We report the ultrasonic spray pyrolysis (USP) synthesis and characterization of composite calcium oxide-based sorbents for carbon dioxide capture. Inclusion of a small amount of Al$_2$O$_3$ into the CaO matrix (as low as Al/Ca: 0.03) yielded significant enhancement of resistance to recycling degradation. The effective homogenous dispersion of additives in the CaO matrix and the relatively high surface area materials obtained via USP explain the sorbent's high performance. All materials were characterized by XRD, STEM, TEM, SEM, and TGA (for CO$_2$ uptake measurements). Two common phases of CaAlO$_4$, Ca$_3$Al$_2$O$_6$, and Ca$_2$Al$_2$O$_6$ were formed during multiple cycles of calcination and CO$_2$ uptake.

Carbon dioxide sequestration has become a subject of extreme interest in recent years as a path towards greenhouse gas mitigation. The combustion of fossil fuels for power generation accounts for over one third of anthropogenic carbon dioxide emission sources, so substantial research has focused on CO$_2$ capture and sequestration from such sources. Many materials are currently under investigation for CO$_2$ capture, both for post-combustion (e.g., silica supported amines, zeolites, activated carbons) and for “pre-combustion”, i.e., after water–gas shift (WGS) but before power generation (e.g., CaO, lithium zirconates, hydroxaluminates, and metal–organic frameworks). Sorbents that operate at relatively high temperature (i.e., CaO) are particularly attractive choices for pre-combustion scheme to integrate with WGS or methane steam reforming processes. A sorption-enhanced water–gas shift reaction process (SEWGS) combines the WGS reaction and CO$_2$ removal into a single process step in an integrated gasification combined cycle (IGCC) power plant. In SEWGS, a solid sorbent is employed to capture the CO$_2$ generated by the WGS reaction. A key technical issue for the SEWGS is to identify and develop sorbents that can capture CO$_2$ under high pressure and high temperature syngas conditions and minimize or even eliminate the need for WGS catalysts.

Calcium oxide has emerged as an attractive material for high temperature CO$_2$ capture because it is inexpensive, has high selectivity, and rapid kinetics. CaO, however, suffers from rapid degradation of capacity after multiple carbonation/calcination cycles due to reduction of surface area. The decline in the performance of CaO materials during cycling are generally attributed to loss of microporosity and sintering.

Several approaches have been taken to improve the performance of CaO over multiple cycles, including the addition of supports and binders such as carbon, magnesium oxide, and calcium aluminates. Some researchers have modified the sorbent microstructure to improve the sorbent stability. Additionally, it has been shown that the sorbent can be partially regenerated upon hydration.

Aerosol synthesis methods have been extensively utilized to prepare a variety of metal oxides, even on an industrial scale. We report here the first use of ultrasonic spray pyrolysis (USP) as a continuous flow method for the facile synthesis of CaO-based materials for CO$_2$ capture applications. In order to improve cyclic reversibility of the prepared sorbents, Al$_2$O$_3$ was incorporated into CaO matrix. It has been previously noted that Al$_2$O$_3$ forms mixed calcium aluminate phases upon reaction with CaO at high temperatures (e.g., Ca$_{12}$Al$_4$O$_{13}$, Ca$_2$Al$_2$O$_6$, CaAl$_2$O$_4$). To synthesize the composite aluminum-doped CaO materials, a solution of calcium nitrate tetrahydrate [Ca(NO$_3$)$_2$·4H$_2$O] and aluminum nitrate nonahydrate [Al(NO$_3$)$_3$·9H$_2$O] in ethanol were nebulized via ultrasound, and the resulting mist was carried through a furnace tube (set at 600 °C unless otherwise stated) by argon gas. Solvent evaporation and precursor
decomposition occurred within the furnace, and the product was collected in ethanol-filled bubblers. A schematic of the USP set-up is presented in the ESI (Fig. S1†). The nitrate salts were selected as precursors for two reasons: first, each salt decomposes completely to the respective oxide leaving no residue behind; and second, the gases created during nitrate decomposition act as porogens and increase the surface area of the sorbent product. Several studies have shown that the performance of CaO sorbents is directly related to the surface area of the material.11,12

Sorbents containing various ratios of Al/Ca were synthesized by USP. XRD of the as-synthesized materials show only crystalline CaCO₃ (Fig. 1a). The Debye–Sherrer formula was used to calculate the CaCO₃ crystallite size based on the six major characteristic peaks of CaCO₃ pattern (ICDD PDF card 04-007-8659) at 23.05, 29.4, 35.9, 39.4, 43.1 and 48.5°. CaCO₃ crystallite size comparison between pure CaCO₃ and Al/Ca materials with an atomic ratio of 0.16 reveals that the presence of Al reduced the grain size from 133 nm to 45 nm, which suggests that the alumina phase exists as an amorphous phase between CaCO₃ grains. USP produces the carbonated form of CaO (CaCO₃) due to reaction with CO₂ produced from the pyrolysis of the solvent, ethanol. In order to confirm formation of a CaAlO phase, a sample with Al/Ca = 0.16 was calcined at 900 °C for 1.5 h; from the XRD pattern (Fig. 1b) small peaks corresponding to mayenite (Ca₁₂Al₁₄O₃₃) phase were observed. As described in more detail later, the sorbents subjected to 15 cycles of calcination/carbonation; XRD characterization of the cycled sample reveals the formation of both Ca₁₂Al₁₄O₃₃ and Ca₃Al₂O₆ phases (Fig. 1c). This indicates that intermediate mayenite phase observed in Fig. 1b turns into the more stable Ca₃Al₂O₆ phase after increased cycles of calcination/carbonation. As expected, increasing the amount of Al in the synthesis produces more pronounced CaAlO peaks.

