Crystallization and Crystallizing Processes to Produce Controlled-Properties Solid Particles†

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Abstract

The need for preparing solid particles with required properties has led to the development of processes allowing control of these properties: high purity, size, size distribution, crystalline form, flowability, packability, or other specific effects. This paper deals with several "new" processes of preparation of solid particles of controlled properties. Most of these processes have been known for a long time but they have not been carried out extensively in production. The potential of such processes is shown.

1. Introduction

Over the past decade, the chemical industry has been faced with a quickening trend towards improvement of product quality in relation to the growing importance attached to fine chemicals, pharmaceuticals, special-effect chemicals and other high-value materials. The need for high-purity powders with controlled properties of size and size distribution, crystalline form, morphology, specific surface area, flowability, packability and specified effects for their use has led to the development of new processes for preparing chemicals in solid form. Most of these processes are based on fundamental principles of crystallization occurring naturally or combined with other operations such as solvent extraction, drying, and granulation. This contribution provides a non-exhaustive review of some of these processes which have already been known for a long time, but whose application to industrial purposes can be considered as rather new.

2. Some principles of crystallization from solutions

The crystallization or precipitation of powders involves the nucleation and growth of solid particles from a supersaturated solution.

Supersaturation can be induced in several ways. Systems in which the solubility of the solute increases with temperature can be brought to supersaturation by cooling the solution. For systems in which the solubility is not sensitive to temperature, supersaturation can be easily achieved by isothermal evaporation of the solvent. These two methods are often combined in the vacuum cooling crystallization process in which a hot concentrated solution is adiabatically flashed to a reduced pressure.

Supersaturation may also be induced by adding other miscible components to the solution in order to reduce the solubility of the solute. This method, extensively used to produce speciality chemicals, is usually called drowning out. In the case of a reaction product present, for example, as an anion in the solution, the addition of excess quantities of a counterion forces the product out of solution. This method is well known as salting out.

In many instances, a chemical reaction in the solution may produce an insoluble species which precipitates out as the reaction proceeds. This occurs for instance in the production of azo pigments and disperse dyes from coupling reactions, and in a lot of inorganic chemical systems. The reactive crystallization is traditionally referred to as precipitation.

Drastic effects on crystallization kinetics and crystal morphology or purity may be related to the presence of impurities in the crystallizing systems. These impurities are often difficult to remove and several steps of recrystallization may be required to produce crystals with their desirable properties. In other cases, controlled trace quantities of selected species may be used specifically as additives to control the crystallization process.

In addition to nucleation and crystal growth, other phenomena may occur in industrial crystallizers. Attrition due to mechanical interactions between crystals and between crystals and moving mechanical
parts results in the generation of small crystals a little larger than those created by nucleation, and makes parent crystals more rounded with free flowing properties. Dramatic damage to parent crystals as a result of high-energy contacts between crystals and moving parts of crystallizers can be induced through breakage with the formation of coarse fragments and a severe size reduction of damaged crystals.

With an opposite effect on the size distribution, agglomeration often takes place when two or more crystals are attracted by any kind of cohesion force and remain together sufficiently long that they grow into stable entities containing individual crystalline particles of irregular shape and usually poor flow properties.

2. Use of tailor-made additives to control crystallization processes

The morphology of a crystal results from the relative growth rates of its various faces, with the general rule that the slower the growth rate, the larger the face. The growth rate of each individual face is determined by intermolecular interaction between molecules in the crystal, as well as by external parameters such as solvent, temperature, supersaturation, impurities. Dramatic modification in crystal morphology may result from changes in any of these factors. In particular, small traces of surface-active impurities may induce morphological changes when adsorbed at specific surfaces of the growing crystal. These impurities can act either by reducing the specific surface energy or by blocking integration of a growing face or by limiting the supply of material to the crystal face. They can be ionic species, surfactants, chemical binding complexes or specific molecules subjected to electrostatic and van der Waals interactions, or tending to form hydrogen bonds with the substrate molecules at the surface. Recently, owing to the increased power of computers and understanding of the solid state, potential energy calculations at the microscopic level and evaluation of molecular interaction in the growth layer faces have led to quantitative prediction of crystal morphology. The effects on crystal habit caused by tailor-made additives whose molecular structures are very close to those of the substrate molecules comprising the crystal have been derived from these analyses. The additive is selectively adsorbed on the host crystal sites only on those faces where its modified part emerges from the crystal surface. On these faces, the additive is bound in a very similar way to a substrate molecule by virtue of interactions between its unmodified part and the neighboring substrate molecule at the surface layer. The regular deposition of oncoming crystal layers becomes thus disturbed, causing retardation of growth normal to these faces with the consequence of a relative increase in their surface area. From there, it is also possible to select inhibitors in order to modify the habit of organic crystals in a desired and controlled manner.

