Spray-Dried Sodium Zirconate: A Rapid Absorption Powder for CO₂ Capture with Enhanced Cyclic Stability

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Improved powders for capturing CO₂ at high temperatures are required for H₂ production using sorption-enhanced steam reforming. Here, we examine the relationship between particle structure and carbonation rate for two types of Na₂ZrO₃ powders. Hollow spray-dried microgranules with a wall thickness of 100–300 nm corresponding to the dimensions of the primary acetate-derived particles gave about 75 wt% theoretical CO₂ conversion after a process-relevant 5 min exposure to 15 vol% CO₂. A conventional powder prepared by solid-state reaction carbonated more slowly, achieving only 50% conversion owing to a greater proportion of the reaction requiring bulk diffusion through the densely agglomerated particles. The hollow granular structure of the spray-dried powder was retained post-carbonation but chemical segregation resulted in islands of an amorphous Na-rich phase (Na₂CO₃) within a crystalline ZrO₂ particle matrix. Despite this phase separation, the reverse reaction to re-form Na₂ZrO₃ could be achieved by heating each powder to 900 °C in N₂ (no dwell time). This resulted in a very stable multicycle performance in 40 cycle tests using thermogravimetric analysis for both powders. Kinetic analysis of thermogravimetric data showed the carbonation process fits an Avrami–Erofeev 2D nucleation and nuclei growth model, consistent with microstructural evidence of a surface-driven transformation. Thus, we demonstrate that spray drying is a viable processing route to enhance the carbon capture performance of Na₂ZrO₃ powder.

Introduction

Powder sorbents for CO₂ at high temperatures are of interest for a number of applications, including the production of H₂ by steam reforming, in which removal of CO₂ shifts the chemical equilibrium in favor of greater H₂ yield and purity. Sorption-enhanced steam reforming (SESR) based on a CaO sorbent (CaOₓ+CO₂(g)=CaCO₃(s)) has been demonstrated at the research level. Calcium oxide sorbents work best at approximately 600–700 °C, and hence, coupled to steam reforming reactions; the sorbent may be regenerated by calcination in air at around 800 °C or above. This type of calcium looping technology has been considered widely for post-combustion capture (PCC) from fossil-fuel-fired power plants (notably, coal-fired) and other single-point industrial emitters.[2] The technology could be implemented using two parallel, fluidized beds operating as carbonator and regenerator, or using fixed-bed reactors with alternating carbonation/calcination reactions by feed-flow control.[2] For the proposed implementation in PCC, the decarbonation step would be performed in a near pure CO₂ stream, necessitating calcination temperatures ≥950 °C.[2] In SESR applications, in which oxygen looping is employed to exchange oxygen with the metal catalyst, air (oxygen depleted) would be the sorbent regeneration stream at temperatures ≥800 °C.[3]

An acceptable sorbent for PCC or SESR should have a high CO₂-uptake capacity per unit mass and remain close to its original CO₂-capture capacity over repeated carbonation/regeneration cycles.[3] Material costs should be low and the sorbent should be mechanically robust, as in the case of calcium oxide (CaO) and other inorganic oxides. CaO from limestone is the most inexpensive and readily available options. CaO however shows serious loss of CO₂ capacity after repeated calcination cycles at 800 °C owing to the effects of partial sintering and loss of surface area and porosity.[4]

A number of additive powders (e.g., SiO₂, Al₂O₃, ZrO₂) have been investigated as means of improving the multicycle stability of CO₂-capture performance of the active CaO component.[3] The greater the volume fraction of the refractory additive the more durable the sorbent, but there is a trade-off in the dilution of the active component that leads to loss of initial capture capacity: 20–30 wt % is a common compromise loading. The added oxide component often reacts with CaO to form a binary compound, and it is this compound, for example,
Ca$_2$Al$_2$O$_{13}$ (mayenite), which acts as the “refractory spacer” second phase designed to inhibit CaO particle sintering and densification.[8–11] A uniform distribution of the second phase is essential to minimize densification of the active CaO phase and suppress multicycle degradation. The performance of a range of CaO-based sorbents is summarized in the study of Zhao et al.[12] The more complex (and costly) the processing technique, for example, sol-gel or chemical templating, the finer the particle size, and the more uniform the dispersion. Consequently, solution-derived composite powders generally have the best multicycle performance relative to the base CaO sorbent material.

