Hydrotalcite-Stabilized MgO-$NaNO_3$ with Improved Cyclic Stability for Intermediate-Temperature CO_2 Capture

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Abstract: $NaNO_3$ significantly catalyzes the dissolution of CO_2 on MgO, but loses stability and capacity after regeneration. In this study, commercially available hydrotalcites with MgO:Al_2O_3 weight ratios of 30:70 and 70:30 were used as stabilizers for MgO-$NaNO_3$ sorbents. Cyclic tests revealed that the 30:70 hydrotalcite-stabilized sorbent attained higher and stable sorption performance as compared to pristine MgO-$NaNO_3$ under multiple cycles, reaching a stable capacity of 30.92 wt% or 37.95% MgO conversion. The sample also showed high capture performance under a modified 15% CO_2 sorption cyclic test with partial desorption, achieving an average capacity of 23.3wt% or 28.1% MgO conversion.

Keywords: magnesium oxide, sodium nitrate, intermediate temperature CO_2 sorption

1. Introduction

MgO is regarded as a promising sorbent for carbon capture due to its abundance in basic sites and lower energy requirement for regeneration. However, its relatively slow kinetics, moderate CO_2 sorption capacity, and large capacity decrease after regeneration greatly limit its applications.[1,2] Although molten salt promoters such as $NaNO_3$ have been reported to catalyze and improve the sorption and regeneration reactions on MgO, the performance of such sorbents significantly decreases after multiple cycles, implying that these sorbents lack stability and may not be efficient and robust for industrial applications.[3–5] To resolve this, we propose the use of commercially available hydrotalcites as stabilizers to maintain the cyclic capacity of $NaNO_3$-promoted MgO and obtain an overall uptake that is comparable to that of MgO-$NaNO_3$.

2. Experimental

The sorbents were synthesized by melting 6.045g of $Mg(NO_3)_2 \cdot 6H_2O$ at 175˚C and adding 0.05g of the hydrotalcite stabilizer (30:70 and 70:30 Mg:Al weight ratio). The mixture was stirred for 12 hrs, removed from heat, and cooled to room temperature before calcining at 600˚C for 3 hrs at a rate of 2˚C/min. $NaNO_3$ was added to the stabilizer-loaded MgO by physical mixing and calcining at 400˚C for 2 hrs at a rate of 2˚C/min. MgO-$NaNO_3$ and an α-Al_2O_3-stabilized samples were also synthesized for comparison. The samples were denoted as S-MgNa where S refers to the support used (e.g. 30:70HMgNa, 70:30HMgNa, Al_2O_3MgNa). X-ray diffraction, BET surface characterization, FE-SEM imaging, and FE-TEM imaging were then performed to characterize the samples. To evaluate the CO_2 sorption performance of the sorbents, temperature sweeping tests from 25°C to 600°C, isothermal tests at desired temperature intervals, and cyclic tests under pure CO_2 sorption (300˚C, 3 hrs) and N_2 regeneration (450°C, 1 hr) were performed via thermogravimetric analysis. A modified cyclic test with partial desorption was also performed to activate the sample towards 15% CO_2 sorption. To do this, the sample was first saturated with 100% CO_2 and partially desorbed before subjecting it under 15% CO_2 sorption balanced with N_2 (300°C, 3hrs).

3. Results and discussion

Optimization tests were first performed to determine the optimum loading of the stabilizer and $NaNO_3$ on MgO. It was found out that a stabilizer loading of 5wt% and a $NaNO_3$ loading of 20wt% gives the highest sorption. It was also found out that the 30:70HMgNa sample gave higher sorption than 70:30HMgNa, and was thus used in the succeeding tests. SEM and TEM images of the bare stabilizers and the stabilizer-loaded MgO with and without $NaNO_3$ reveal that the stabilizer was evenly distributed within the sorbent, while EDX results show that $NaNO_3$ was also evenly dispersed.

