Improved $CaO/CaZrO_3$ adsorbents with potential applications in sorption enhanced steam reforming

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Introduction

CaO is the natural choice for many applications such as CO_2 post-combustion capture for fossil fuel fired power plants or steam reforming for hydrogen production. In both these applications, CaO suffers from CO_2 capacity loss after multiple calcination cycles [1], hence a lot of effort is being put into finding different ways to improve its stability. This is translated into the retention of at least 0.3g CO_2/ g sorbent sorption capacity over multiple sorption/desorption cycles [2].

One way of inhibiting the CaO matrix densification is to add refractory "spacer" particles [3] which not only physically separate the particles, but also due to differential thermal expansion effects and differential sintering rates of the different components.

Materials and Methods

Calcium and zirconium hydroxides suspended in ethanol were prepared through the precipitation of the precursors with ammonium hydroxide. The two dispersions were mixed together, dried and then calcined at 800°C for 30 minutes in air. The $CaZrO_3$ content was controlled by varying the amount of zirconium component.

Thermogravimetric analysis was involved in assessing the CO_2 capacity and stability of the prepared sorbents. Additionally, other characterization tools such as XRD, SEM and TEM were used for materials characterization at different stages.

Results and Discussion

Table 1 presents the CO_2 uptake and the carbonation of the as-prepared samples over up to 30 cycles [4].

Table 1. Net CO_2 uptakes and carbonation percentages for cycle 1, 10 and 30 under 'mild' conditions (carbonation: 15% CO_2, 650°C, 15min; calcination: air, 800°C, no dwell time).

	Net CO_2 uptake ($g\text{-}CO_2/g\text{-sorbent}$)			Carbonation (%)		
	1st	10th	30th	1st	10th	30th
$10CaZrO_3$:90CaO	0.310	0.373	0.365	43.8	52.7	51.6
$18CaZrO_3$:82CaO	0.251	0.320	0.312	39.0	49.7	48.4
$30CaZrO_3$:70CaO	0.175	0.251	0.267	31.8	45.6	48.5

The reason for "self-reactivation" observed for all the samples reported here, with the most predominant being characteristic to sample 3, has been investigated as part of this work.

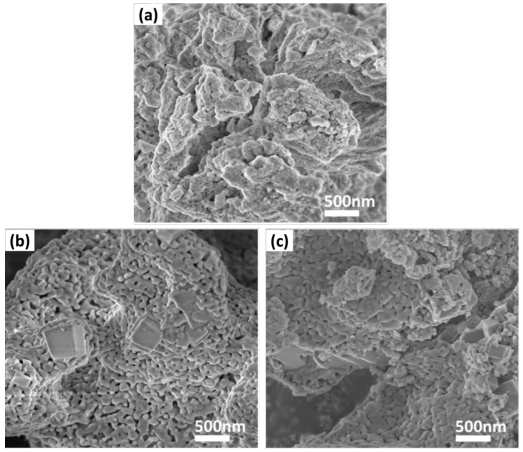

Figure 1. SEM images of porosity development within Sample 3, the $30CaZrO_3$:70CaO sorbent after the 'mild' TGA cycles ending on calcination (carbonation: 15% CO_2, 650 °C, 15min; calcination: air, 800°C, no dwell time). (a) Fresh form, (b) after 10 cycles, (c) after 30 cycles. The cuboid particles evident in b and c are identified as $CaZrO_3$ micro-particles by TEM.

At cycle 10 the powder matrix was more porous, containing <100 nm pores within a matrix of <200 nm CaO particles. This development of a more porous matrix in the first 10 carbonation-calcination cycles accounts for the observed rise in CO_2 capacity; progressive changes to this microstructure in the earlier cycles would give rise to the gradual increase in CO_2 uptake that is observed.

Significance

Under severe calcination, 950°C in 100% CO_2 (calcination 650 °C in 100 % CO_2, 15 min), the most durable composition, 30%$CaZrO_3$:70%CaO demonstrated an uptake of 0.36 $g\text{-}CO_2$/g-sorbent in cycle 1 decreasing to 0.31 by cycle 30, superior to many other spacer materials.

References

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