Another approach to avoid multicycle powder densification problems has been to use alternative sorbent materials to CaO, such as Li$_2$SiO$_4$ and Li$_2$ZrO$_3$.[13] The latter has received considerable attention for both post- and pre-combustion capture, and for SESR applications. Li$_2$ZrO$_3$ absorbs CO$_2$ according to the reversible reaction: Li$_2$ZrO$_3$ + CO$_2$ $\rightleftharpoons$ Li$_2$CO$_3$ + ZrO$_{2\,\delta}$ (giving a maximum increase in sorbent mass of 28%). It also acts as a basic catalyst that has the advantage of promoting tar degradation in SESR processes. However, its utilization has been inhibited by poor reaction kinetics at low CO$_2$ partial pressures (< 0.02 MPa) and high temperatures (> 500 °C). The more active, metastable, tetragonal crystal structure—the major contributor to CO$_2$ chemisorption—is potentially transformed to a less reactive monoclinic form during high-temperature cycling. The Li$_2$ZrO$_3$-based sorbents are best suited to processes operating at temperatures < 550 °C such as steam reforming of simple compounds such as methane, ethanol, or glycerol. Solid solutions of Li$_2$ZrO$_3$ with Na$_2$ZrO$_3$ have also received attention.[16]

There are also reports on the use of Na$_2$ZrO$_3$ and K$_2$ZrO$_3$ as CO$_2$ sorbents.[17] From thermodynamic considerations, Na$_2$ZrO$_3$ and K$_2$ZrO$_3$ absorb CO$_2$ at lower CO$_2$ partial pressures and higher temperatures than Li$_2$ZrO$_3$. However, K$_2$ZrO$_3$ sorbents are more difficult to regenerate. To reach a good balance between ease of capture and regeneration at high temperatures (≈ 650–750 °C), Na$_2$ZrO$_3$ is more promising than either Li$_2$ZrO$_3$ or K$_2$ZrO$_3$.

The CO$_2$ uptake and regeneration of Na$_2$ZrO$_3$ proceed according to the reversible reaction: Na$_2$ZrO$_{3\,\delta}$ + CO$_{2\,\delta}$ $\rightarrow$ Na$_2$CO$_3$ + ZrO$_2$. Conventionally, Na$_2$ZrO$_3$ sorbents are synthesized by a SS reaction between Na$_2$CO$_3$ and ZrO$_2$ at high temperatures (> 1000 °C), resulting in large (micrometer) agglomerated particles, with long diffusion paths for subsequent carbonation.

To reduce the particle size of Na$_2$ZrO$_3$ sorbents, a number of solution-based synthesis routes were developed.[17,18] These result in faster carbonation rates since a greater proportion of the CO$_2$ uptake occurs through interfacial solid–gas reactions, and the diffusion lengths for ion migration in the later stages of the reaction (in which the rate of mass transfer is controlled by SS diffusion) are reduced.

Herein, we use scanning and transmission electron microscopy with energy-dispersive analysis of X-rays (EDX) to investigate the microstructural differences between Na$_2$ZrO$_3$ particles produced by spray drying a mixed acetate solution, and powders prepared by conventional SS reaction. The structural differences we identify account for much faster rates of carbonation in spray-dried (SD) forms. A CO$_2$ conversion of approximately 0.18 g$_{\text{CO}_2}$ g$_{\text{sorbent}}$ (= 75% of theoretical capacity) is demonstrated for the SD powder after only 5 min exposure to 15 vol% CO$_2$ at 700 °C, namely, under carbonation conditions pertinent to SESR. Stable multicycle performance is demonstrated for both powder types over a 40 cycle thermogravimetric testing program (decarbonation at 900 °C) but because of the slower rate of carbonation for the conventionally prepared Na$_2$ZrO$_3$, its conversion is only about 50% of the theoretical capacity under these conditions (which are relevant to implementation in SESR). Finally, we link our microstructural observations to kinetic modelling of the CO$_2$-absorption profiles measured during carbonation to gain mechanistic insights into the surface-driven absorption process.

