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Review on the nanoparticle fluidization science and technology☆

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article info abstract

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1. Introduction

Powder is a dry, bulk solid composed of a large number of very fine solid particles. Nano-structured particulate materials consisted of various spheres, flakes, tubes, and rods possess unique mechanical, electrical, optical, electrochemical, and thermal properties. Recently, novel advanced nano-structured materials for energy conversion and storage, environmental, catalysis, materials engineering, biology, drug, sensors, devices, information technology are highly concerned. This emerges the opportunity for extending the knowledge base of chemical engineering [\[1\].](#page--1-0) Usually, these pristine nanoparticles belong to group C particles according to Geldart's classification, which were extremely fine powders and therefore the most cohesive particles [\[2\]](#page--1-0). Fluidization of most Group C particles was difficult to achieve, which may require the introduction of external forces (e.g. mechanical agitation). Accordingly, the nanomaterials with tunable structures and extraordinary properties are strongly considered by both scientific communities and industrial engineers, and the related nanomaterial processing becomes an emerging research area.

Fluidization has an ability to turn static particles to fluid-like dense flow, which greatly makes improved heat transfer among porous powders and highly efficient solid processing become reality. Many excellent review publications have been appeared to well illustrate the

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Gas fluidization has an ability to turn static particles to fluid-like dense flow, which allows greatly improved heat transfer among porous powders and highly efficient solid processing to become reality. As the rising star of current scientific research, some nanoparticles can also be fluidized in the form of agglomerates, with sizes ranging from tens to hundreds of microns. Herein, we have reviewed the recent progress on nanomaterial agglomeration and their fluidization behavior, the assisted techniques to enhance the fluidization of nanomaterials, including some mechanical measures, external fields and improved gas injections, as well as their effects on solid fluidization and mixing behaviors. Most of these techniques are effective in breaking large agglomerates and promoting particulate fluidization, meanwhile, the solid mixing is intensified under assisted fluidization. The applications of nanofluidization in nanostructured material production and sustainable chemical industry are further presented. In summary, the fluidization science of multidimensional, multicomponent and multifunctional particles, their multi-phase characterization, and the guideline of fluidized bed coupled process are prerequisites for the sustainable development of fluidized bed based materials, energy and chemical industry. © 2015 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

> importance of fluidization science and fluidized bed technology [3–[12\].](#page--1-0) However, with the rise of nano research, the cutting edge knowledge between chemical engineering, physics, materials, as well as nanoscience is growing rapidly.

> In this contribution, the recent progress on the science and technology of nanomaterials fluidization has been reviewed. The nanoparticle building blocks belong to group C particles and their fluidization is extremely difficult. However, some nanoparticles can be smoothly fluidized in the form of agglomerates. Therefore, we tried to review the essence of nanoparticle agglomeration, their fluidization phenomena, and the assisted techniques to enhance the fluidization. In addition, the applications of fluidization for mass production of nanomaterials and novel chemical engineering process were also included.

2. The Fluidization Science of Nanomaterials

Nanomaterials with morphological features on the nanoscale (smaller than 100 nm in at least one dimension) have been strongly considered. Their controllable synthesis by novel processes such as high gravity controlled precipitation [\[13\],](#page--1-0) gas combustion [\[14\],](#page--1-0) microfluid [\[15,16\],](#page--1-0) hydrothermal reaction [\[17\]](#page--1-0), and fluidized bed chemical vapor deposition [\[18,19\],](#page--1-0) has been well documented. Usually, the nanomaterials prefer to aggregate into multi-scale agglomerates [20–[22\]](#page--1-0), and the agglomerates behave similar to porous particles. When the gas passes through the nanoparticles, their agglomeration, fluidization behavior and related characterization are quite different from the routine Group A and C powders. New insight into nanoagglomerate fluidization is the first step to understand the unique fluidization behavior and develop nanomaterial process.

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2.1. Nanoparticle agglomeration

When the size of powder became small, the interactive forces between nanoparticles significantly increase. Therefore, the nanoparticles prefer to be coalesced into aggregates. The properties of the primary nanoparticles determine the architectures of the agglomerates that control the behavior of the two-phase flow in a fluidized bed reactor. As shown in Fig. $1(a, b)$, the SiO₂ aerogels with a size of 7 to 16 nm form micro-agglomerates by several steps with different bonding mechanisms [\[20\].](#page--1-0) The cohesive force between nanoparticles and the gravity force on the agglomerates are effectively diminished by the porous hierarchical multi-stage agglomerate structure, thus, even with a fairly high bed expansion, these $SiO₂$ agglomerates still form bubbleless fluidized beds that have a texture much closer to the particulate fluidization of a liquid–solid system. This system obeys the Richardson–Zaki relation, as opposed to the aggregative bubbling regime in many gas– solid beds. Moreover, the structure of the agglomerates as well as their size, apparent weight, and the interactive forces significantly influence the hydrodynamic and their group behavior of nanoparticle agglomeration based on Geldart's classification. For instance, the multi-stage agglomerates consisted of Group C primary nanoparticles exhibited the fluidization behavior that was similar to Group A particles (Fig. $1(c)$). Recently, de Martin and co-workers [\[23,24\]](#page--1-0) studied the multidimensional structure of nanoparticle agglomerate with combined neutron scattering and image analysis. They indicated that the fluidized agglomerates had three fractal dimensions: the first was sintered aggregates from synthesis, the second was agglomerates formed during storage, and the last was large agglomerates broken under fluidization.

The particle densities, shapes, surface roughness, sizes, and size distributions are important parameters affecting the operating range of fluidized beds as well as the gas–solid mixing and heat/mass transfer. Among these solid properties, particle size and size distribution are of the primary elements, which significantly affect the interaction between the individual particle and its neighboring particles, the movement of particles in a group, and the fluid-particle mixing and contacting during fluidization. A force analysis shown in [Fig. 2](#page--1-0)(a) is presented to reveal the relationship of the ratio between the gravity and cohesive force and the drag force, $(F_g + F_c) / F_d$, vs. particle size range [\[25\].](#page--1-0) With the decrease of particle size, the gravity force decreases continuously and the cohesive force increases sharply. The cohesive force becomes nearly the same as the drag force at a certain particle size d_p^* . Thus, the particles with a size of less than d_p^* afford strong interparticle van der Waals force between fine particles that induces strong aggregation [\[25,26\].](#page--1-0) Consequently, the elutriation rate constant and other hydrodynamic behaviors differ from those particles where the gravity and drag forces are in dominance as the particle size varies.

From the theoretical consideration, Johnson–Kendall–Roberts model [\[28\]](#page--1-0), Deryaguin–Muller–Toporov model [\[29\],](#page--1-0) and their extended/modified models, have been developed to calculate the adhesion force between smooth surfaces undergoing elastic deformation. However, the measured adhesion force for particles between 10 and 100 μm is always less than the theoretical results due to the surface roughness which reduces the contact area between two contiguous bodies with respect to the case when contacting surfaces are perfectly smooth [\[30\].](#page--1-0) The adhesion force between two rough spheres is composed of the attraction between two parent spheres representing the large scale curvature of the surfaces and the adhesion between an asperity and the parent spheres [\[30\]](#page--1-0). And the asperities can dramatically reduce the interparticle adhesion force by surface coverage with nanosized particles ([Fig. 2](#page--1-0)(b)). Recently, Chen and his co-workers proposed

Fig. 1. (a) Chain-structure and (b) multi-stage of SiO₂ nanoparticles [\[20\]](#page--1-0); (c) group transition behavior of nanoparticle agglomeration based on Geldart classification.

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