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FLUIDIZATION OF NANOPOWDERS: EXPERIMENTS, MODELING, AND APPLICATIONS

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FLUIDIZATION OF NANOPOWDERS: EXPERIMENTS, MODELING, AND APPLICATIONS

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ABSTRACT

Nanopowders are applied in a wide range of processes, and their use continues to increase. Fluidization is one of the best techniques available to disperse and process nanoparticles. However, nanoparticles cannot be fluidized individually; they fluidize as very porous agglomerates. Often, it is needed to apply an assisting method, such as vibration or microjets, to obtain proper fluidization. In this paper, we give a brief review of the developments in nanopowder fluidization.

INTRODUCTION

Nanoparticles and nanostructured materials such as aerogels are being widely used in many industrial and environmental remediation processes because of their unique properties and large surface area that make them suitable as supports for catalysts and microorganisms, and as effective sorbents in separations. Nanoparticles are also of special interest to the pharmaceutical industry because their enhanced bioavailability can be used to advantage in drug delivery systems. Furthermore, they can be used in nanostructured materials for hydrogen storage, in Li-ion batteries, and in fuel cells.

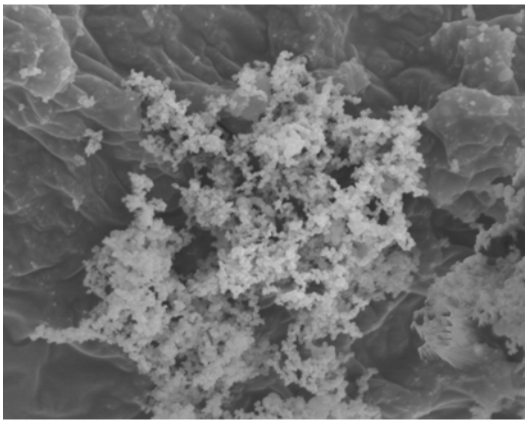

Figure 1. SEM image of agglomerate of silica nanoparticles.

While the vast majority of nanoparticle research is aimed at liquid-phase processing of nanoparticles, we believe that gas-phase processing has a number of important advantages. Due to the absence of liquid-solid interactions, it is easier to develop generic processing approaches. Moreover, gas-phase processing reduces contamination and separation problems, and allows easier scale-up. Fluidization is one of the best techniques available to disperse and process fine powders, but nanoparticles cannot be fluidized individually, and fluidize as large, very porous, fractal structured agglomerates due to the large cohesive forces between them (see, e.g., 1-3); Figure 1 shows an example us such an agglomerate. During fluidization of nanopowders several problems such as bubbling, channeling, clustering, and elutriation of particles are encountered. These problems do not allow for a good dispersion of the powder in the gas phase and lead to appreciable gas bypassing. Various assisting methods, all based on adding an external force field, have been developed to overcome these problems and enhance the fluidization of nanopowders. The quality of the fluidization obtained by applying these assisting methods is evaluated by measuring the minimum fluidization velocity, pressure drop, bed expansion, agglomerate size, degree of mixing, suppression of bubbling, amount of particles elutriated, and by visual observations.

Nanopowders have been classified as either agglomerate particulate fluidization (APF) or agglomerate bubbling fluidization (ABF) (3). APF is characterized by the absence of bubbles, low minimum fluidization velocity, and a large bed expansion. When these nanopowders are conventionally fluidized, the bed expansion is several times (3 to 5) the initial bed height before reaching the minimum bubbling velocity. Nanopowders that show this behavior are Aerosil 200, R974, 300 and R972, among others. Other nanopowders such as Aeroxide TiO_2 P25, Aeroxide Alu C and Aerosil 90 are classified as ABF type because of the presence of large bubbles at gas velocities higher than the minimum fluidization velocity. These nanopowders show a limited bed expansion (less than twice the initial bed height), a high minimum fluidization velocity when conventionally fluidized, and an abundance of bubbles that makes the fluidized bed interface unclear.

APPLICATIONS

Using one or more of the assisting methods to obtain homogeneous liquid-like fluidization, the nanoagglomerates can be further processed in large quantities in the dry state using unit operations such as reaction, coating, granulation, mixing, drying, and adsorption. Fluidization is already used in the large-scale production of carbon black and titanium dioxide. Fluidization of nanoagglomerates can also be used for the production of more advanced materials via coating processes such as chemical vapor deposition (CVD; see 4,5), atomic layer deposition (ALD; see 6-8), and molecular layer deposition (MLD; see 9). ALD coating of silica nanoparticles using fluidized beds, assisted by vibration or mechanical stirring has shown that although large nanoagglomerates are fluidized, individual silica nanoparticles are uniformly coated by the ALD process (6). The film thickness of the coating material is of the order of a few nanometers, is uniform throughout the entire bed, and the coating thickness depends on the number of ALD cycles used (6). While Weimer and co-workers perform particle ALD at low pressure, typically in the order of 100 Pa (6,7), van Ommen and co-workers recently showed that ALD on fluidized particles can also be carried out at atmospheric pressure (8). Figure 2 shows a TEM picture of the coated material.