### Results and Discussion

**Phase analysis and particle structure: as-prepared powders**

X-ray diffraction (XRD) patterns confirmed that both SD and solid-state (SS) powders contained crystalline Na$_2$ZrO$_3$, in the form of hexagonal and monoclinic polymorphs. Figure 1 presents the XRD pattern for the SD powder. Minor peaks of ZrO$_2$ (monoclinic) and very weak peaks of Na$_2$CO$_3$ were detected, consistent with residual intermediate phases from the following reaction [Reaction (R1), only inorganic products are represented]:

$$2\text{Na(CH}_3\text{COO)} + \text{Zr(CH}_3\text{COO)}_4 \rightarrow \text{Na}_2\text{CO}_3 + \text{ZrO}_2$$  (R1)

The very weak Na$_2$CO$_3$ peaks relative to the XRD peaks for ZrO$_2$ are consistent with the former being poorly crystallized.

![Figure 1. XRD pattern for the Na$_2$ZrO$_3$ SD powder (top figure) with indexing to a mixture of the hexagonal and monoclinic phases. An expanded intensity scale in the lower figure aids the identification of small quantities of residual intermediate Na$_2$CO$_3$ and ZrO$_2$ phase.](image-url)
The conventional SS powder gave similar diffraction patterns to the SD material (Figure S1 in the Supporting Information).

SEM (Figure 2) revealed the SD powders to be hollow, perforated, and partially collapsed spherical granules. These ranged in size from 1–10 μm (Figure 2a). The walls of the granules were composed of interlocking primary particles (100–300 nm in size, Figure 2b) and were a single particle in thickness (the 100–300 nm wall thickness is illustrated in Figure S2 in the Supporting Information). We have observed similar particle structures previously, for example, in ZrO2 granules that were spray dried from acetate solution.[9] This type of structure is consistent with a formation mechanism in which liquid atomized droplets, upon entering the heated chamber of the spray dryer, first develop a solid, pliable surface in salt particles that surrounds a liquid core. After continued heating, pressure builds up and is released by bursting of the outer solid skin, resulting in characteristic surface rupturing of the hollow granule. If the outer skin remains pliable at this stage, the walls collapse to create deformed, hollow spheres. The expelled liquid from the interior of the droplet forms as secondary aerosol, which results in a series of smaller granules. A schematic of the proposed SD granule formation mechanism is shown in Figure 3.

The SS powders were composed of densely agglomerated granules, tenths of μm in size, typical of a conventionally prepared mixed-oxide ceramic powder; primary particle size was approximately 0.05–1 μm. (Figure 2c, d).

Carbonation characteristics and effect on particle structure

To assess the baseline CO2-uptake performance of the SD and SS powders, the response to prolonged exposure to 15% CO2 at 700 °C was analyzed (Figure 4). The SD powders reached a steady-state increase in mass after about 10 min, equivalent to 0.20 gCO2 g−1sorbent uptake and a molar conversion of approximately 85% of theoretical capacity. After 5 min, the uptake was about 0.18 gCO2 g−1sorbent. The SS powder approached a similar steady-state level of carbonation but required a dwell period of almost 25 min as opposed to only 10 min for the SD powder, indicating a much slower rate of carbonation in the conventional SS powder.

The XRD patterns of both powders collected after the end of the isothermal thermogravimetric analysis (TGA) experiment were similar. The pattern for the SD powder is shown in Figure 5, indicating a mixture of Na2CO3 and ZrO2, with no evidence of unreacted Na2ZrO3 (Figure 5). The carbonated SS powder pattern is shown in the Supporting Information. This confirms the carbonation reaction of the Na2ZrO3 phase contained in the calcined starting powder [Reaction (R2)] had reached completion (subject to XRD detection limits).

\[
\text{Na}_2\text{ZrO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{ZrO}_2 \quad \text{(R2)}
\]

The SEM images of the powders produced after 25 min isothermal carbonation revealed the carbonated SD granules retained the general structure of the as-prepared material Figure 6a (compared to Figure 2b); likewise, there was little change in the general form of the SS agglomerates (Figure 6c compared to Figure 2c). The surface of the carbonated SD granules revealed localized pockets with a smooth, glass-like appearance.