Figure 1 shows modifications of the habit of (E)–cinnamide crystals in the presence of additives obtained by substituting a bulkier functional group for a corresponding one of the substrate molecule.

A new form of engineering, namely morphological engineering, is now emerging and tailor-made additives are being designed, including surfactants. The important feature of this methodology is the specificity of tailor-made additives in technological applications. Besides changes in crystal morphology, additive design is starting to be used as an effective means of separating products from racemic solutions in relation to chiral products, and of controlling the production of a desirable polymorph even at the expense of the stable form.

3. Hydrothermal synthesis of ultrafine crystalline powders

Fabrication of ceramic materials such as titanates, magnetic materials such as ferrites or of other component materials suitable for living bodies such as hydroxyapatites involves the sintering of powders whose required characteristics are usually high purity, high degree of crystallinity and ultrafine size with narrow size distribution. The hydrothermal process has been successful for preparing powders with the required specificities. It allows liquid-phase reactions that do not occur below 100 °C to proceed appreciably. It consists in precipitating the product under a non-crystalline gel-like state in a first step at room temperature as the result of a reaction between two aqueous solutions, and then subjecting the suspension to the hydrothermal treatment in an autoclave at controlled heating rate and stirring speed, and maintaining it for several hours at a fixed temperature, generally between 100 and 300 °C. In the case of Ni-, Co- and Zn-ferrite synthesized by Kumazawa et al., round ultrafine particles were formed whose size ranged from 6 to 16 nm dependent on hydrothermal conditions, and whose size
distribution could be described by a log-normal function with a geometric standard deviation of about 1.2. The crystallinity degree increased with temperature.

4. Precipitation of microsized particles from supercritical fluid solutions

Hannay and Hogarth observed the remarkable ability of supercritical fluids (SF) to dissolve solids as early as 1879. In recent years, there has been a growing interest in using SF as a solvent in a number of crystallization and precipitation processes to ensure the manufacture of crystalline and amorphous powders with morphologically uniform particles and narrow size distribution. An important advantage of SF used as solvents is the high sensitivity of the solubility of solids with respect to temperature and pressure. Due to the high compressibility of SF, small changes in pressure result in large changes in density and solvent power. Addition of small amounts of a cosolvent to SF can also enhance solvent power by a very significant factor. Moreover, as pressure perturbations propagate very quickly within SF, the medium is essentially uniform whereas in conventional crystallization, the suspension undergoes temperature gradients. The consequence is that nucleation generates particles more uniform in morphology and narrower in size distribution than those produced in conventional crystallizing systems.

4.1 Crystallization in the supercritical region

Tavana and Randolph have reported experimental results of the crystallization of benzoic acid in SF CO₂. The operation was run in a similar way as a conventional batch cooling crystallization. In conventional batch cooling crystallization, a saturated solution is cooled from an initial temperature at which the solute is highly soluble to a final lower operating temperature, with lower solubility, along an optimal cooling curve followed to maintain a reasonable level of supersaturation as crystallization proceeds. When the solute-laden solution is a SF, supersaturation can be induced by varying either temperature or pressure. It is more convenient to choose pressure as the main variable. Depressurisation curves can be fixed in order to promote formation of small or large-sized particles as desired. The crystallization process remains in the supercritical region. The authors have shown that nucleation and growth mechanisms are the same as those involved in liquid solvents, but the process in SF offers the potential to change particle size distribution very easily without the
4.2 Use of supercritical fluid as an anti-solvent

Some processes involve SF for their anti-solvent effect on the product to be crystallized. They consist in preparing a solution of the solute with a classical liquid solvent. Mixing the solution with the non-solvent SF leads to the formation of two phases. The lighter one mainly contains the SF with a certain amount of the solvent without the solute. The heaviest one consists of the solvent, a large amount of the SF, and the solute whose solubility is considerably reduced so that it precipitates out. This process has been used successfully to produce crystals of cyclotrimethylene trinitramine, RDX, commonly called plastic, by adding SF CO₂ to a solution of RDX in cyclohexanone. Other applications relate to pigments for paints, explosives, polymers, magnetic materials, semiconductors, superconductors, and piezo-elastic materials.

