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PUTTING STRUCTURES INTO FLUIDIZED BEDS - FROM CONCEPT TO INDUSTRIAL APPLICATIONS

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ABSTRACT

Structures of particles, particle agglomerates, distributors, and internals have significantly influence on hydrodynamics and transfer behaviors of the dense gas-solid fluidized bed. For nanomaterial production, the particle surface and their agglomerated structures directly influence the fluidization behaviors; while for coal to chemical process, the distributors, internals play an important role in regime transient, and hydrodynamics. Carbon nanotubes mass production, coal to chemicals process, and fuel production were employed as examples to describe the concept of putting structures into fluidized bed, and then to put these structures into industrial applications.

The asymmetric surface of solids plays a very important role in material functions, such as its reactivity, catalytic performance, adsorption, and transfer behaviors, which were rapidly developed with the growth of nanotechnology and information technology. Recently, nano-structured granular materials, which are consisted of various flakes, tubes, and rods, possess unique mechanical, electrical, optical, electrochemical, and thermal properties. Novel advanced functional nanomaterials for energy conversion and storage, environmental, catalysis, materials engineering, biology, drug, sensors, devices, information technology are highly concerned. Those particles usually belong to group C particles according Geldart classification, which were extremely fine powders and therefore the most cohesive particles. The fluidization of Group C particles was difficult to achieve, which may require the application of some external forces, such as mechanical agitation. Recently, with the fast development of nanotechnology, nanomaterials with tunable structures and extraordinary properties were widely investigated.

In fluidized bed, the particles become fluid-like dense flow. Thus, the heat transfer between fluid and solid phase is over thousand times of that on porous catalysts, which is an important step for high-efficiency solid processing. For fluidization

behavior, the symmetric spherical particles and cylinder fluidized beds always the first and simplest choice. While for the academic researches and industrial applications, it is quite important to let materials or catalysts well fluidize, and to control their fluidized states as well as transfer behaviors. Structured internals in a fluidized bed reactor have significantly influences on regime transition. Recently, they were also widely used in a fluid catalytic cracking (FCC) stripper. To get high yield of intermediate products, plug flow fluidized bed with high efficient heat transfer were highly required. Structured distributors and internals can also play an important role in control of the backmixing and heat transfer of the fluidized bed. When the fluidized bed reactor is coupled with special structures for various functions, excellent heat and mass transfer properties as well as the multifunctional properties were provided by the particles. This significantly enlarges fluidized bed reactor applications for chemical or material production, or even device manufacture. When putting those structures into fluidized bed, a series of scientific questions were proposed: 1) Can those structures be smoothly fluidized? 2) Can we use fluidized bed to produce structures in large scale? 3) Can we use structure to improve the efficiency of fluidized bed process?

To answer these questions, we briefly review our recent progress on putting structures into fluidized bed reactor, and demonstrate several examples in mass production of carbon nanotubes (CNTs), high efficient catalytic reaction for coal to chemicals and particle sensors for detection of fluidization state.

FLUIDIZATION SCIENCE: NANOPARTICLE AGGLOMERATION AND ITS FLUIDIZATION

Nanomaterials with morphological features on the nanoscale (smaller than 100 nm in at least one dimension) have become the focus of science because of many interesting properties that make them attractive for various applications. Interactive forces between nanosized particles significantly increase with decreasing particle size, so nanoparticles coalesce easier than micron-sized particles. The properties of the primary particles determine the properties of the agglomerates that control the behavior of the two-phase flow in a fluidized bed. For instance, as shown in Fig. 1, the SiO₂ aerogels with a size distribution of 7 to 16 nm form agglomerates, called multi-stage agglomerates (MSA), by several steps with different bonding mechanisms.^[2] The cohesive force between nanoparticles and the gravity force on the agglomerates are effectively diminished by the porous MSA 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–solids system and which obeys the Richardson–Zaki relation, as opposed to the aggregative bubbling regime in many gas–solids systems. In the region of $U_g =$

0.01–0.08 m/s, the average hydrodynamic diameters of the fluidized complex agglomerates are 230–331 μm . The structure of the agglomerates as well as their size, apparent weight and the interactive forces between them significantly influence the hydrodynamic behavior of agglomerating fluidization.