Close inspection indicated that a similar phase was also interspersed within the interlocking submicron particles that made up the remainder of the granule surface (Figure 6a). The SEM/EDX elemental maps indicated the smooth regions to be Na-rich (Figure 6b), and therefore, we attribute these to be

![Figure 2](image-url)

**Figure 2.** a, b) SEM images of the SD sorbent powders showing partially deflated, hollow granules 1–10 μm in size with a substructure composed of 100–300 nm primary particles; c, d) conventional powder prepared by SS reaction with solid agglomerates 10 μm in size and primary particle size ≈ 1 μm.

![Figure 3](image-url)

**Figure 3.** Schematic of Na2ZrO3 particle formation during spray drying showing the likely formation route of hollow, ruptured granules; the released liquid goes on to form secondary smaller granules.

![Figure 4](image-url)

**Figure 4.** TGA profiles of SD and SS powders carbonated under isothermal conditions (700 °C, 15% CO2).
Na₂CO₃, which under the carbonation conditions employed had softened and flowed into isolated islands. The remainder of the carbonated-granule structure was made up of interlocking faceted particles that were Zr-rich (Figure 6b)—these are assumed to be the ZrO₂ phase identified by XRD. There was also some localized glass-like phase interspersed within the (crystalline) ZrO₂ particles. The SS agglomerates showed similar evidence of a glass-like Na-rich phase surrounding Zr-rich particulate material (Figure 6d).

Multicycle carbonation/decarbonation performance

The multicycle performance of the SD powder and the conventional powder over 40 TGA carbonation/decarbonation cycles, is summarized in Figure 7 (multicycle TGA plots are shown in the Supporting Information). An increase in the level of CO₂ uptake was observed over the first 3 cycles for each powder; this type of self-activation has been observed for other oxide sorbent powders, for example, CaO, and can be attributed to the generation of porosity in the powder owing to outgassing in the first few decarbonation cycles. After the initial self-activation period, the uptake capacity of both the SD and SS powders showed a remarkable stability, indicating high durability to be an intrinsic feature of Na₂ZrO₃ sorbents (as discussed below). The variation in mass conversion of the SD powder was <5% between cycles number 3 and 40. The CO₂ uptake level was approximately 0.18 g CO₂ g⁻¹ sorbent (4.1 mmol g⁻¹) in cycle 4 corresponding to a molar conversion efficiency of about 75%. Because of the slower rate of carbonation of the SS powder (as identified in Figure 4) the level of uptake after the set 5 min carbonation within multicycle experiments was lower, 0.12 g CO₂ g⁻¹ sorbent (2.7 mmol g⁻¹) or about 50% conversion by mass under multicycle conditions.

SEM micrographs showed the particle structure of decarbonated SD and SS powders after 10 and 30 TGA cycles, indicating a more porous structure (Figure 8a,b) than for the as-
prepared example (Figure 2). This is consistent with reports for other oxide sorbents for which an initial increase in porosity owing to self-activation associated with the first few carbonation/decarbonation cycles is shown.\textsuperscript{10,11} The cycled SS powders were also more porous than the as-prepared SS samples (Figure 8c,d).

**TEM of spray-dried powder**

Analysis by TEM of the carbonated SD powder after one TGA cycle and dispersion in heptane is shown in Figure 9a. Only fragments of the granules could be imaged as full-size granules are not electron transparent. The fragment shows a polycrystalline substructure (top right image in Figure 9a). Lattice imaging of this region reveals crystalline particles in a glassy matrix (bottom right image) with fast Fourier Transform (inset) showing the lattice spacing of the particles identified in the red box to be 2.89 nm, consistent with the ZrO\textsubscript{2} (111) spacing (ICDD ref. file 00-037-1484). EDX spectra (bottom left, Figure 9a) show that the polycrystalline regions (red) are Zr and O rich whereas EDX spectra of the glassy regions (black) are Na and C rich, consistent with Na\textsubscript{2}CO\textsubscript{3} (the background Cu signal is from the support grid). These findings are in agreement with the information inferred by SEM/EDX of full-size SD granules imaged following extended carbonation experiments (Figure 6) and confirm that the walls of the hollow granules are composed of a network of interlocking submicrometer, crystalline ZrO\textsubscript{2} particles with regions of partially glassy Na\textsubscript{2}CO\textsubscript{3} phase interspersed between them (only partially glassy because XRD identifies a minor amount of crystalline Na\textsubscript{2}CO\textsubscript{3}).

