber, and Kasper (2003) demonstrated this method for the study of the fragmentation behavior of different particle materials. Seipenbusch, Toneva, Peukert, and Weber (2007) used such a setup to compare the binding strength of different metal agglomerates bound by van-der-Waals and magnetic forces. The influence of the degree of sintering on the stability of silica agglomerates was studied by Seipenbusch et al. (2010), who found a clear correlation between a reduction in fragmentation and the sintering temperature. Gensch and Weber studied the influence of the impaction angle and the rebound behavior of particles (Gensch & Weber, 2014, 2017). Ihalainen et al. studied the simultaneous breakup and bounce of different materials in a micro-orifice uniform deposit impactor (Ihalainen, Lind, Torvela, Lehtinen, & Jokiniemi, 2012). They found that the bounced fraction of the particles and the deposited fraction resulted in similar size distributions. Furthermore, they found that the degree of fragmentation depends on the primary particle size with agglomerates of smaller particles being harder to fragment (Froeschke et al., 2003; Ihalainen, Lind, Arffman, Torvela, & Jokiniemi, 2014). Since the degree of fragmentation depends on the particle material as well as the cross-sectional area of contact between primary particles, a coating of a more rigid material on the agglomerate should improve its stability during impaction.

There are multiple methods for coating nanoparticles with different shell materials, many of which use liquid-phase processes. However, while these liquid-phase methods may lead to homogeneous and defined coatings, they often require many process steps to extract the powder in the desired purity, such as removal of by-products, washing, and filtering. In contrast, gas-phase processes generally involve fewer steps and can be more easily coupled with subsequent powder modification or measurement methods. Common gas phase coating techniques include the flame synthesis (Qi, Moiseev, Deubener, & Weber, 2011; Teleki, Heine, Krumeich, Akhtar, & Pratsinis, 2008) or the atomic layer deposition (George, 2010). However, both often expose the powder to elevated temperatures during the process, which can lead to restructuring or sintering of the particles. Hence, if thermally unstable particles need to be coated, alternative coating techniques are preferable. Some plasma assisted processes provide a chemically reactive environment without the necessity of high temperatures. Furthermore, they allow the continuous coating of particles directly in the gas-phase and are for the most part independent of the particle synthesis method. The dielectric barrier discharge (DBD) is a relatively simple way to produce a non-thermal plasma and can be used for the coating of particles with different materials. Examples include the work of Vons, Creyghton, and Schmidt-Ott (2006), Nessim, Boulos, and Kogelschatz (2009), Marino, Huijser, Creyghton, and van der Heijden (2007) and Lei, Tang, Li, Luo, and Zhang (2007). The coating of particles is often accomplished directly in the plasma discharge. However, due to the strong electric fields this can result in the deposition of particles or coating material on the reactor walls, which decreases the long-term stability of the process. In the present work, a post-discharge plasma process was used (Post, Jidenko, Weber, & Borra, 2016; Post, Wurlitzer, Maus-Friedrichs, & Weber, 2018; Post & Weber, 2018). Here, neither the particles nor the precursors pass the discharge volume. Instead, the post-discharge environment of a DBD reactor is used to provide the reactive species necessary for the chemical vapor deposition (CVD) coating reactions. The precursors used here were tetraethyl orthosilicate (TEOS) and hexamethyldisiloxane (HMDSO), both of which are common for silica coatings. In this post-plasma process, the use of TEOS results in inorganic SiO_x coatings on the particles, while HMDSO-based coatings are silica-organic in nature (Post, Wurlitzer, et al., 2018). Two different variations of the post-plasma process were used. One process is performed at ambient temperature, which requires residence times in the range of minutes and a second method operates at elevated temperatures of up to 200 °C during the coating formation, requiring residence times of only a few seconds. While TEOS can be used in both, HMDSO requires the more reactive environment at elevated temperatures.

In the present work, highly agglomerated model Pt particles, produced in a spark discharge generator (SDG), are modified with a thin silica or silica-organic coating in the post-discharge process. The mechanical stability of these particles is quantified in a low pressure impactor by impaction onto a surface and the subsequent analysis of the deposited particles. It will be shown that these coatings improve the rigidness of the agglomerates by reducing the degree of structural changes. The aim of the work is not to provide a conclusive model of the impaction and cohesion physics, but instead to demonstrate a relatively simple way to modify and study the mechanical stability of nanoparticles.

2. Material and methods

The experimental setup can be divided in two main parts. The first one comprises the particle synthesis and the subsequent coating of these particles, while the second part concerns the stability measurement. Particles were synthesized with a spark discharge generator and then coated with a plasma assisted CVD process. The stability measurements were conducted with a low pressure impactor. Fig. 1 shows an overview of the setup. Both parts of the setup were coupled and enabled the direct measurement of the coated aerosol without any intermediate steps. However, while the particles were synthesized and coated at ambient pressure (1 bar), the stability measurements required low pressures. The transfer between the pressure regimes was accomplished with a critical orifice at the inlet of the impactor. Earlier studies with the setup have shown that the sheer forces acting on the particles in this critical orifice are too small to fragment the Pt agglomerates (Gensch & Weber, 2014).

2.1. Particle synthesis and coating

The particles were continuously produced in a spark discharge generator (SDG) (Tabrizi, Ullmann, Vons, Lafont, & Schmidt-Ott, 2009). A spark discharge generator produces particles by ablation of electrode material and subsequent particle nucleation and condensation in the gas-phase (Feng et al., 2016). Platinum was used as particle material, since the produced primary particles were typically small (single digit nm) and agglomerated quickly to much larger fractal structures with thin and long branches. This