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Calcium oxides for CO_2 capture obtained from the thermal decomposition of $CaCO_3$ particles coprecipitated with Al^{3+} ions

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Abstract

Calcium-carbonate powders were coprecipitated with Al^{3+} and then decomposed in air and/or under a CO_2 flux between 590 °C and 1150 °C. The data were analysed using a consecutive-decomposition-dilatometer method and the kinetic results were discussed according to the microstructure analysis done by N_2 adsorption isotherms (78 K), SEM and FT-IR measurements. Below 1000 °C, $CaCO_3$ particle thermal-decomposition was pseudomorphic, resulting in the formation of a CaO grain porous network. When the CaO grains were formed, the Al^{3+} diffused among them, producing AlO_4 groups that promoted the CaO grain coarsening and reduced O^{2-} surface sites available to CO_2 adsorbed molecules to form ${CO_3}^{2-}$. In pure CaO, ${CO_3}^{2-}$ diffused through the grain boundary, enhancing Ca^{2+} and O^{2-} mobility; AlO_4 groups reduced ${CO_3}^{2-}$ penetration and CaO sintering rate. Above 1000 °C, the sintering rate of the doped samples exceeded that of the undoped, likely because of Al^{3+} diffusion in CaO and viscous flow.

Keywords: Limestone decomposition; Sintering; CO_2 capture; Al ions; Dilatometer

1. Introduction

The separation of CO_2 from flue gases using conventional air-blown combustion systems and the storage of CO_2-rich gases in underground geological formation or in the deep ocean are approaches suggested for reducing the greenhouse effect of CO_2. Among the separation processes, the carbonate looping process for postcombustion CO_2 capture appears to be a promising technology.[1–4] This method involves the use of a fluidised bed where lime reacts with a fuel gas and another fluidised bed, the calciner, where the adsorbent is regenerated and pure CO_2 is produced. The choice of natural limestone as the CO_2 carrier is an attractive option because it is a cheap and abundant material with large and important applications in steel making,[5,6] building, cultural heritage,[7] and environmental applications.[8–10]

Regarding CO_2 capture technology, the porous lime particles obtained from the thermal decomposition of limestone need to have high efficiency in CO_2 capture and the capacity to endure a high number of carbonate looping cycles.

This requires that the porous calcium oxide particles obtained in the calciner are characterised by optimal and stable values for surface area, porosity and pore shape for the subsequent CO_2 adsorption from the flue gases. Because both fluidised beds are in air and in CO_2 flux, the surface area and porosity values of high surface porous calcium oxide (CaO) particles are rapidly reduced due to the temperature and catalytic effect of CO_2 on CaO sintering.[11–13]

For these reasons, CaO obtained from the thermal decomposition of limestone particles in air/CO_2 environments is characterised by surface area values of approximately $1 \times 10\,m^2/g$. Although the sintering of these oxides in CO_2 proceeds extremely slowly,[12] it has been found that the surface and porosity values of CaO-adsorbent particles obtained from calciners are reduced after a large number of cycles.[14,15]

Regarding new lime adsorbents with enhanced durability, previous studies[16–24] reported promising materials with a reasonable stable uptake of CO_2 obtained by mixing CaO on the

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molecular level with an inert supporting material with a high melting point, such as Al_2O_3, MgO or TiO_2. Improvements in obtaining these adsorbents have been made[25] by using CaO coprecipitation and hydrolysis methods.

Despite the promising results obtained by testing these materials in pilot plants, according to the opinion of the authors, the mechanism explaining how and why the uptake of CO_2 by these materials is more efficient than that of CaO obtained by the thermal decomposition of limestone/calcium carbonate particles remains to be elucidated.

This is not surprising because, as far as we are aware, the ultimate mechanism by which CO_2 catalyses the sintering of CaO has not been established.

In this paper, we concentrate our efforts on explaining this mechanism by using $CaCO_3$ particles precipitated from $CaCl_2{\cdot}2H_2O$ solutions in the presence and absence of $AlCl_3{\cdot}6H_2O$ salts as starting materials.

The background for this study is derived from previous experimental findings[12,26,27] of the sintering effects of gases such as CO_2 and H_2O on CaO and MgO.

In one of those papers,[27] we stated that any gas used as a catalyst for the sintering of a solid oxide must be chemically adsorbed to the surface of the oxide surface and then it must penetrate into the oxide in its bulk phases.