4.3 Rapid expansion of supercritical fluid solutions (RESS)

Several researchers have performed studies on the production of fine particles as the result of a rapid expansion of SF solutions. Battelle has developed a process called the RESS process (Figure 2). It typically involves the dissolution of a solid in a solvent at increased temperature and pressure to enhance the solubility. The resulting solution is heated to supercritical conditions in a pre-expansion region. Then it is allowed to expand rapidly through a short nozzle into a low-temperature and low-pressure environment where the solvent power of the fluid is negligible. The time scale of the expansion ranges between 10⁻⁸ and 10⁻⁵ seconds. This provokes the rapid nucleation and growth of the particles, provided that sufficient solute density exists in the expansion jet (Figure 2).

Two situations can arise. Under proper pre-expansion conditions, the solvent passes from the SF state to the gaseous state and the product is collected essentially dry. When the pre-expansion temperature is not high enough, a two-phase gas-liquid region is traversed during the expansion producing droplets. This technology offers the potential to produce thin films, fibers, and fine powders with narrow size distributions in crystalline or amorphous form, dependent on the pre-expansion and post-expansion conditions. As well as on the flow properties of the nozzle across which the expansion is allowed to occur.

4.4 Production of aerogels by supercritical drying

Aerogels have been used as catalysts for more than fifty years. Their production involves synthesizing a sol-gel by using alkoxides. This begins by the formation of a sol which is a suspension of solid particles in a liquid, then of a gel which is a diphasic material with the solid encapsulating a liquid. The liquid can be removed from the gel by conventional drying, but drying with supercritical extraction (supercritical drying) gives better qualities to the product. Especially the surface area is twice as large and the pore volume is almost an order of magnitude higher. In addition, it remains amorphous after being

![Fig. 2 Principle of RESS process (from reference 26)]
heated up to 500 °C. This process was developed by Teichner (19) in the 1960s. It could be carried out to produce other materials than aerogels (pharmaceuticals, optical fibers, catalysts, composite materials).

4.5 Other processes involving supercritical fluids to produce solid particles

Garabos et al (26) have reported several processes, all under study, involving supercritical fluids to produce solid particles. These processes will not be described in this paper. However, it can be noted that hydrothermal synthesis in a SF medium, which has been known for fifty years, is fairly analogous to the hydrothermal synthesis in a liquid medium presented in Section 3. This process allows the preparation of uniform-sized powders with very high chemical purity and very high crystallinity.

Recent studies have shown that reverse microemulsions can be formed in a continuous supercritical phase whose properties are the same as those generated in conventional liquid solvents at atmospheric pressure. The small droplets, whose diameter ranges between 3 and 20 nm, act as local microreactors and enhance interactions between the product in solution within the droplets and the continuous phase as a result of very high diffusivities in SF. This allows the generation of very fine particles with a very narrow size distribution.

SF has also been used as a reaction medium for a long time. The best example is polymerisation of ethylene at very high pressure (over 150 MPa) in supercritical ethylene. The polymer formed is dissolved in the SF monomer and is withdrawn continuously. It has been possible to produce many powders as the yield of reactions carried out in SF media, with the advantage of very easy recovery by expansion of the supercritical medium. Such processes allow one to operate at higher temperatures without any risks of damaging the reactants and products. TiO₂ has already been obtained in the form of a very fine crystalline powder (less than 100 nm) from titane isopropoxide in supercritical ethanol at 360 °C.

5 Spherical crystallization for the development of pharmaceutical preparation

Most dosage forms are solid: capsules, pellets, tablets. They are made from powders whose properties must be reproducible. Generally, crystallization and granulation are the two steps necessary to equip the initial powder with adequate properties (flowability, packability). Spherical crystallization can be seen as a new technique combining crystallization and agglomeration processes by which the crystals obtained are directly agglomerated into spherical form (28, 29). Developed by Kawashima (22), this process proceeds according to two steps: the precipitation of the drug crystals and then their agglomeration thanks to the addition of a bridging liquid which wets the crystals preferentially. A very interesting method consists in using a three-solvent system: a solvent, a non-solvent and a third solvent that is miscible with the other two solvents. For instance, in the case of salicylic acid, water-chloroform-ethanol is a representative solvent combination. Crystallization occurs in the shaded region of the diagram shown in Figure 3. Liberation of small quantities of chloroform induces wetting of the salicylic acid crystals and provokes their agglomeration into spherical-form aggregates. These spherical aggregates can be directly compressed into tablets, whereas it is difficult to directly compress salicylic acid crystals due to their characteristic needle shape which is responsible for their poor flowability and packability (Figure 3).