This specific Al/Ca ratio (0.16) was chosen as a representative sample for characterization purposes for several reasons. First, this composition has been previously studied heavily in the literature,13 so it is a good choice for comparison. Second, a sample with Al/Ca = 0.16 corresponds to a composition of 75 : 25 wt% CaO : Ca₁₂Al₁₄O₃₃ after full transformation to the calcium aluminate phase; 75 : 25 is obviously arbitrary, but certainly representative. Third, lower ratios of Al/Ca make the XRD identification of the aluminate phase difficult due to the low intensity of the calcium aluminate peaks.

STEM-EDX analysis was done on a particle with Al/Ca = 0.16 as shown in Fig. 2. The particles are macroporous with a homogenous distribution of Al and Ca throughout, as seen in Fig. 2b and c. The ratio of maximum counts of Ca and Al Kα signals is ~0.17 which is consistent with the atomic ratio for the sample composition (Al/Ca = 0.16). TEM images for various sorbent compositions (Fig. S2†) reveal the change in particles’ morphology from hollow to solid structure upon increasing alumina content in the sorbents. Pure CaCO₃ particles are mostly hollow spheres (Fig. S2a†), and increasing the Al/Ca ratio tends to make a solid macroporous morphology. N₂ BET surface analysis (Table S1†) shows that the surface areas of each sorbent is ~25 m² g⁻¹.

As a control, the effect of synthesis temperature on the sorbent’s stability for the pure CaO sorbents was investigated. As shown in Fig. S3†, the synthesis temperature does not have much influence on the cycling stability of the materials nor does it change the morphology. Also, as indicated throughout the literature,14 regeneration conditions (temperature and CO₂ concentration) have a stronger influence on the stability of the CaO sorbents than preparation parameters. Therefore, we chose the lowest synthesis temperature for which we obtained the complete decomposition of nitrate precursor to oxide (i.e., 600 °C). Then CO₂ uptake of composite CaO-based sorbents was compared for various sorbent compositions during 15 cycles of calcination/carbonation (Fig. 3). Initial CO₂ uptake decreases

**Fig. 1** XRD patterns of the sample with Al/Ca = 0.16; (a) immediately after collection from the USP setup, (b) after calcination at 900 °C for 1.5 h and (c) after 15 cycles of calcination/carbonation. The XRD peak labels given for CaCO₃, Ca₁₂Al₁₄O₃₃, Ca₃Al₂O₆ and CaO are from ICDD PDF cards 04-007-8659, 00-009-0413, 04-008-8069 and 04-005-4757 respectively.

**Fig. 2** (a) STEM image and EDX line scan analysis of a particle with Al/Ca 0.16; (b) Ca Kα signal with 268 max counts, and (c) Al Kα signal with 46 max counts. The red line in (a) indicates the line scan analysis path (~1.7 μm, 15 analysis points).
from the addition of inert Al₂O₃, whereas the recycling stability showed a significant improvement even with low concentrations of Al₂O₃ present (e.g., as low as 0.03 Al to Ca ratio). Carbonation and calcination cycles were performed at 710 °C for 30 min under 100% CO₂ and carbonation at 710 °C for 30 min under 100% CO₂. Incorporating low concentrations of Al₂O₃ significantly improves the cycling stability over 15 cycles.

In summary, we have synthesized a series of macroporous CaAl₉O₁₄ materials for CO₂ capture via ultrasonic spray pyrolysis. USP provides a facile and scalable route for materials synthesis. The formation of calcium aluminate phases greatly stabilizes the CO₂ capacity of the sorbent over 15 calcination/carbonation cycles and provides a more stable sorbent than traditional batch preparations. Over 15 cycles, the optimum Al/Ca ratio is about 0.08.

Acknowledgements

This research was supported by U.S. Department of Energy/National Energy Technology Laboratory (DOE/NETL) through Cooperative Agreement no. DE-FE-0000465 and Illinois Department of Commerce and Economic Opportunity, through the Office of Coal Development and the Illinois Clean Coal Institute under Contract no. 10/US-2 and DEV11-1 and in part by NSF (DMR 1206355). Characterizations were carried out in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which is partially supported by the U.S. Department of Energy under grants DE-FG02-07-ER46453 and DE-FG02-07-ER46471.
References