Except nanoparticles, 1D nanomaterials, such as CNTs which consist of graphene sheet wrapped around to form cylindrical tubes, were selected as model to demonstrate their fluidization behavior. The dependences of bed expansion and pressure drop on gas velocity in a CNT nano-agglomerate fluidize bed is shown in Fig. 2.^[3] A smooth and highly expanded fluidization was achieved, but a strong hysteresis exists in the CNT fluidization curve. On the defluidization branch, similar to Geldart-A particles, particulate fluidization, ABF, turbulent, and fast fluidizations can be successively observed. However, U_c and U_{se} of the CNTs were relatively lower than that of Geldart-A particles, due to the weak interaction among the CNT agglomerates and their highly porous structure. This indicated that good fluidization behavior can be achieved only with strong turbulence of the fluidized bed, because of strong interaction between agglomerated CNTs.

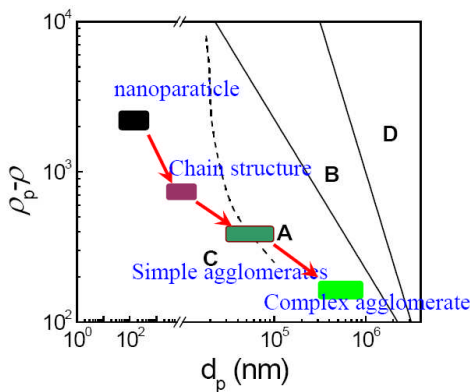


Fig. 1. Nanoparticle agglomeration behavior on Geldart classification.

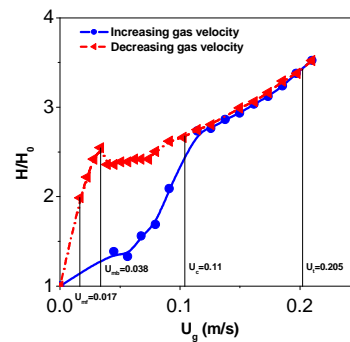


Fig. 2. Dependence of bed expansion and pressure drop on gas velocity in a CNT nano-agglomerate fluidized bed.^[3]

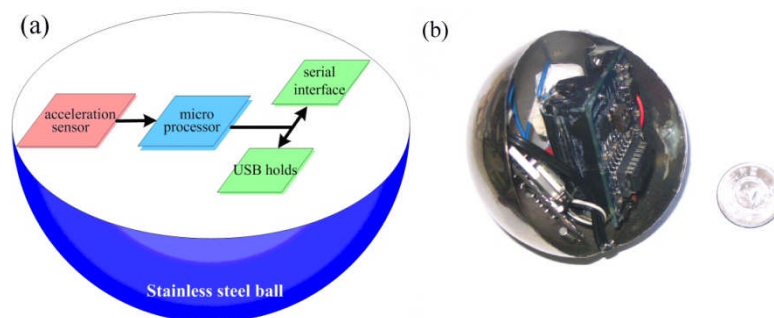


Fig. 3. (a) Design of prototype PMS. (b) A PMS prototype.^[4]