To reveal more information on the spatial distribution of the component phases, two other TEM samples were prepared: a sample collected after one TGA cycle, the other after 20 cycles. This time powders were dispersed in acetone instead of heptane. Acetone is a polar solvent in which Na\textsubscript{2}CO\textsubscript{3} and any hydroxyl–carbonate phases that may form upon storage in air, or on exposure to moisture present in dispersant liquids (e.g., bicarbonate), are soluble and leach out of the granule fragments. TEM showed that the acetone-dried samples were indeed more porous (Figure 9b), suggesting that the soluble (Na\textsubscript{2}CO\textsubscript{3}) material had originally been located between the ZrO\textsubscript{2} nanoparticle networks, corroborating the interpretations of SEM images (which showed glassy material amongst ZrO\textsubscript{2} particles in addition to segregated pockets of Na\textsubscript{2}CO\textsubscript{3}). In some areas of the 20 cycle image, the leached carbonate phase has re-precipitated in an acicular morphology.

**Carbonation reaction: kinetic analysis**

A set of isothermal TGA carbonation experiments were designed to identify the reaction model that best describes the carbonation process of the SD and SS powders and to derive apparent kinetic parameters.

Conversion [Eq. (1)] was calculated by finding the minimum and maximum measured TGA masses over the cycle step considered (a cycle consisting of carbonation followed by calcination). For carbonation, the minimum mass is the initial mass at \( t = 0 \) (\( m_0 \)), whereas the maximum is the final mass at \( t = t_f \) (\( m_f \)).
\[ \alpha(t) = \frac{m(t) - m_0}{m_f - m_0} \]  

Conversion versus time data (\( \alpha \) vs. t) can then be represented using several models of SS (gas) reactions. Hancock and Sharp's method\(^{[12]}\) assigns a model or a family of models according to the value of \( m \), as defined in Equation (2):

\[ \ln[-\ln(1-\alpha)] = m \ln t + \ln B \]  
in which \( B \) is a constant, the conversion values (\( \alpha \)) range typically between 0 and 0.5, and plotting \( \ln[-\ln(1-\alpha)] \) versus \( \ln t \) produces a straight line fit with gradient \( m \).

Figure 10a shows the linear fit for the SD and SS powders carbonating at 700°C with best fit values of \( m \) and \( \ln B \).

According to Hancock and Sharp,\(^{[12]}\) the SD and SS powders exhibited \( m \) values of 1.86 and 1.69 respectively, both corresponding to Avrami–Erofeyev (also known as JMAEK) models close to \( m=2 \), termed A2 models. Avrami–Erofeyev AN models, with values of \( N \geq 1 \), are known as "nucleation and nuclei growth models". In the case of the carbonation of the SD and SS Na\(_2\)ZrO\(_3\) crystals, with fitted values of \( m \) of 1.9 and 1.7, both close to \( N=2 \), disc-like are the most likely nuclei shapes.

Further confirmation of the Avrami–Erofeyev model being identified as best fitting the SD and SS Na\(_2\)ZrO\(_3\) carbonation reactions is found using the method described by Khawam and Flanagan.\(^{[13]}\) In this method, the shape of the plot \( d\alpha/dt \) versus \( \alpha \) is used to determine the most likely reaction model, with Avrami–Erofeyev displaying a unique dome-like profile with the apex located at \( \alpha \) values between 0.3 and 0.4 for model A2. Figure 10b shows that the carbonation of both the SD and SS Na\(_2\)ZrO\(_3\) powders exhibited dome shapes with apices between 0.3 and 0.4, corresponding roughly to the A2 model.

Reaction kinetics of the Avrami–Erofeyev AN models can be described by the equation relating the integral-conversion function (\( g(\alpha) \)) to the reaction time following Equation (3):

\[ g(\alpha) = k \times t = (-\ln(1-\alpha))^{1/N} \]  
in which the rate constant \( k \) typically follows Arrhenius’ law [Eq. (4)]:

\[ k = A \times \exp(-E/RT) \]  
in which \( A \) is the pre-exponential factor, \( E \) is the activation energy, \( R \) is the universal gas constant, and \( T \) is the temperature in K.