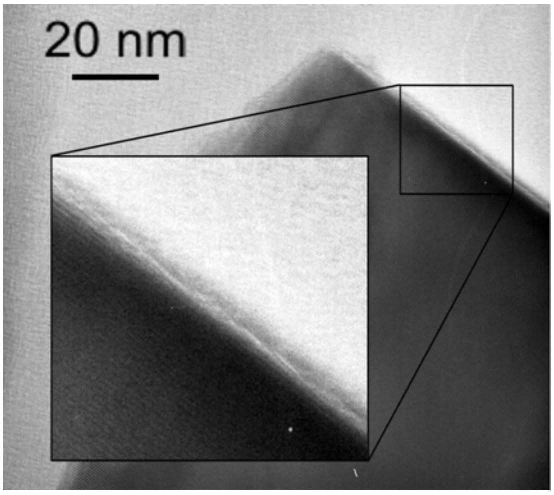

Figure 2. TEM picture of a $LiMn_2O_4$ particle coated with a thin layer of alumina (five ALD cycles) at atmospheric pressure. Such nanoparticles can be used as cathode material in Li-ion batteries (8).

ASSISTED FLUIDIZATION

Various assisting methods have been developed to enhance the fluidization of nanopowders. These methods include vibration (10), acoustic waves (11,12), magnetic particles excited by a magnetic field (13), alternating electric fields (14), use of a centrifugal field (in a rotating fluidized bed) (15), and use of a secondary flow in the form of micro-jets (16). In this brief review, we will focus on the latter two methods.

The use of a rotating fluidized bed for processing nanopowders has some distinct advantages over a conventional fluidized bed including less elutriation of powder, fluidization at much higher gas velocities resulting in a much higher gas throughput per unit area of distributor, smaller footprint, and shallow beds resulting in very small bubbles and therefore very little gas bypassing. For example, the minimum fluidization velocity for Aerosil R974, an APF type powder, in a RFB at a centrifugal acceleration (*G*) of 10 times gravity is about an order of magnitude higher than that observed in a conventional fluidized bed of the same powder (15). The minimum fluidization velocity increases linearly with *G*, but the fully expanded bed height is found to decrease with increasing *G*. Furthermore, the mean agglomerate size of Aerosil R974 nanoparticles is dramatically reduced by a factor of as much as 4 in an RFB for high *G* (40 times the acceleration of gravity) as compared to the mean agglomerate size measured in a conventional fluidized bed (1*G*). As expected the agglomerate density in an RFB is larger than that in a conventional fluidized bed and is also larger than in vibration and magnetic assisted fluidized beds. However, similar to the results obtained for vibration and magnetic assisted nanofluidization, when fluidizing 2 different species of nanopowders in the RFB, good mixing was found to occur on the micro-scale, but not on the nano-scale (17).

When a secondary flow, using a downward facing micro-nozzle, is introduced into the fluidization system in the form of a high velocity (sonic) micro-jet, the fluidization quality of agglomerates of nanoparticles is greatly improved (16). Of all of the assisting methods tried, the use of reverse micro-jets placed above the distributor give the best results. APF type nanoagglomerates can show as much as a 50-fold increase in bed height (as compared to the stationary bed height) when processed by the high velocity micro-jet. The larger bed expansion signifies a much better dispersion of the agglomerates in the dilute phase, while maintaining particulate fluidization behavior and showing a well defined interface with the absence of bubbles. Furthermore, when agglomerates of ABF type nanoparticles are exposed to the jet, the fluidization behavior is changed to APF type, showing a bed expansion as much as 5 times the initial bed height with the absence of bubbles. Figure 3 shows an example of the obtained increase in bed height. The micro-nozzles studied ranged from 125 up to 500 μm in diameter, producing a jet with sufficient velocity (hundreds of meters per second) and shear to break-up large nano-agglomerates, prevent channeling, curtail bubbling, and promote liquid-like fluidization. Recent research using discrete particle modelling indicates that agglomerate-agglomerate collisions play an important role the size reduction of the agglomerates (18). When two different species of nanoparticles were fluidized with micro-jet assistance, TEM-EELS images showed that mixing occurred on the nano-scale (16). Unlike some of the other nano-fluidization assistance methods described above, the use of micro-jets is effective, simple to use, does not require expensive equipment or adding foreign materials to the bed, uses less energy, is easily scaled-up and can be used to mix and blend different species of nano-particles on the nano-scale to form nano-composites.

