

# Application-Driven Fine Particle Solutions

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## ABSTRACT

Working closely with end-users and partners, Cabot SMP is developing solutions and manufacturing fine particle products for energy materials, electronics, displays, and other applications. In this manuscript, we address the importance of understanding the applications requirements and provide selected examples of application-driven particle manufacturing and processing. The implementation of fine particle solution for catalysis and development of dispersions and formulations for electronics and other applications will be discussed. This paper will focus on development of revolutionary sorbent materials for absorption-enhanced natural gas reforming for production of high purity hydrogen. The advantages of CSMP spray-based manufacturing method to produce advanced CaO-based reversible CO<sub>2</sub> sorbent powders will be described. The sorbent materials produced using CSMP's manufacturing method have been formed as extrudates and shown greatly improved durability, retaining high CO<sub>2</sub> absorption capacity and carbonation/de-carbonation kinetics through multiple cycles required for a commercial application. The presentation will also discuss the manufacturing challenges associated with production and processing of engineered ultra-fine particles for applications in electronics, lighting, and displays. In particular, special attention to the development of conductor type materials for inkjet processes for these applications will be addressed.

*Keywords:* engineered particles, spray, aerosol, sorbents, catalysts.

## 1 INTRODUCTION

The continuous push for performance enhancement in important existing and emerging applications has generated substantial interest in engineered fine particles. There are many examples of the improved optical, electronic, and physical properties achieved by controlling the morphology, composition and surface functionality of fine particles. To realize fully the broad benefits of fine particle solutions, it is necessary to implement an application-based approach to solving R&D problems and implementing commercially viable solutions. Some of the conventional particles manufacturing methods often have limited capability to provide control over various particle properties which are needed to satisfy increasingly stringent application requirements. For example, the conventional manufacturing methods for producing sorbent powders are liquid precipitation and impregnation, followed by forming of the powders into extrudates or monoliths. Typically targeted properties for these materials are high surface area and desired pore size distribution with precise control over the

porosity, crystalline phases, surface composition, impurities and dispersion of the active phase. Such control is often difficult to achieve simultaneously for various properties due to limitations in the liquid precipitation processes. CSMP has developed a patented spray-based powder-manufacturing platform that is capable of producing a wide variety of sorbent materials with unique microstructures combined with economic suitability for high volume manufacturing. The uniqueness of the spray-based method to construct specific microstructures and compositions derives from the sequential application of liquid phase and solid-state chemistries that can be resolved by both temperature and time. A key feature of the process is that the physical (surface area, porosity, dispersion) and/or chemical (composition, phase) evolution of the particles can be arrested at any stage by quenching the reaction media. The fact that this process can involve a relatively high processing temperature for a relatively short amount of time while maintaining control over the particle size is valuable for the formation of complex composition materials such as mixed metal oxide sorbents.

## 2 REVOLUTIONARY SORBENT MATERIALS FOR NATURAL GAS REFORMING

The conventional methods for natural gas reforming for this application, steam methane reforming (SMR) and autothermal reforming (ATR) lead to relatively low hydrogen content gas streams. The fuel feeds are highly contaminated by CO and CO<sub>2</sub> and require extensive purification prior the delivery to a fuel cell stack.<sup>1-3</sup> Therefore, it is highly desirable to develop a method of natural gas reforming in which a high concentration, high purity H<sub>2</sub> stream is produced. This can be achieved by an absorption enhanced reforming (AER) process (Reaction 4) that combines SMR (Reaction 1), the WGS (Reaction 2), and CO<sub>2</sub> sorption (Reaction 3) to produce a synthesis gas with relatively high hydrogen purity and low CO<sub>2</sub> and CO content. The potential benefits are well known and have been the subject of a number of studies.<sup>4-6</sup>



Figure 1 illustrates the degree to which the CO<sub>2</sub> sorption shifts the chemical equilibrium to the product side. At 600°C in the presence of a CO<sub>2</sub> sorbent, AER can achieve at least 98% conversion to H<sub>2</sub> as compared to only 75 % conversion according to thermodynamic calculations under normal conditions of SMR or ATR. To achieve a similar

equilibrium conversion for SMR, it is necessary to operate at 720°C. For this reason it is desirable to remove the CO<sub>2</sub> during the reforming step as opposed to post WGS CO<sub>2</sub> removal.