Here, the carbonation having been performed at 700°C, one value of \( k \) was obtained for each of the materials tested (SD and SS Na\(_2\)ZrO\(_3\) powders).

Inverting Equations (1) and (3) allows the calculation of a modeled value of mass increase (in %) as function of time according to Equations (5) and (6):

\[
\text{Mass increase}_{\text{model}}[\%] = 100 \times \frac{m(t) - m_0}{m_f} = \alpha \times \frac{(m_t - m_0)}{m_0} 
\]

With \( \alpha = 1 - \exp[-((kt)^N)] \)

Figure 11 compares the experimentally obtained % mass increases versus time of the SD and SS Na\(_2\)ZrO\(_3\) powders during carbonation at 700°C with their modeled counterpart using Equations (5) and (6), and provides a final test of the suitability of the chosen models with their derived kinetic rates. It can be seen that an excellent match between experimental and modeled mass increases was obtained for both materials.

Both modelling methods indicate 2D nucleation and nuclei growth for the carbonate phase, which when combined with the SEM observations (Figures 2 and 6) suggest a surface-driven transformation of the Na\(_2\)ZrO\(_3\) granules, consistent with a porous Na\(_2\)CO\(_3\) and ZrO\(_2\) surface layer discussed in another Na\(_2\)ZrO\(_3\) study.\(^{[14]}\)

In summary, SD Na\(_2\)ZrO\(_3\) granules exhibit rapid CO\(_2\) uptake reaching 0.18 g\(_{\text{CO}_2}/g\) under within only 5 min (15% CO\(_2\) at 700°C), some 50% greater conversion within this process-relevant time period than the conventionally prepared SS powder. Both powder types are highly durable, showing minimal decay (<5%) in uptake capacity after the 40 cycles test under conditions relevant to steam reforming.

Thus, we demonstrate the intrinsically superior durability of Na\(_2\)ZrO\(_3\), and that the rate of carbonation may be improved through simple spray drying, which is an industrially scalable process that provides a fine primary particle size within...
a porous granular structure. Confirmation of a higher surface area in the SD powders, as suggested by the SEM images, was obtained from N₂-adsorption isotherms (Figure 12). The BET (Brunauer–Emmett–Teller) surface areas of the SD powder were ≈20 m² g⁻¹ compared to only ≈2 m² g⁻¹ for the SS powder.

Hysteresis in the isotherms indicates mesoporosity. Pore volumes measured by the Barrett–Joyner–Halenda (BJH) method were ≈0.039 cm³ g⁻¹ for the SD powder and 0.007 cm³ g⁻¹ for the SS powder. This difference is consistent with SEM observations of hollow-perforated microgranules in SD powders, and dense agglomerates in SS powders. The hollow and perforated microstructure of the SD granules provides easy access of CO₂ to the inner and outer surfaces of the granule walls. This, allied to the thin wall dimensions, results in a higher proportion of the carbonation process involving a rapid gas–solid reaction (the linear segment of the TGA profile) than is the case for the densely agglomerated SS Na₂ZrO₃ powder.

Crystalline Na₂ZrO₃ naturally possesses lattice-scale intimate mixing of refractory ZrO₂ and active Na₂O constituents. The crystal structure of the monoclinic form is represented in Figure 13. The lattice-scale distributions of each component represents ideal mixing of a composite metal-oxide material suited to high-temperature operation, and account for the remarkable durability of Na₂CO₃ in multicycle operation. This scale of mixing cannot be achieved by mechanical mixing or chemical precipitation of two-phase sorbent and refractory spacer powders.

During carbonation, the Na₂ZrO₃ crystal lattice decomposes in a surface-driven process to a truly nanoscale composite of ZrO₂ and Na₂CO₃. From SEM and TEM examination of the walls of the hollow SD granules, a poorly crystallized/glassy carbonate phase segregates. The reverse reaction to regenerate crystalline Na₂ZrO₃ occurs readily during the temperature and gas-swing decarbonation step, once again creating a sorbent with ideal crystal lattice scale distributions of “active” and “spacer” components ready for the next carbonation step. The net result is a very durable single-phase high-temperature sorbent.