To identify a particle trace in a fluidized bed, an intelligent particle spy capable of detecting, transferring, and storing data, is proposed under the name of Particle Measurement Sensor (PMS) (Fig. 3).^[4] The mobile PMS can be appended to the measurement system to sense movement information, including acceleration, velocity, distance between particles, and so on. A prototype 60-mm-dia PMS was tested and served as a particle spy in a fluidized bed delivering the *in situ* acceleration information it detects. With increasing superficial gas velocity in the fluidized bed, the acceleration felt by PMS was observed to increase. The variance of the signals, which reflect the fluctuation, increased at first and then reached a maximum at the gas velocity (U_c), which marks the transition from bubbling to turbulent fluidization. The probability density distribution peak can be divided into the emulsion phase peak and the bubble phase peak. The average acceleration of emulsion and bubble phase increased, while the variance of both phases reached a maximum at U_c , at the same time. However, the difference between the variances of two phases reached the maximum at U_c . The solids mixing behavior of nanoparticle in a fluidized bed were also investigated.^[5] The axial and radial solids dispersion coefficients of nanoparticles were two orders of magnitude lower than those in fluid catalytic cracking (FCC) catalyst systems. The axial solids dispersion coefficient increased with increasing superficial gas velocities, and ranged between 9.1×10^{-4} and 2.6×10^{-3} m²/s. There was a step increase in the axial solids dispersion coefficient between the particulate fluidization regime and bubbling and turbulent fluidization regimes. As the superficial gas velocity increased, the radial solids dispersion coefficient increased gradually, from 1.2×10^{-4} to 4.5×10^{-4} m²/s. The much smaller D_a and D_r , compared to regular fluidized systems, is mainly due to the reduced density difference between the fluidized particles and fluidizing medium.

PARTICULOGICAL DESIGN: NANOSTRUCTURE PRODUCTION IN A FLUIDIZED BED

The fluidization technique has been an efficient route for materials production. However, how to produce tunable nanostructured materials in a fluidized bed is still an open area. We selected CNTs as a typical advanced nanostructured materials to describe their mass production via fluidization bed chemical vapor deposition (CVD).^[1, 6] CNTs possess extremely high tensile strength, high modulus, large aspect ratio, low density, good chemical and environmental stability, and high thermal and electrical conductivity. It is a new type of carbon nanomaterials with high performance that are in demand for different potential applications, including both the large-volume applications (such as supercapacitor or battery electrodes, battery electronic additives, conductive, high-strength composites, etc.) and limited-volume applications (such as electronic devices, etc). Recently, CNTs have been used as fillers in advanced battery electronic additives, supercapacitor or battery electrodes,

and light high-strength composites at a scale of hundreds of tons. Mass production of CNTs with desired structure at a low cost is the first step.



Fig. 4. The pilot plant facility for MWCNT production.^[1]

Among various ways to synthesis CNTs, the CVD method has the advantages of mild operation, low cost, and controllable process, and is the most promising method for the mass production of CNTs. In CVD methods, the carbon source is deposited with the assistance of a catalyst at temperatures lower than 1200 °C. Tubular CNTs are deposited at the catalyst site. Fe, Co, Ni particles, always show high activity for CNT growth. With sustainable growth of CNTs, the as-grown tubes will cluster into agglomerated or aligned CNTs. The CNT aggregates were nanocarbon products in which CNTs are randomly entangled with each other, while the CNT arrays were nanocarbon products in which CNTs are nearly parallel to each other.

The agglomerated CNTs are 3-dimensional network structure composed with large amounts of CNTs. They are very easy to be synthesized for the reason that CNTs are

prone to entangle with each other during the growth on powder catalysts.^[7] If the wall number of CNTs decreased and became double/single-walled, then the as-obtained CNTs will be very flexible. S/DWCNTs were confined grown in the porous catalyst.^[8] S/DWCNT growth needs not only a good dispersion of the active metal components on the catalyst support and a suitable large BET surface area, but also a proper catalyst structure. Layered double hydroxides (LDHs), also known as hydrotalcite-like materials, which are a class of two-dimensional nanostructured anionic clays whose structure is based on brucite ($Mg(OH)_2$)-like layers, can be used as a novel catalysts for SWCNT growth with a huge BET surface area of $1289\text{ m}^2/\text{g}$.^[9]

