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Assessment of limestone treatment with organic acids for CO_2 capture in Ca-looping cycles

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ABSTRACT

The main challenge for CO_2 capture in calcium looping cycles is the decay of CO_2 carrying capacity of the CaO-based sorbents with increasing number of cycles. In this work, limestone was treated with organic acids and tested for CO_2 capture in calcium looping cycles to understand how practical and reliable the treatment is for CO_2 looping capture. The results showed that after 20 cycles the carbonation conversions of limestone treated with acetic acid, vinegar, formic acid, and oxalic acid were 33.1%, 21.1%, 31%, and 35.2%, respectively, compared to 18.9% for untreated limestone. The treatment with organic acids clearly improves the sintering-resistance properties of the modified sorbent. However, the activity of these sorbents was found to decline in similar fashion to that of untreated limestone. It was concluded that although limestone treatment with organic acids enhances CO_2 capture capacity, the enhancement is marginal in most cases while the treatment increases the cost of CO_2 capture significantly. Accordingly, the treatment may not be an adequate approach if the goal is to maintain low-cost capture of CO_2; moreover, treated sorbents which perform well for CO_2 capture do also perform well for SO_2 capture, causing their capacity to decline at least as rapidly as a natural untreated sorbent and often more so.

1. Introduction

Carbon dioxide (CO_2) emissions through human activities, such as the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, have increased rapidly in recent decades contributing to the greenhouse gas effect [1]. Carbon capture and storage (CCS) has been proposed for the power generation sector (being the main source for CO_2 emissions) as an effective option for reducing CO_2 emissions [2]. In the CCS approach, capturing CO_2 is the most challenging and costly stage. Currently, the commercially-applied technique for CO_2 capture is based on amine scrubbing technology [3,4]. However, this approach is energy intensive, in addition to the economic penalties due to the degradation of the expensive solvents [5]. Calcium looping (CaL) is an emerging technology for high-temperature post-combustion CO_2 capture [6]. In CaL cycles, CO_2 reacts with CaO to form $CaCO_3$ at 600–700 °C, followed by the reverse reaction of $CaCO_3$ to regenerate the material at 850–950 °C. The capture cycles are proposed to take place in a dual-fluidized bed circulating system, as shown in Fig. 1, which presents a schematic diagram of the CaL process. The carbonation and calcination reactions are made to occur in the carbonator (reactor A) and calciner (reactor B), respectively.

Limestone has been identified as an attractive source of CaO; it is abundant and inexpensive. For an economically feasible process, the sorbent must be capable of being regenerated and reused repeatedly. However, previous studies have shown that the cyclic reactions of CaO-based sorbents are far from reversible in practice, where the activity of the sorbent declines gradually from cycle to cycle due to sintering [7–9]. Consequently, more fresh sorbent is required to make up for the spent sorbent [10]. To minimize this loss of activity and to improve the life cycle performance of limestone several methods have been proposed including treatment of limestone with organic acids. The reaction between an organic acid and limestone (calcium carbonate, $CaCO_3$) proceeds according to the following equations:

With acetic acid:

$$CaCO_{3(s)} + 2CH_3CO_2H_{(aq)} \rightarrow Ca(CH_3CO_3)_{2(g)} + H_2O_{(1)}. \quad (1)$$

When heated $Ca(CH_3CO_2)_2$ decomposes to acetone (C_3H_6O) and $CaCO_3$, following the reaction:

$$Ca(CH_3CO_2)_{2(s)} \rightarrow CaCO_{3(s)} + C_3H_6O_{(g)}. \quad (2)$$

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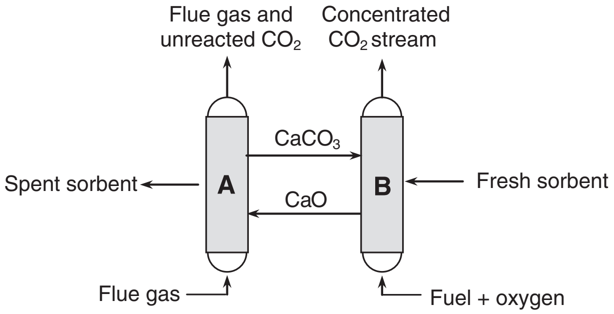

Fig. 1. CaL cycles system.