6. Preparation of solid particles of controlled properties in emulsions

6.1 Emulsion-solvent-diffusion method for preparing agglomerated crystals

With the same purpose as the spherical crystallization, Kawashima et al. (30) have developed a new emulsion-solvent-diffusion method (Figure 4) to agglomerate the crystals of poorly compressible pharmaceuticals during crystallization without using...
any binder. In this process, the drug X is dissolved in a solvent S at temperature $T_1$ in a storage tank. A non-solvent, NS, miscible with S and containing small quantities of an emulsifier, E, is kept agitated at temperature $T_2$ ($T_2 < T_1$) in the crystallizer. Then the X-S solution is fed at a constant flow rate from the storage tank to the crystallizer through a capillary tube. The crystallization system is thermally controlled at temperature $T_2$. An emulsion of small droplets of X-S solution is formed in the NS continuous phase due to the presence of the emulsifier E. The temperature of droplets is rapidly reduced. Simultaneously, the solvent S in the droplets diffuses to the outer continuous phase while the non-solvent NS enters the inner phase (droplets). These heat and mass transfers lead the droplets to their supersaturation limit from which nucleation occurs. Crystals grow within the droplets, and spherical drug crystal agglomerates are finally produced while retaining the initial shape of the emulsion droplets first formed. The tensile and shear tests of the resultant agglomerated crystals prove their appreciable flowability and packability. They can be easily compressed into tablets without capping (Figure 4).

This technique has been extended recently to include direct encapsulation of a drug in biodegradable polymeric nanospheres serving as the carrier of the drug.

6.2 Chemical reactions in microemulsions to obtain ultrafine particles.

Ultrafine particles can be obtained as a result of chemical reactions in microemulsions acting as micro-reactors in order to control their growth. The method described by Lopez-Quintela and Rivas consists in preparing two microemulsions formed by nanodroplets of water dispersed in oil, each containing an appropriate reactant. Once the right microemulsion systems are obtained, they are mixed (Figure 5). An interchange of the reactants A and B takes place during the collision of the nanodroplets in the microemulsions. This interchange is very fast and the reaction occurs rapidly, leading to nucleation and growth of the crystals produced inside the droplets which control the final size of the particles. Microemulsions should be chosen in such a way that the

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**Fig. 4** Schematic process for emulsion-solvent diffusion method (from reference 30)
curvature radius is similar to the natural radius so that the surfactant film cannot be opened during collisions which would lead to an interchange of nuclei and would hinder the droplets in controlling the final size of the particles (Figure 5).

6.3 Precipitation in liquid membrane systems

A new technique to control the particle size in precipitation processes has been developed by Yang et al. (34) and Stewart et al. (35) using a liquid surfactant membrane emulsion (LSME). An LSME is actually a double emulsion in which an aqueous-in-oil type emulsion, stabilized by a surfactant, is dispersed in a second aqueous phase (oil/aqueous/oil LSMEs can also be formed). One of the reactants is transported from the outer aqueous phase via an oil phase containing a facilitating carrier to an internal aqueous phase of another reactant. A precipitation reaction takes place, and particles nucleate and grow at the internal aqueous/oil interface of the emulsion. The size distribution of the particles within the emulsion is found to be related to the emulsion drop size distribution. This technique was applied to produce copper oxalate crystals (34) with controlled size distribution. A further study (35) has shown that the morphology of the particles formed depends on the nature of the surfactant present in the organic phase.

6.4 Formation of ultrafine particles in reverse micelles

With the objective of preparing and stabilizing uniform ultrafine particles by preventing uncontrolled aggregation, processes involving crystallization in reverse micelles have been developed (36,37) and models have been proposed to explain them. Hirai et al. (36) have studied the formation mechanism of TiO₂ ultrafine particles in AOT/iso-octane reverse micelles by means of hydrolysis of titanium tetra-butoxide (TTB) by following the process via the UV-visible absorption spectra. They have observed that the increase of TTB concentration and water content facilitates particle formation, which is also controlled by the number of micelles. They have proposed a scheme which fits well with the observed data.

Conclusion

The need for preparing solid particles with required properties — either to be used directly in the form they are obtained or, more generally, to be further processed to yield dispersions, tablets, pastes, powders, etc., as pharmaceuticals, dyestuffs, agrochemicals, polymers or basic materials of electronics components or advanced construction materials — has led to the development of processes allowing control of these properties. Most of these processes have been known for a long time but they have not been carried out extensively in production. They are based mainly on the fundamental principles of crystallization and precipitation, as was mentioned at the beginning of this contribution. A non-exhaustive presentation of some of these “new” processes has been made, including control of simple crystallization operations by tailor-made additives, hydrothermal synthesis of ultrafine crystalline powders, use of supercritical fluids as solvents, anti-solvents or reaction medium, rapid expansion of supercritical fluid solutions, supercritical drying, reverse microemulsion in a continuous supercritical phase, spherical crystalization, emulsion-solvent-diffusion method and chemical reaction in microemulsions, in liquid membrane systems and in reverse micelles.
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