As mentioned in the Introduction, there is a wide literature on other high-temperature powder sorbents for CO₂ capture, most notably for CaO powders in which refractory additives are introduced, for example, ZrO₂,[15] to suppress the natural densification (partial sintering) and loss of porosity that degrades cycle on cycle the CaO performance, as outlined in the Introduction. Often, very complex chemical solution precipitation reactions are employed to promote adequate mixing of the two components. In 2012, we proposed a temperature-induced volume-expanding phase change additive to disrupt densification,[16] others later adopted this concept. However, we found that the volume expansion that occurred between regeneration and carbonation was accommodated in the residual pore spaces and did not induce microcracking to open up porosity prior to the next carbonation step. All of these second-phase additives to a sorbent powder require complicated processing to achieve significant improvements in durability as performance is only improved if there is intimate mixing of “refractory” additive and sorbent. Even the best chemical or mechanical synthetic processes only give mixing of the two particle types on the submicron scale.

There are a number of literature reports of Na₂ZrO₃ as a sorbent for CO₂: the conditions used for sorption/desorption vary...
between the different publications. Martínez-dlCruz and Pfeiffer[7d, e] prepared Na₂ZrO₃ by a similar SS route to our SS powder but with calcination at 850 °C for 6 h and found that addition of 20% excess Na₂ZrO₃ produced a phase-pure product (by XRD). The surface area of this product was approximately 3 m² g⁻¹, comparable to the surface area of the SS powder presented herein. Their 20 cycle sorption/desorption studies were conducted in 100% CO₂ (as opposed to 15% herein): temperatures between 550 and 700 °C were found to give the highest uptakes; desorption in N₂ was conducted at ≤ 800 °C. Sorption-dwell times of 30 minutes were adopted, the samples exhibited CO₂ uptakes corresponding to 18.5–19 mass%.[7d, e] Our SS powder exhibited similar uptake after similar total time periods to these reports (Figure 4) but we adopted a shorter (5 minute) carbonation period in multicycle TGA as this replicated more closely the conditions of a working sorbent. The same group studied the microstructure of their SS powders and concluded that a mesoporous structure was formed on the surface of the agglomerates at sorption temperatures of 300–550 °C, but sintering of this shell layer at temperatures above 550 °C eliminated the porosity and at that stage sorption kinetics were controlled by diffusion processes through a dense Na₂CO₃ + ZrO₂ shell.[7a] This is consistent with our TEM analysis. The effect of relative humidity on the carbonation and decarbonation processes at low temperatures (30–80 °C) for powders produced by SS reaction shows that high humidity has a positive effect, which was attributed to bicarbonate formation at the surface.[17]

Several solution routes have been used to produce Na₂ZrO₃ sorbent powders. This includes simple evaporation of sodium acetate and zirconium acetyl acetate in ethanol and uptakes of CO₂ of about 21 wt% by TGA over four cycles were recorded involving sorption in 80% CO₂ at 600 °C (for > 100 minutes) and regeneration in argon at 800 °C.[7a, e] Spray drying of these precursor solutions was also investigated.[8] Unlike the SD granules of the present work, their spherical granules disintegrated on calcination to produce a nanosized powder of similar particle sizes (∼50 nm) to the powders produced by simple evaporation drying. Hence, both SD and simple evaporation powders within the study of Zhao et al.[8] exhibited similar CO₂-capture properties, achieving around 17.5 wt% mass increase after 200 s in 100% CO₂ at 575 °C. Multicycle performance in 50% CO₂ up to 11 cycles indicated an uptake of almost 15 wt%.[9] Sodium oxalate and zirconium nitrate, sodium citrate and zirconyl nitrate aqueous solutions as well as sodium acetate and zirconyl chloride solutions have been used to produce Na₂ZrO₃ in an evaporation/drying/calcination process reported by Ji et al.[16] and Memon et al.[19]

The CO₂-capture kinetics of our SD powders compare favorably to other Na₂ZrO₃ sorbent powders, although performance comparisons between different laboratories is complicated by the variability in sorption and desorption conditions employed. We demonstrate distinctive microstructural features that lead to high surface areas, which explain the reasons for the characteristic rapid rates of carbonation. The direct like-for-like comparison to SS tested under identical TGA conditions provides an unequivocal demonstration of the superior performance of SD. For comparisons with other alkaline metal or alkaline-earth ceramic sorbents, the reader is directed to a comprehensive review article by Memon et al.[19]

