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Effects of rapid calcination on properties of calcium-based sorbents

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ABSTRACT

The calcination process may influence subsequent fragmentation, sintering and swelling when CaO derived from limestone acts as a CO_2 or SO_2-sorbent in combustion, gasification and reforming. Sorbent properties are affected by CO_2 partial pressure, total pressure, temperature, heating rate, impurities and sample size. In this study, the effect of calcination heating rate was investigated based on an electrically heated platinum foil. The effects of heating rate (up to 800 °C/s), calcination temperature (700–950 °C), particle size (90–180 μm) and sweep gas velocity were investigated. Higher initial heating rates led to lower extents of limestone calcination, but the extents of carbonation of the resulting CaO were similar to each other. Calcium utilization declined markedly during carbonation or sulphation of CaO after calcination by rapid heating. Experimental results show that carbonation and calcium utilization were most effective for carbonation temperatures between 503 and 607 °C. Increasing the extent of calcination is not the best way to improve overall calcium utilization due to the vast increase in energy consumption.

1. Introduction

The increasing use of fossil fuels to meet energy needs has led to higher carbon dioxide (CO_2) and sulphur dioxide (SO_2) emissions into the atmosphere. Increasing attention has been focused on chemical looping of limestone involving calcination and carbonation for carbon dioxide separation during combustion, gasification and reforming. Gaseous CO_2 reacts with lime to yield calcium carbonate during carbonation

$$CaO + CO_2 \rightarrow CaCO_3 \quad \Delta H_{298K} = -178\,\mathrm{kJ/mol}, \tag{1}$$

and the lime is then regenerated by calcination, i.e.

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H_{298K} = 178\,\mathrm{kJ/mol}. \tag{2}$$

Lime derived from calcium-based sorbent (limestone or dolomite) is also commonly utilized to capture SO_2 in fluidized bed combustors via

$$CaO + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 \quad \Delta H_{298K} = -426.5\,\mathrm{kJ/mol}. \tag{3}$$

It is important to understand whether the manner in which the calcination takes place affects the subsequent carbonation and sulphation processes. In this paper, we investigate the effects of calcination rate and conditions on the subsequent performance of calcium-based sorbents.

2. Calcination

Calcination of limestone involves five steps:

(1) Heat transfer from the surroundings to the exterior of a particle.
(2) Heat transfer from the external surface to the interior reaction interface.
(3) Heat absorption and thermal decomposition at the reaction interface.
(4) Diffusion of CO_2 formed by the reaction through a porous layer of CaO.
(5) Diffusion of CO_2 from the particle exterior surface to the surroundings.

Several investigations [1,2] have shown that decomposition of calcium carbonate occurs at a well-defined boundary between the CaO and $CaCO_3$ phases. This boundary migrates towards the centre of the particle. Dennis and Hayhurst [3] and Silcox et al. [4] used the shrinking core model to predict their experimental results, whereas Borgwardt [5] assumed a homogeneous reaction throughout the sorbent for particles smaller than 90 μm. Khinast et al. [6] concluded that simple models such as the shrinking core and uniform conversion models only apply in extreme cases. Rao et al. [7] assumed gradual conversion in pellets of size ~6.5 mm, with the mass transfer in the porous shell controlling the reaction. Later, Hu and Scaroni [8]

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observed by SEM analysis different conversion levels inside partially calcined 63 μm limestone particles.

Both heat and mass transfer have been found to influence the rate of calcination. Improved thermal conductivity of the selected sweep gas increases the rate of calcination [9]. Previous studies [2,10,11] have indicated that the kinetics of decomposition of calcium-based sorbents depend greatly on the experimental system and conditions.

The porosities of calcined samples vary over a wide range (0.32–0.51) depending on the limestone. The apparent activation energies of large limestone particles calcined in thermogravimetric analyzers or in differential reactors at temperatures <900 °C range from 79 to 280 kJ/mol [5,7,11–15], while the activation energy has been determined to be 209 kJ/mol [16,17]. Garcýa-Calvo et al. [15] found values from 110 to 194 kJ/mol depending on the limestone impurities. These values are higher than those (33 to 92 kJ/mol) obtained in entrained-flow reactors [4,14,18] for particles smaller than 100 μm and temperatures up to 1200 °C. Mai [19] attributed the higher activation energies to inadequate sorbent/gas mixing or slow particle heat-up. Results were similar for dehydration of calcium hydroxide. Activation energies between 79 kJ/mol [12] and 280 kJ/mol [13] were higher than ~67 kJ/mol obtained in a drop tube reactor [14,19]. The activation energy for calcination of Omyacarb limestone, 96 kJ/mol, was similar to that obtained by other authors under similar experimental conditions. However, values of 36 and 50 kJ/mol, reported by Fierro et al. [20], were lower than those obtained by other authors.

Khraisha and Dugwell [21] studied the thermal decomposition of a limestone in a thermogravimetric analyzer at heating rates up to 80 K/min and temperatures to 950 °C. They also summarized a wide range of data from other workers with activation energies and frequency factors varying from 33 to 4002 kJ/mol and 10^2 to 10^{69} s^{-1}, respectively.