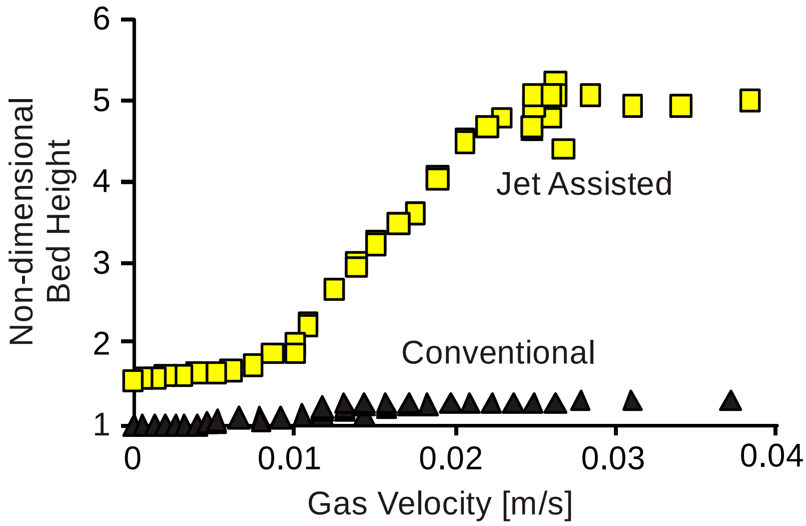

Figure 3. Comparison of the non-dimensional fluidized bed height as a function of gas velocity for conventional and microjet assisted fluidization of Aeroxide TiO_2 P25 (ABF nanopowder) in a 12.7 cm diameter column. The jet diameter is 254 μm, and the jet velocity is 320 m/s.

MODELLING AND MEASURING AGGLOMERATE SIZE

A number of theoretical models have been proposed to predict the mean agglomerate size during nanofluidization. All of these models incorporate the Richardson–Zaki equation, which was developed for particulate, smooth, liquid-like fluidization. Hence, these models can only be used for nanoparticles that show APF type behavior and cannot be used for nanoparticles that produce large bubbles (ABF type behavior). They also cannot predict the mean agglomerate size as a function of gas velocity. One of these models based on fractal analysis and a modified Richardson-Zaki equation to predict the agglomerate size, density and external bed porosity was compared with images taken with a CCD camera in the splash zone above the bed illuminated by a laser sheet and relatively good agreement was obtained (19-22). However, it is not known whether the mean agglomerate size and size distribution measured in the splash zone is actually representative of the mean agglomerate size and distribution in the bed itself.

In situ agglomerate size measurements and imaging of fluidized nano-agglomerates were achieved by reducing the electrostatic charge in the bed by bubbling the gas fed to the distributor through an ethanol-water solution and using Focused Beam Reflectance Measurement (FBRM) and Particle Vision Measurement (PVM) probes from Lasentec (23). The probes successfully characterize the number weighted and volume weighted agglomerate size distributions for both APF and ABF type nanopowders. At higher gas velocity, the concentration of agglomerates (counts) is seen to be lower, which is consistent with the increased bed expansion and higher porosity observed. The FBRM probe also shows that the mean agglomerate size tends to increase slightly with gas velocity, in contrast with the measurements made by photographing agglomerates in the splash zone, which show a decrease in mean agglomerate size with increasing gas velocity. The FBRM data and PVM images show that the probes are able to differentiate between different types of nanopowders (such as Aerosil R974 and Aerosil 90) and can also evaluate the effects of the micro-jet assisting method on the agglomerate concentration and agglomerate size; that is, the results show that the agglomerates are reduced both in size as indicated by the size distributions and in density as shown by the images.

CHALLENGES AND OUTLOOK

Proper fluidization of nanoparticles is often not possible without an assisting method. Experiments have shown that the fluidization behaviour of nanoparticle agglomerates is greatly enhanced by adding a secondary flow in the form of a high-velocity jet produced by one or more micronozzles pointing vertically downward toward the distributor. However, the exact working of these microjets is not yet fully understood. Also some of the other assisting methods, such as the use of acoustic waves, need further research to fully understand and optimize them. Another virtually unexplored field is the modelling of reactions involving fluidized nanopowders. Given the large range of length scales that play a role – one nanoparticle agglomerate easily consists of billions of particles – a multi-scale modelling approach will be needed.

We anticipate that in the coming years, nanoparticles will find more and more applications, for example in pharma, catalysis, and energy storage. In some cases simple, single-material nanoparticles can be applied, but several applications ask for more complex, nanostructured particles such as core shell particles or aerogels. It will be crucial to scale-up production processes while precisely maintaining the specifications of the particulate product. We believe that fluidization of nanoparticles will play an important role in this.

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EXPERIMENTS AND MODELLING OF MICRO-JET ASSISTED FLUIDIZATION OF NANOPARTICLES

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KEYWORDS

Nanoparticles, agglomerates, microjet, assisted fluidization, review, atomic layer deposition.