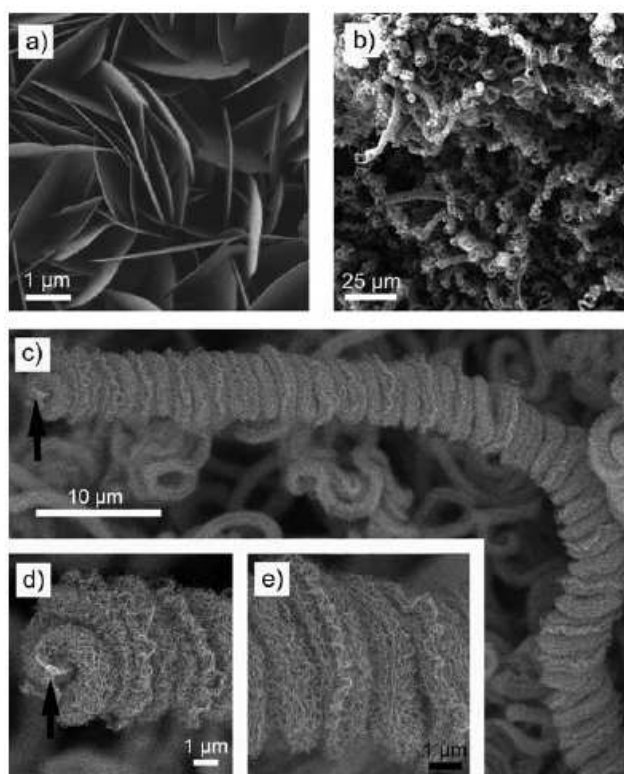


Fig. 5. CNT-array double helices grown on Fe/Mg/Al LDH flakes. a) As-obtained Fe/Mg/Al LDH flakes; b) a large number of CNT-array double helices; c) dextrorotatory CNT-array double helices grown on LDH flakes; d,e) calcined LDH flakes and middle section of (c);

Based on catalyst concept design, multiphase flow of CNTs, and process scale up rules, A pilot plant for producing high quality and purity MWCNTs was designed (Fig. 4).^[1] Based on the fluidized bed technologies developed, we realized a commercial production of MWCNTs with a capacity of 560 tons per year, and SWCNTs with a capacity of 8 tons per year in the middle of 2009.

The aligned structures of CNTs were always obtained via a bottom-up self-assemble process during thermal/floating CVD. The synchronous growth of a CNT forest induced by stress was found.^[10] Based on CNT growth and agglomeration mechanism, various effective strategies for VACNT mass production have been proposed. It is commonly reported that aligned CNTs can be synthesized on a flat surface. However, the surface area of the flat substrate is often limited and its mobility is poor. Only 1 g/h VACNT arrays can be obtained with flat silica as substrate. If a substrate with a larger surface area is used, such as spheres, more VACNT

arrays can be produced. We have recently large scale synthesized VACNT arrays on spheres,^[11] quartz fibers^[12] and flakes.^[13] Left or right handed CNT arrays were twisted into a double helix on a LDH flake through a self-organization process during growth by chemical vapor deposition (Fig. 5).^[13a] The wall number and diameter of CNT in the double helix can be tuned by chemical precursor mediated process.^[13b] To avoid the damage caused by the collisions among CNT arrays during the transport or fluidization process, a strategy of intercalating VACNTs into layered compounds and directly constructing a layered hybrid nanocomposite composed of alternate CNT films and inorganic sheets was proposed (Fig. 6).^[14] This is a successful way for the mass production of VACNT arrays in a fluidized bed reactor. A 3.0 kg/hr VACNT array productivity was realized in a fluidized bed reactor with a diameter 500 mm.^[15] The CNTs in the as-grown arrays were with good alignment, and can be easily purified by facile acid treatment.