The results of the cyclic tests carried out in this study are shown in Fig. 1. The $MgONaNO_3$ sorbent synthesized in this study follows the same behavior as those obtained in literature (Fig. 1a).[3–5] The adsorbent initially attained a capacity of 37.4 wt%, corresponding to 42.8% MgO conversion, and gradually dropped in the succeeding cycles. At the end of the 8th cycle, the sorbent was only able to maintain a capacity of 17.4 wt% or 19.9% MgO conversion, showing a capacity drop of 53.6% as compared with the first cycle. On the other hand, Fig. 1b shows the cyclic adsorption test for 30:70HMgNa. The sample initially attains a sorption capacity of only 11.50 wt% or 13.86% MgO conversion, and continuously increased in the following cycles, reaching a stable capacity of 30.7 wt% or 36.9% MgO conversion at the fourth cycle until the 8th cycle. The sorbent achieved a cumulative CO_2 uptake of 49.7 mmol/g, while $MgONaNO_3$ only achieved 43.2 mmol/g. Thus, although there is an initial capacity-stability trade-off, 30:70HMgNa still performed better after longer use and is thus favorable for practical applications. The stabilizing ability was proven to be unique for 30:70HMgNa, as the α-Al_2O_3-loaded sample did not show the same stable cyclic performance (Fig. 1c).

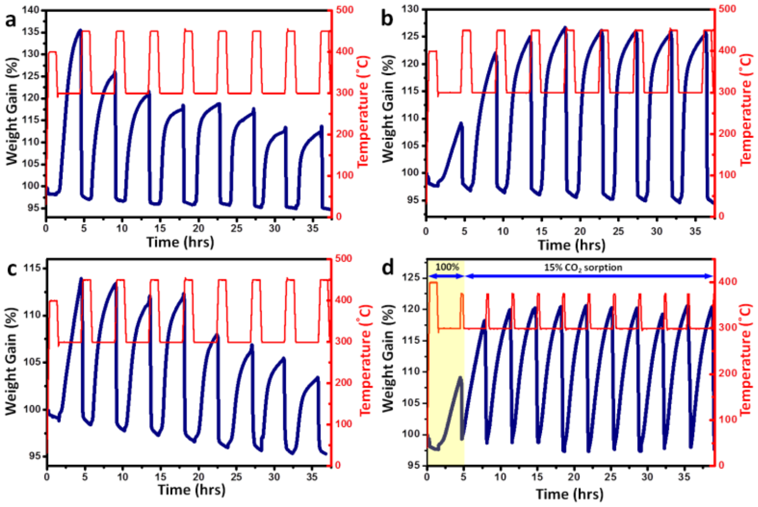

Figure 1. Cyclic test for (a) $MgONaNO_3$ (b) 30:70HMgNa, and (c) Al_2O_3MgNa under pure CO_2 sorption (300˚C, 3 hrs) and N_2 regeneration (450°C, 1 hr) (d) CO_2 sorption performance of 30:70HMgNa under 15% CO_2 sorption (300°C, 3 hrs) and N_2 regeneration (375°C, 13 min).

XRD patterns of cycled $MgONaNO_3$ and 30:70HMgNa sorbents were obtained. Results reveal that the crystallite size of $MgCO_3$ on $MgONaNO_3$ greatly increased after 4 cycles (40.0 nm) while maintaining the size of MgO crystals. On the other hand, the MgO crystals on 30:70HMgNa samples were found to decrease after multiple cycles. Moreover, $MgCO_3$ crystals formed after the 4th cycle were also found to be smaller (35.1 nm) than those formed on $MgONaNO_3$, showing that the hydrotalcite stabilizer inhibited the formation of large $MgCO_3$ crystals, resulting to the improved stability.

Lastly, a modified cyclic test was done to demonstrate the potential of30:70HMgNa for practical use. Fig. 1d shows that the sorbent can achieve a stable capacity of 23.3wt% or 28.1% MgO conversion under 10 cycles of dilute CO_2 sorption, showing that the sorbent may be developed for commercial use.

4. Conclusions

In summary, it was demonstrated that hydrotalcites are capable of stabilizing the CO_2 uptake of $NaNO_3$-promoted MgO sorbents, achieving a significantly higher total uptake than bare $MgONaNO_3$. The hydrotalcite restricts the formation of large $MgCO_3$ crystals after regeneration, resulting to the increased stability obtained. Moreover, the 30:70HMgNa sample achieved an average stable sorption of 23.3wt% or 28.1% MgO conversion after 10 cycles under a modified cyclic test using 15% CO_2, thus further demonstrating the efficiency of the sorbent for industrial use. With these findings, it can be concluded that hydrotalcite-stabilized $NaNO_3$-promoted MgO has high potential for practical CO_2 capture applications.

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