With formic acid:

$$CaCO_{3(s)} + 2CH_{2(aq)} \rightarrow Ca(CHO_2)_{(aq)} + CO_{2(g)} + H_2O_{(1)}. \quad (3)$$

When heated $Ca(CHO_2)_2$ decomposes to formaldehyde (CH_2O) and $CaCO_3$:

$$Ca(CHO_2)_{2(s)} \rightarrow CaCO_{3(s)} + CH_2O_{(g)}. \quad (4)$$

With oxalic acid:

$$CaCO_{3(s)} + C_2H_2O_{4(aq)} \rightarrow CaC_2O_{4(s)} + CO_{2(g)} + H_2O_{(1)}. \quad (5)$$

When heated $CaC_2O_{4(s)}$ decomposes to carbon monoxide (CO) and $CaCO_3$:

$$CaC_2O_{4(s)} \rightarrow CaCO_{3(s)} + CO_{(g)}. \quad (6)$$

At high temperatures, e.g., >800 °C, $CaCO_3$ decomposes to CaO and CO_2 according to the following equation:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}. \quad (7)$$

Although the reaction of $CaCO_3$ with organic acids has been used for some applications, various studies have suggested this treatment for high-temperature CO_2 capture. Li et al. [11] showed that a limestone treated with acetic acid solution exhibited significantly higher pore surface area and pore volume than the untreated one. In addition, the grain size of the treated sorbent was ~50% smaller than that of the parent material after 20 carbonation/calcination cycles. A pressurized CO_2 capture with acetified limestone was also investigated [12], and showed enhanced CO_2 uptake with acetified sorbent compared to the natural sorbent. The enhancement in CO_2 capture with this modified sorbent was attributed to the alteration in sorbent porosity due to acid treatment. Previous workers generally concluded that the treatment improves the sintering resistance of the modified sorbent by altering the porous structure, which as a result enhanced CO_2 capture capacity over multiple cycles.

We have carried out a comprehensive body of work on the treatment of limestone with organic acids for CO_2 capture in CaL cycles. In this work, we present an assessment of the treatment of limestone with organic acids to explore how practical this approach is for modifying sorbents and determine whether the treatment process meets the goal of CaL cycles from both technical and economical perspectives.

2. Experimental

2.1. Sorbents

A batch of Cadomin limestone (0.5–1.4 mm in diameter) was crushed and sieved to powder with a particle size of <53 μm (designated as CD). Four organic acids, namely acetic acid, commercial vinegar (cooking grade, 5 vol.% acetic acid), formic acid, and oxalic acid were used. In the treatment with acid, 2.5 g CD was placed in a small beaker. 20–mL of 10 vol.% acid solution (except for vinegar) was added slowly to the beaker inside a fume hood and the contents were shaken for a few seconds to ensure homogeneity. The contents were then left for 5 min followed by evaporation and drying at 120 °C. The product was left exposed to air overnight at ambient temperature. Samples were designated according to the first letter of the acid. It is important to note that according to the decomposition in Eqs. (2) and (4), modified sorbents release acetone or formaldehyde, respectively. These gases are flammable, and if oxygen is present in the high-temperature calcination atmosphere they will burn with flame, thus caution must be exercised.

2.2. Characterization

The elemental content of CD was obtained using a Rigaku Primus II WD-XRF spectrometer, and the content of major elements is given in Table 1. Porosity characterization was performed with N_2 at −196 °C using a Micromeritics TriStar II-3020. Brunauer–Emmett–Teller (BET) specific surface area was obtained from multiple point measurements, while Barrett–Joyner–Halenda (BJH) total specific pore volume was obtained at relative pressure (P/P_o) of ~0.99. BJH pore size distribution was derived from N_2 adsorption data for pore surface area, and from the corresponding desorption data for pore volume. Prior to N_2 isotherm measurements, samples were calcined at 850 °C for 2 h in N_2. Quantitative X-ray diffractometry (XRD) analysis for the uncalcined powders was conducted on a Rigaku Ultima IV X-ray diffractometer to identify and quantify crystal phases.

2.3. CO_2 capture cycles

CO_2 capture cycles were performed in a Mettler Toledo TGA/SDTA851 thermogravimetric analyzer (TGA). The procedure consists of heating the sample from ambient temperature to 850 °C at a heating rate of 25 °C/min in N_2 (a limited number of tests were done with CO_2, but this appeared to degrade sorbent performance even faster, so that the difference between treated and untreated sorbents was smaller after even fewer cycles). After reaching the target temperature, the calcination continued for 5 min, followed by cooling down to 650 °C for carbonation in an atmosphere of 15% CO_2 (N_2 balance) for 20 min. The carbonation was allowed proceeding for 20 min before the next calcination. Gas flow rate for both reactions was kept constant at 0.04 dm^3/min.

3. Results and discussion

3.1. Sorbent morphology

The results of nitrogen physisorption analysis are presented in Table 2, which shows BET surface areas and BJH pore volumes calculated from N_2 isotherms. Sorbents obtained from treatment with acetic acid (CD-A), vinegar (CD-V) and formic acid (CD-F) exhibited a significant drop in pore surface area, from 5.2 m^2/g for the parent CD to 2.7, 3.8,

Table 1
XRF elemental results for Cadomin limestone.

Component	wt.%
SiO_2	1.14
Al_2O_3	1.12
Fe_2O_3	0.38
CaO	51.96
MgO	0.47
K_2O	0.25
LOF	41.50*
Sum	96.82

* LOF: Loss on Fusion.