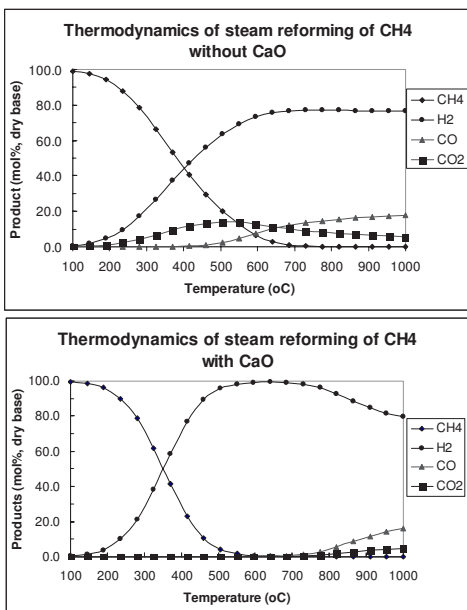


Figure 1. Reformate composition (dry basis) predicted by Gibbs free energy minimization.

The major barrier to the implementation of this approach has been the development of a recyclable CO<sub>2</sub> sorbents with a performance (CO<sub>2</sub> absorption capacity) that does not degrade significantly over the number of cycles required for a commercial product.<sup>4-6, 8, 9</sup> The problem of reduced absorption capacity for conventional sorbent materials stems from the fact that the product of the carbonation reaction, CaCO<sub>3</sub> has a much lower density than the reagent CaO. Therefore, for a fixed mass of CO<sub>2</sub> sorbent in a reactor bed,

there is a large increase in volume as CaO is converted to CaCO<sub>3</sub>. Due to the high temperature typically required for decarbonation, particle sintering occurs leading to a massively reduced CO<sub>2</sub> absorption capacity on the second cycle. Therefore a strategy that achieves a high absorption capacity through the production of a high surface area CaO powder based on small primary particle CaO alone will not lead to retention of a high capacity in subsequent cycles.

CSMP has addressed this problem by applying a spray-based powder manufacturing to design and produce materials with the necessary microstructure and composition to achieve the required high capacity and performance over multiple cycles. In the current work we use a unique spray-based powder manufacturing approach to develop and produce powders that have been specifically designed for absorption enhanced reforming using logical materials design concepts.<sup>12,13</sup> The materials are specifically designed for pelletization with tailored and optimized catalyst/sorbent proximity in the mm to nm length scale and with additional compositional and microstructural features that lead to enhanced carbonation/decarbonation kinetics and WGS activity.

CSMP has developed this patented spray-based powder manufacturing platform and has demonstrated that this powder production method is capable of producing a wide variety of materials and microstructures.<sup>13</sup> The major attributes of this approach are the extreme flexibility to achieve combinations of compositions and microstructures that cannot be achieved by other powder manufacturing methods, combined with economic suitability for high volume manufacturing. The flexibility to achieve unique combinations of compositions and microstructures comes from the fact that the spray process combines chemistries from both liquid phase and solid state processing.

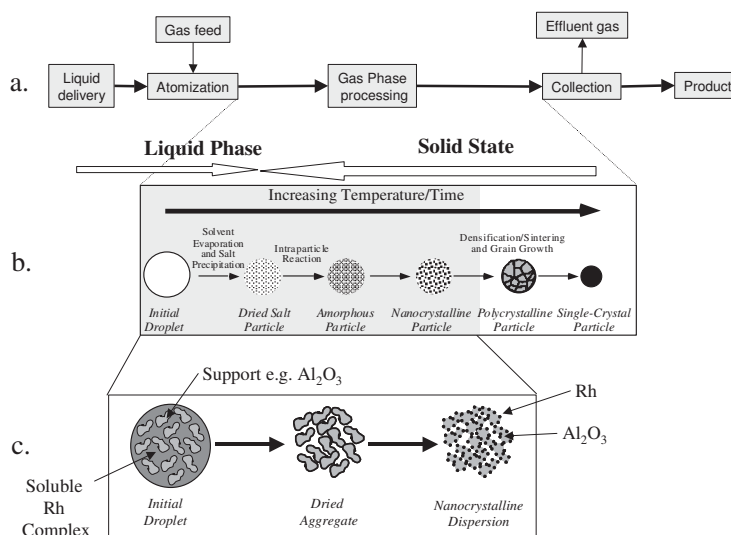
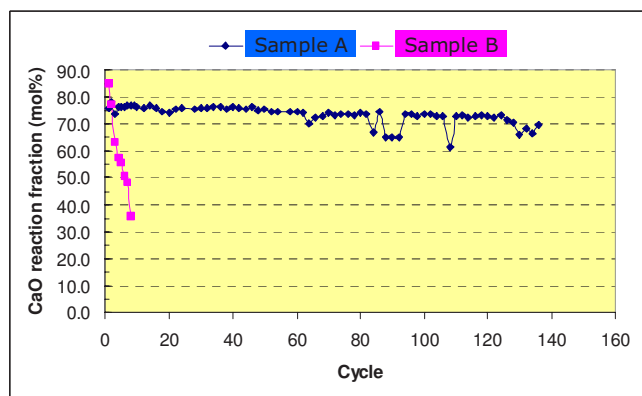


Figure 2. a. Schematic representation of spray-pyrolysis process flow; b, Schematic representation of processes occurring during spray-based production of unsupported materials; c, Schematic representation of processes during the spray-based production of supported catalysts.