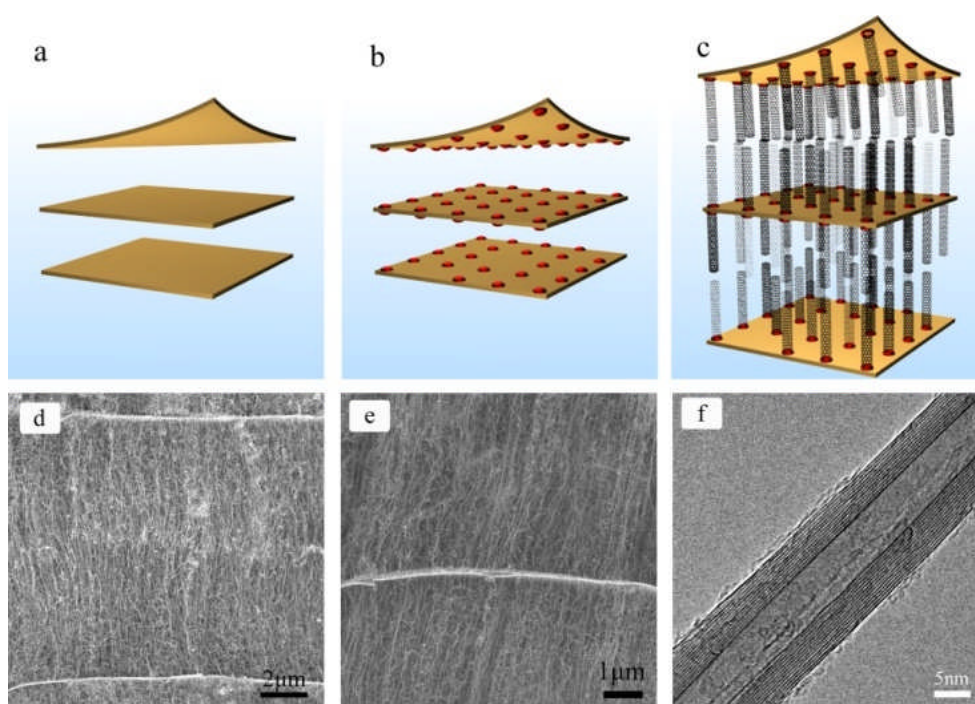


Fig. 6. Illustration of the formation of hybrid composites by intercalating vertically aligned CNT films into layered inorganic compounds, showing stacked layers in the original vermiculite (left panel), catalyst particles adhering to the surface of the layers after impregnation (middle), and aligned CNTs between the layers after the CNT growth process (right); d) SEM image showing an enlarged view of a single interlayer with aligned CNTs and an interlayer distance of 20nm. e) SEM image showing CNT growth on both sides of a vermiculite layer. f) Transmission electron microscopy image of a multiwalled CNT.

For the horizontally aligned CNT formation, the gas flow, which makes the CNTs grow in a way similar with a flying kite, is efficient for super long (20 cm) CNT growth at a fast rate (80-90 $\mu\text{m/s}$).^[16] The growth rate of CNT is very high, and the weight space velocity can reach $10^8 \text{ g}_{\text{CNT}}/\text{g}_{\text{cat}}\text{h}$, which is millions of times of that of agglomerated CNTs on porous catalyst. The synthesis of HACNTs on movable or free substrates in a fluidized bed to obtain long CNTs is still an important issue.

Based on particuological concept design, the agglomerated CNTs and aligned CNTs have been successfully mass produced in ton scale via fluidized bed process, and are available in the market. This will greatly promote the bulk applications of CNTs, and provide a sustainable route for the development of the novel advanced materials.

INDUSTRIAL APPLICATION: MULTI-FUNCTIONAL STRUCTURE FOR ADVANCED CATALYTICAL FLUIDIZATION TECHNIQUE

The last level of structure in fluidized bed is in macro-scale of fluidized bed, such as the distributors, internals or bluffs in a fluidized bed reactor. Chemical looping concept for high efficient fossil fuel conversion by a family of configurations with different reactors or regions of fluidized bed have also been explored.^[17] Many applications of internals in fluidized bed have been employed for acrylonitrile, aniline, vinyl acetate and vinyl chloride monomer synthesis,^[18] and fluid menthol to propylene. The influence of internals on hydrodynamics and mixing in fluidized bed and related reactor performance will also be presented.