The experiments designed in this paper will prove that the above statement holds when CaO in the presence and absence of Al^{3+} ions is exposed to CO_2 in the temperature range of 590–1000 °C. Thus, the rule that CO_2 and H_2O must diffuse as ${CO_3}^{2-}$ and OH^- ions, respectively, into the oxide through grain boundary paths to be effective catalysts will be applied as a solid scientific basis to understand how and why ions smaller than Ca^{2+} can be used to stabilise the surface area and porosity of new CO_2 adsorbents in the carbonate looping process.

2. Experimental

2.1. Materials

The starting materials were $CaCl_2{\cdot}2H_2O$, $AlCl_3{\cdot}6H_2O$, 33% ammonia (NH_3) solution (each from Sigma–Aldrich), and 99.999% CO_2 gas (Air Liquide).

All inorganic chemicals were used without purification. A stock solution of $CaCl_2$ was freshly prepared by adding distilled water to reach the concentration of 1 mol/l. To produce the aluminium-doped $CaCO_3$, another solution was prepared by adding 2.41 g of $AlCl_3{\cdot}6H_2O$ to 1 l of $CaCl_2$ 1 M. Ammonium carbonate solution was prepared bubbling CO_2 into a 2 M NH_3 solution until a pH value of 8.47 was reached. The $CaCO_3$ powder was prepared by adding into the water-jacketed beaker containing 600 ml of the $(NH_4)_2CO_3$ solution and 500 ml of $CaCl_2$ solution. With respect the 1:1 ratio required by the stoichiometric reaction between $(NH_4)_2CO_3$ and $CaCl_2$, the $(NH_4)_2CO_3$ results the 20% greater. The solution was continuously stirred for 20 min, the reaction temperature was kept constant at 25 °C and changes in pH were recorded both for the precipitation without and with $AlCl_3$. A rapid decreasing of the pH down to 6.5 followed by an increasing to pH 8 was observed when $AlCl_3$ is not present, while in the case of doped material, the minimum pH was around 6.2 and the final one was 7.14. The precipitate was aged for 24 h. After sedimentation, the powders were collected and washed with distilled water until chloride ions were completely removed. The chlorine ion concentration in the liquid phase was checked with a 0.1 N $AgNO_3$ solution.

The obtained precipitates were settled by centrifugation and dried at room temperature in a desiccator for 1 week.

2.2. Methods

Cylindrical pellets of 8 ± 0.1 mm in diameter and 7.6 ± 0.1 mm were prepared with an uniaxial cylindrical mould. Due to the importance of the pelletisation step, great care was paid to obtain pellets of doped/not doped calcium carbonate with the same initial density.

230 mg of doped/not doped calcium carbonate powders as they have been obtained after the precipitation process and after the drying step were introduced in stainless cylinder without using lubricants at the wall to avoid contamination.[28] A two steps pressing procedure was adopted. The first step had a stop point at 100 MPa for 2 min, the second one had a maximum value of 195 MPa for further 2 min. Final density of the sample was evaluated trough weight – geometrical volume measurements. The final density of all the sample turned out to be fairly constant and equal to 1.9 ± 0.01 g/cm^3 for both the carbonates. This value corresponds to a relative density of 0.7 compared with the theoretical density of calcite.[29]

2.3. Thermogravimetry (TG)

Dynamic TG measurements were performed in a static air atmosphere using a Netzsch STA 409 equipped with platinum TG-DSC thermal analyser in the sensitivity range of ±0.1 mg and with a Netzsch 410 furnace temperature controller system. It is well known[30] that in dynamic thermal decomposition the actual temperature of the sample might be different from the one actual measured at the time *t*, due to thermal transport phenomena. These transport phenomena are different for pellets and for powders even if the chemical nature is the same. Since in this paper we are interested to the differences in the decomposition between doped and non doped samples, both pellet and powders were heated at 10 °C/min in air. Effects of the heat transport and of crucible height[31] will result by the difference in the decomposition behaviour between the same kind of pellets and powders.

Platinum crucible of 6 mm in diameter and 3 mm in height was used, while the pellet was directly placed on the platinum sample holder. The temperature range between 20 °C and 1200 °C was explored when the furnace was kept in static air atmosphere.

To minimize the transport heat phenomena[32] in decomposition of doped and non doped powders, a "quasi-isothermal" run was made keeping the heating rate at the minimum value that the instrument allows, i.e. 0.1 °C/min and reducing the weight of the loose powder sample to 20 mg to minimize the absorption–desorption phenomena of CO_2 in the powder bed.[33]