Particle size influences the calcination rate. For small particles (1–90 μm), chemical reaction controls the calcination rate [5,14]. Heat transfer becomes important [7] for particles larger than 6 mm. For intermediate size particles, reaction and internal mass transfer are the main resistances controlling calcination. Their relative importance also depends on the pore structure. The calcination rate increases with decreasing particle size because pore diffusion is less important for smaller particles. The relative importance of heat transfer is also greatly influenced by particle size [6,8,22].

From the numerical simulation of Hu and Scaroni [8], the intraparticle average temperature is lower than the sweep gas temperature, and there are large temperature gradients within the particle, especially for larger particles. Wernick [23] attributed the difference between activation energies of limestones to different calcination temperatures. He proposed that the activation energy is higher at low temperatures. Bischoff [24] found an activation energy of 185 kJ/mol in the temperature range between 550 and 800 °C in moist or dry sweep air, whereas Ar and Dogu [25] obtained values between 410 and 1470 kJ/mol, depending on the heating rate and gas composition.

3. Carbonation

The possibility of using the carbonation reaction to capture CO_2 from a gas stream was considered as early as the 19th century [26]. Calcined limestone may be able to remove CO_2 in fluidized bed combustion environments and, by subsequent calcination, to produce a nearly pure CO_2 stream for sequestration in a chemical looping process [27–30]. This scheme involved a fluidized bed combustor–carbonator where the fuel burned in an excess of lime which, depending on operating conditions, removed 80% or more of the CO_2 and effectively all of the SO_2, and a calciner where sorbent was regenerated releasing a gas of high CO_2 concentration. However, experimental results indicate a rapid decline in sorbent effectiveness, especially if SO_2 is present [31].

Carbonation involves three different processes according to the unreacted shrinking core model, any of which can be rate-controlling:

(1) Mass transfer from the gas phase to the surface.
(2) Diffusion of gaseous reactant inside the particle pores or through the product layer.
(3) Chemical reaction.

The gas–solid CO_2–CaO reaction proceeds through two rate-controlling regimes [32,33]. Reaction occurs rapidly by heterogeneous reaction at the surface in the initial stage. A compact layer of product $CaCO_3$ then develops on the outer region of the particle, causing the rate of reaction to decrease due to the diffusion limitation through this layer [33]. The reaction does not proceed to complete conversion of CaO, instead giving ultimate conversions of 70–80% [34] or up to 90% [35]. To describe such gas–solid reaction kinetics, various models have been proposed.

Structural limitations prevent the attainment of 100% conversion. Dedman and Owen [36] obtained a CO_2 uptake of about 0.23 g of CO_2/g of CaO (~30% conversion) in 30 min at 600 °C. Bhatia and Perlmutter [34] reached ~70% conversion for 81–137 μm particles. Mess et al. [37] reported 82% conversion at 1050 °C and 11.74 atm CO_2 pressure after 32 h for 15–20 μm particles. The limitation on total conversion stems essentially from the initial pore size distribution of the CaO sorbent. Microporous sorbents (pore size<2 nm) are very susceptible to pore blockage and plugging through formation of a higher-molar-volume product (molar volume of CaO = 17 cm^3/mol, whereas molar volume of $CaCO_3$ = 37 cm^3/mol). CaO sorbents from naturally-occurring precursors are usually microporous. At the end of the kinetically controlled regime, diffusion through the product layer controls the reaction rate. Wei et al. [38] suggested that a mesoporous structure which maximizes porosity in the 5–20 nm pore size range would be less susceptible to pore pluggage, while providing sufficient surface area to ensure rapid kinetics. The modified precipitation technique [32] resulted in a mesoporous $CaCO_3$ structure with high BET surface area (60 m^2/g). Barker [39] obtained repeated 93% conversions over 30 cycles at 629 °C on 10 nm CaO particles. Gupta and Fan [35] modified calcium carbonate precipitation to achieve higher (>90%) carbonation conversions.

4. Reactors for calcination

To develop accurate predictive models and to simulate the calcination process, it is necessary to measure the reaction rate as a function of time and temperature. Heating rates can vary from fractions to tens of thousands of °C/s. The reaction is affected by a combination of heat transfer, mass transfer and chemical reaction, which are in turn affected to different extents by such factors as particle physical shape, heat capacity, emissivity and thermal conductivity.

A variety of reactors have been employed including induction heating, laser heating, fluidized beds, plasma and shock tubes, entrained-flow reactors, and wire-mesh reactors. An electrically heated wire-mesh reactor was first used by Loison and Chauvin [40]. They were subsequently widely employed in coal kinetics studies, e.g. by Anthony et al. [41,42], Suuberg [43] and Fong [44] at MIT; Gibbins et al. [45–47], Kandiyoti [48,49] at Imperial College, and Mill [50] at the University of New South Wales. The time of heating in this type of apparatus can be precisely controlled, and good material balances can be obtained, to an accuracy of a few percent [51]. The fundamental problems are the weighing and measurement of particle temperature during heat-up and calcination. The thermal properties and thermal response of the particles may differ significantly from the thermocouple attached to the wire mesh. These differences are important if a significant temperature gradient exists between the