Due to the worldwide crude oil shortage and the rapidly increasing demands for light olefins, the methanol to olefins (MTO) process and dimethyl ether to olefins (DTO) process were selected as the alternative ways for the production of light olefins. Because of the strongly exothermicity of MTO/DTO reactions and fast deactivation of SAPO-34 zeolite catalyst, a fluidized bed was the preferred reactor for industrial application.^[20] Consequently, the MTO/DTO catalysts needed to be prepared for facile fluidization. Herein, a hierarchical SAPO-34 zeolite with high crystallinity and excellent hydrothermal stability was directly synthesized in the nanoscale confined environment provided by the natural layered material kaolin (Fig. 7).^[19] The hierarchical sample showed a much higher conversion than the conventional zeolite. The overall olefin selectivity was as much as 96.7%, which was 4–7% higher than that of the conventional zeolite. The presence of the mesopore structure shortened the diffusion path, thus, the primary products could easily diffuse out of the zeolites and secondary reactions were avoided. Therefore, higher propylene selectivity and overall olefin selectivity were obtained. This expected to be a facile and economically

feasible way to prepare more effective catalyst for fluidized MTO/DTO process. A fluidized bed methanol to propylene (FMTP) industrial technology was developed. The industrial practice of fluidized bed for FMTP process at Huainan with a 470 hours of continuous operation at full capacity were carried out, and high yield of propylene was reached (Fig. 7c).

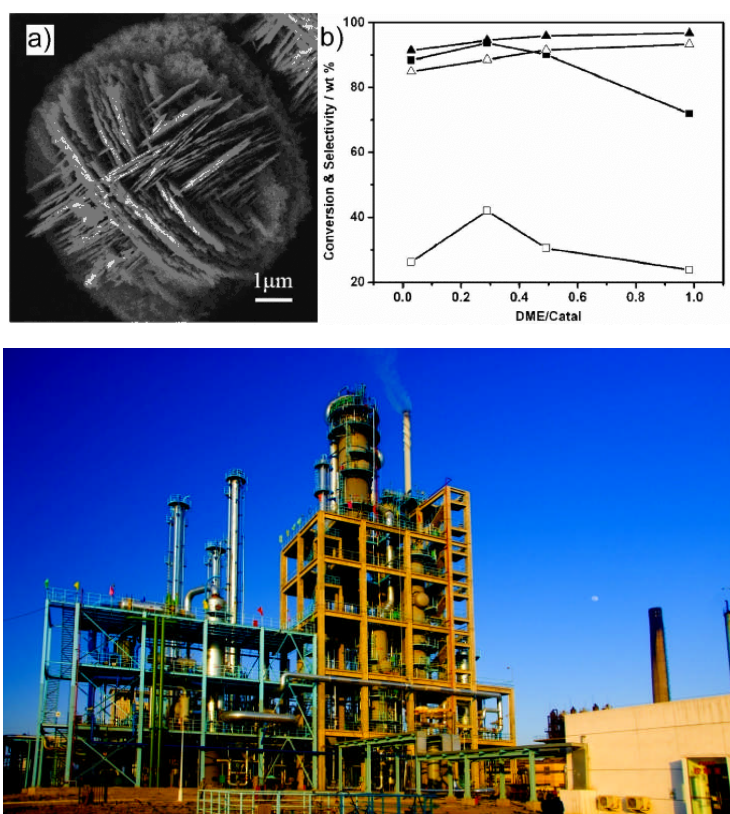


Fig. 7. a) As synthesized hierarchical SAPO-34 zeolite; b) DME conversions and overall olefin selectivities (Conversion on hierarchical (■) and conventional (□) SAPO-34; selectivity on hierarchical (▲) and conventional (Δ) SAPO-34.^[19] c) 300kT/a multistage fluidized bed FMTP unit

Polyvinylchloride (PVC) is second largest general plastics in the world, the very low space velocity makes gas-phase catalytic hydro-chlorination of C_2H_2 on $HgCl_2$ /activated carbon (AC) catalyst only can be carried out in packed bed at high conversion. However, if a multistage fluidized bed (MSFB) is applied into this process, a high conversion of C_2H_2 at 130-140 °C at a high space velocity of C_2H_2 , while maintaining high selectivity to vinyl chloride monomer (VCM), could be obtained by efficiently inhibiting the back-mixing of gases between stages. The new catalyst with a coconut-shell-type AC as the support shows much higher mechanical strength for stable fluidization with a proper pore structure for the dispersion of $HgCl_2$ and a high thermal stability, as compared to a catalyst with coal-based AC as the support in

conventional packed bed reactors. The catalyst lifetime estimated by simulation and a rapid sublimation experiment fits in well with the data from the pilot plant test. These results suggest that the combination of a MSFB and the new catalyst described here is a novel technology for producing VCM on a large scale at low cost. The scale-up of MSFB through a series of small hot model, 3000 ton/a pilot-plant and 100 kT/a industrial plant was demonstrated and reactor modeling of the scale up of the MSFB was carried out, as shown in Fig. 8.