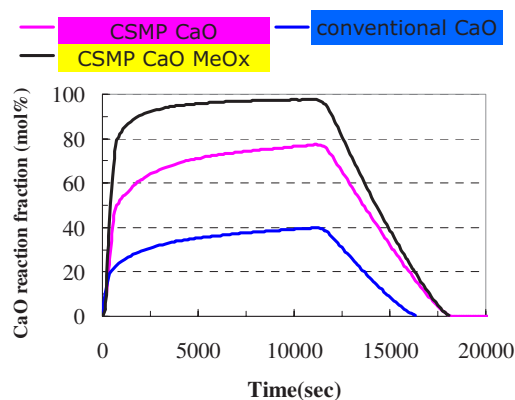
A schematic representation of the spray-based process is illustrated in Figure 2 and has been described elsewhere in detail.<sup>12,14</sup> It starts with the formulation of a liquid that contains either dissolved or suspended reagents which act as precursors to the final product. The liquid, together with a gas, is then fed to an atomization unit where the liquid is converted into an aerosol. The size and size distribution of the droplets that comprise the aerosol are carefully controlled because each droplet becomes a particle (or aggregate in the case of supported catalyst powders) after gas phase processing. Many methods of droplet formation exist providing a broad spectrum of droplet sizes, atomization rates (measured by the amount of liquid phase atomized per unit time) and droplet size and size distribution. The gas stream containing the aerosol is then heated in a gas phase processing unit to effect the physical and chemical conversion of the droplets to the final powder. The final powder is separated from the gas stream using conventional powder collection methods, leaving only a gaseous effluent (no liquid effluent to be disposed). The final powder microstructure and composition depends on the residence time, temperature, the reactive nature of droplet components and the composition of the gas. A schematic representation of these processes is provided in Figure 2b and typically involves solvent evaporation, thermally or

chemically induced liquid phase and/or solid state reactions, crystal nucleation and crystal growth. *The uniqueness in the ability to construct specific microstructures and compositions is derived from the sequential application of liquid phase and solid state chemistries that can be resolved by both temperature and time.* The physical and/or chemical evolution of the particles can be arrested at any stage by quenching of the reaction media. Therefore this process can be used to produce a wide variety of materials compositions combined with unique microstructures and morphologies. A number of CaO-based powders have been synthesized and their CO<sub>2</sub> sorption capacity evaluated. Figure 3 shows an examples of two samples with large variation in their sorption capacity and stability as measured by Thermo-gravimetric Analysis (TGA) under the following conditions: carbonation: 600°C; decarbonation: 750°C. These data show that the reactivity of the sorbents (in terms of CaO reaction fraction) of a properly designed material can be extremely high (over 70 % for sample A, Figure 3) and that it can be retained after multiple cycles of carbonation and decarbonation. To our knowledge this is the best performance observed for these type of materials and while this is only a relatively small number of cycles (over 140) it demonstrates the feasibility of the proposed approach.



**Figure 3:** Comparison of reversible CO<sub>2</sub> uptake in commercial in two CSMP sorbents

The recycle time in the fuel processing system is dictated by the size of the CO<sub>2</sub> sorbent beds, the number of beds present and the rate at which the CO<sub>2</sub> is absorbed and removed. High and reproducible rates of carbonation and decarbonation are desirable. Based on the initial studies of the materials produced to date and the nature of the equilibrium between CaO + CO<sub>2</sub> and CaCO<sub>3</sub>, it can be concluded that the carbonation reaction has a relatively high rate at a lower temperature compared to the rate of decarbonation during the calcination step. This assumes that by controlling the microstructure, we can avoid the formation of an impervious CaCO<sub>3</sub> layer, which has been shown in the literature to limit the rate of CO<sub>2</sub> uptake after all the exposed surfaces of CaO have reacted.



**Figure 4:** Comparison of the rates of carbonation and decarbonation in CSMP spray-produced sorbents

The more difficult problem to solve is achieving decarbonation kinetics that is sufficiently rapid to ensure that this step does not limit the recycle time. Increasing the temperature can increase the rate constant for the decarbonation reaction, but this may lead to some sintering of the material and reduce the cycle life. Therefore, alternative strategies need to be employed to minimize the time required for decarbonation. Figure 4 shows a plot of the carbonation and decarbonation rates under the conditions specified for a spray-based material compared to a standard CaO sample. In this experiments, the CO<sub>2</sub> is present in large excess.

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