Conclusions

The microstructural reasons for faster rates of CO₂ capture by spray-dried (SD) granules of Na₂ZrO₃ relative to a powder prepared by conventional solid-state (SS) synthesis method have been established using a combination of scanning and transmission electron microscopy, surface area measurements, and kinetic modeling. The hollow and perforated granular structure of SD powders presents a higher surface area than the densely agglomerated conventional powder and promotes the surface-driven carbonation reaction. This permitted about 75% of the theoretical mass conversion within 5 min exposure to 15% CO₂ at 700 °C, compared to only around 50% for the benchmark conventional SS powder. Although segregation of Na₂CO₃ and ZrO₂ occurs during carbonation, crystalline Na₂ZrO₃ is reformed by heating to 900 °C and immediately cooling, ready for the next carbonation step in a multicycle sorption/desorption process. High multicycle durability is an intrinsic feature of Na₂ZrO₃, as the active soda component is held within a stable crystal structure. This contrasts to alternative high-temperature sorbents such as CaO-based materials in which sintering degrades durability.

Experimental Section

SD powders were prepared from a starting solution produced by dissolving Na(CH₃COO)·3H₂O (50 mmol) and Zr(CH₃COO)₂ (25 mmol) in dilute nitric acid (300 mL) (Sigma–Aldrich reagents) to form a clear solution. This solution was spray dried using a benchtop spray dryer (SD-05 Lab-Plant, UK). The operation conditions were: inlet temperature 200 °C, aspirating air flow at 40 m³ h⁻¹, peristaltic pump speed 0.6 dm³ h⁻¹, and compressor pressure of 0.18 MPa. Collected powders were calcined in a box furnace at 900 °C for 2 h to promote formation of Na₂ZrO₃. The conventional SS powder was prepared by ball-milling Na₂CO₃ (Acros Organics) and ZrO₂ (Dynamic Ceramics) powders for 16 h, followed by calcination at 900 °C for 2 h. Nitrogen adsorption/desorption isotherms were measured using a Quantachrome Instruments Nova 2200: surface areas were measured by the BET method and pore volumes by the BJH method. Samples were outgassed under vacuum at 200 °C for 3 h prior to analysis.

The first assessment of the carbonation characteristics of the SD and SS powders involved isothermal TGA in which a sample was exposed to CO₂ at 700 °C (Mettler Toledo star 1 TGA/DSC). The sample was first heated to 900 °C (20 °C min⁻¹) in N₂ to remove any traces of hydrated/carbonated surface phases formed during storage. After cooling (20 °C min⁻¹) to 700 °C, the gas was switched to 15% CO₂/85% N₂, and held at this condition for 25 min. Multicycle performance up to 40 cycles was evaluated using 700 °C, 15% CO₂/5 min carbonation and regeneration (desorption) achieved by switching to N₂, and heating at 20 °C min⁻¹ to 900 °C and immediately cooling at 20 °C min⁻¹ to 700 °C. XRD data were collected using a Bruker D8 diffractometer (CuKα, λ = 1.5416 Å). Owing to the small quantities of powders generated in the TGA experiments, the powders were deposited on a silicon
sample holder. The resulting XRD patterns were analyzed using X’Pert HighScore Plus software (Version 3.0e). The diffraction patterns were compared to standard patterns in the ICDD PDF4 database (International Center for Diffraction Data).

The microstructures of as-prepared powders, carbonated powders, and powders after multiple carbonation/decarbonation cycles were characterized by using SEM with energy dispersive EDX elemental analysis (LEO 1530 Gemini field emission gun, FEG-SEM). All samples for SEM were sputter-coated with a layer of platinum, ≈5 nm in thickness. TEM was used to analyze an SD sample after 1 and 20 successive TGA cycles, ending on a carbonation step (Philips CM200 Field emission gun TEM/STEM with Supertwin Objective lens, and an Oxford Instruments SD 80 mm2 X-ray EDX system running INCA software). Powders were prepared for TEM by dispersing in either acetone or heptane (as detailed) and drop-casting onto standard holey carbon films supported on copper grids (Agar Scientific Ltd).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: absorption • Co2 capture • kinetic analysis • sodium zirconate • spray drying

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