Fig. 8. Top: Internal structured fluidized bed reaction; Bottom: Multistage fluidized bed reactor for VCM production scale-up process: Left: small hot model test unit; Middle: 3 kT/a pilot plant; Right: 100kT/a multistage fluidized bed CVM unit

The flow structure of gas-solid can significantly regulated the flow directions. The gas-solid downward flow (downer) reactor can reduce axial gas and solids backmixing by 30 times in comparison with upward flow riser reactor. Downer is therefore acknowledged as a novel multiphase flow reactor with great potential in high-severity operated processes, such as the short contact time reactions with the intermediates as the desired products.^[21] Compared with the riser reactor with the same feeds and catalysts, the LPG and propylene yield increased by 8.15 and 4.30 wt%, respectively. The gasoline octane number likewise reached 94.8 with 28 wt% olefin content. However, dry gas is significantly suppressed, and the coke has little

change in yield even with the increased catalyst to oil ratio. With some gasoline recycling, the LPG and propylene yield increased by 11.45 and 5.06 wt %, respectively. The olefin content in gasoline significantly decreased to 22 wt %; the high octane number (95.4) is maintained. The computational fluid dynamics (CFD) coupled with a 6-lump kinetic model is also applied to simulate the FCC process for the industrial trials. The yield of propylene and butylene and the temperature profile along the axis direction demonstrated consistency between the simulation results and the experimental data. The axial solid mixing mechanisms in gas-solids cocurrent upflow and downflow circulating fluidized bed systems revealed that among the many influencing factors, flow direction has the most profound influence on the axial solids mixing. When the flow is in the direction of gravity (downflow in the downer), axial solids dispersion is very small and the flow pattern approaches plug flow; when the flow is against gravity (upflow in the riser), axial solids dispersion is significantly larger and the flow pattern deviates significantly from plug flow. Solid mixing is found to be mainly due to the dispersion of dispersed particles in the downer; however, in the riser, both the dispersion of dispersed particles and particle clusters were co-existed in the riser.. In both the riser and the downer, the dispersion of the dispersed particles is very small, indicating that dispersed particles pass through the system in a near plug flow pattern. Dispersion due to particle clusters in the riser, on the other hand, is very significant, contributing to the large axial solids backmixing and the bimodal solids residence time distribution in the riser.

CONCLUSIONS

Development of fluidization technique has spanned several decades, attesting to the importance of this technique in chemical engineering, thermal engineering, and metallurgy. When nanostructured granular materials were used for fluidization, some kinds of nanoparticles (such as SiO₂, carbon nanotubes) are agglomerated into multi-stage agglomerates for stable fluidization. The structure of the agglomerates as well as their size, apparent weight and the interactive forces between them significantly influence the hydrodynamic behavior of agglomerating fluidization. The concept of a particle spy was tested in the form of an encapsulated prototype PMS was proposed to *in situ* detect the phase structure of fluidized bed. The axial and radial solids dispersion coefficients were both two orders of magnitude lower than those in FCC systems. Based on the scientific understanding of nanomaterials fluidization, the fluidization process was successfully employed for nanomaterial (both agglomerated and aligned CNT) production. Multi-functional nanostructures, such as hierarchical SAPO-34 zeolite, were employed as advanced catalysts for catalytic fluidized bed route for methanol to olefin process. Novel fluidized bed reactor, such as the novel riser-downer coupling reactor for the FCC process and a two-stage fluidized-bed for gas-phase catalytic hydrochlorination of acetylene, were

also proposed. More efforts should be paid on new scientific challenges for nanomaterials fluidization and novel industrial process for nanomaterial production and (nano)structure enhanced fluidization technology for advanced materials, novel chemical production, and energy conversion.

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