



ELSEVIER

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

On the negative activation energy for limestone calcination at high temperatures nearby equilibrium



Jose Manuel Valverde

Faculty of Physics, University of Seville, Avenida Reina Mercedes s/n, 41012 Sevilla, Spain

HIGHLIGHTS

- Limestone calcination at high and fixed ratios of CO₂ pressure to equilibrium pressure is analyzed.
- The reaction rate is influenced by CO₂ desorption and CaO structural transformation.
- At high temperature the exothermic CaO structural transformation yields negative activation energy.
- Experimental results are shown demonstrating this anomalous trend with temperature.

ARTICLE INFO

Article history:

Received 25 February 2015

Received in revised form

5 April 2015

Accepted 17 April 2015

Available online 27 April 2015

Keywords:

Calcination

Limestone

CO₂ capture

Calcium looping

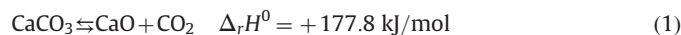
ABSTRACT

The study of limestone calcination under high CO₂ pressure and high temperature has gained an extraordinary practical importance due to the recently emerged Ca-looping technology for post-combustion CO₂ capture, which uses natural limestone (CaCO₃) as precursor of the CO₂ solid sorbent (CaO). A critical issue of this promising process is the necessity of producing CaO by calcination of limestone under high CO₂ partial pressure. Experimental measurements on the kinetics of limestone calcination usually show that the rate of the endothermic calcination reaction is increased with temperature according to an Arrhenius law with an activation energy similar to the reaction enthalpy change. In situ microscopic observations have demonstrated that the reaction involves a crystallographic structural transformation of CaO. Calcination is started by chemical decomposition leading to the development of metastable CaO* nanocrystals after which CO₂ is desorbed while stable CaO cubic crystals grow. In calcination environments with low CO₂ partial pressure P (as compared to the equilibrium pressure: $P/P_{eq} \ll 1$), desorption of CO₂ and the exothermic structural transformation of CaO* to its stable CaO form occur extremely fast and do not play a role on the reaction kinetics, which is just determined by chemical decomposition. However, at high values of P/P_{eq} the reaction rate may be significantly influenced by the structural transformation above a critical temperature. As a main consequence, the reaction mechanism proposed in the present paper shows that, above a critical temperature, limestone calcination is characterized by a negative activation energy in agreement with the experimental results shown.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Calcination of limestone (CaCO₃)



to produce lime (CaO) is at the root of a vast number of industrial applications as well as natural processes and has been the focus of a large number of studies over many years (Hyatt et al., 1958; Boynton, 1980; Zsako and Arz, 1974; Beruto et al., 1984, 2004;

Fuller and Yoos, 1987; Criado et al., 1992, 1995; Khinast et al., 1996; Dollimore et al., 1996; Koga and Criado, 1998; Garcia-Labiano et al., 2002; L'vov et al., 2002; Michele et al., 2011; Rrodriguez-Navarro et al., 2009). In 1966, Boynton stated in his book: *this is probably the most basic and the simplest of all chemical reactions. But, while it is theoretically very prosaic, there are many complexities attendant to this reaction. In spite of incontrovertible scientific data delineating calcination, this process still remains, to some extent, a technique or an art that only an experienced lime burner comprehends* (Boynton, 1980). To these days, and despite the great number of experimental and theoretical works devoted to understanding limestone calcination, the fundamental physics and chemistry that govern

E-mail address: jmillan@us.es

this gas–solid decomposition reaction remain elusive (L'vov et al., 2002). Most of the works carried out have been focused on analyzing the reaction kinetics as determined by the calcination temperature T , calcination atmosphere and CaCO_3 conversion degree α (defined as ratio of mass of CaCO_3 decarbonated to the initial mass). Experimental results show that the rate of conversion can be in general well fitted to an Arrhenius type law:

$$\frac{d\alpha}{dt} = r(T, P)f(\alpha) \quad (2)$$

$$r(T, P) = A \exp(-E/RT) \left(1 - \frac{P}{P_{eq}}\right)^\gamma \quad (3)$$

where r is the surface reaction rate, $f(\alpha)$ is a mechanistic-rate function, A is a pre-exponential term, γ is an empirical exponent of order unity, $R=8.3145 \text{ J/mol}\cdot\text{K}$ is the ideal gas constant, P is the CO_2 partial pressure in the calcination environment and $E > 0$ is the so-called activation energy. The CO_2 partial pressure at equilibrium (P_{eq}) is given by

$$P_{eq}(\text{atm}) \approx 4.083 \times 10^7 \exp(-20474/T) \quad (4)$$

as inferred from thermochemical data (Barin, 1989; Garcia-Labiano et al., 2002; Stanmore and Gilot, 2005).

In regards to the dependence of the conversion rate on the degree of calcination conversion α , it is usually described from the function $f(\alpha)$, which would take into account the influence on the reaction progress of several rate-limiting mechanisms such as nucleation in crystal defects and geometrical constraints related to particles' shape and pore size distribution (Khawam and Flanagan, 2006; Koga and Criado, 1998). Nevertheless, the possibility of expressing the conversion rate dependence on the degree of conversion by means of a separate function $f(\alpha)$ has been questioned as some studies show a variation of the apparent activation energy with α (Michele et al., 2011). Moreover, the values of the kinetic parameters (A and E in Eq. (3)) reported in the literature are controversial even when calcination experiments are made using single calcite crystals to mitigate the effect of solid's imperfections. In general, values of the activation energy are found to be similar to the reaction enthalpy change albeit they are spread in a wide range (mainly between 100 and 230 kJ/mol, Galwey and Brown, 2002). The broad dispersion of reported data on the calcination kinetic parameters is usually explained from the uncontrolled influence of the working conditions, which prevents drawing a clear physical meaning of the activation energies obtained (Zsako and Arz, 1974). For example, it is estimated that self-cooling due to the endothermicity of chemical decomposition might cause a decrease of temperature in the sample by 4–8 °C leading to an overestimation of the activation energy for calcination under vacuum (Rouquerol, 1973; L'vov et al., 2002). Furthermore, self-cooling would lead to a significant dependence of the kinetic parameters upon sample weight and heating rate (Gallagher and Johnson, 1973; Beruto and Searcy, 1974; Gallagher and Johnson, 1976). Sample cleaning, which tends to remove nucleation sites, and de-gassing, which probably removes water vapor, have been shown to have also an important effect on the kinetic parameters (Wang and Thomson, 1995). Results from calcination experiments in air and pure CO_2 atmospheres (Zsako and Arz, 1974; Gallagher and Johnson, 1976) indicate that the kinetic parameters follow the general compensation effect by virtue of which any variation in the experimental conditions that causes E to change will induce a compensating change in A according to the exponential law $A = B \exp(aE)$, where B and a are constants. Even though the mechanism that drives the compensation effect (observed for a broad class of heterogeneous surface reactions) is unclear it has been related to the stability of intermediate species (Bligaard et al., 2003), which suggests that the calcination reaction might be influenced by the effect of calcination conditions on the rate of elementary steps.

Besides chemical decomposition, the transformation from a metastable CaO^* form to the stable CaO structure has been hypothesized as

an additional step for calcination to be fully achieved (Hyatt et al., 1958; Searcy and Beruto, 1976; Beruto et al., 2004; Valverde et al., 2015). In situ transmission electron microscopy coupled with selected area electron diffraction (TEM-SAED) and 2D-XRD analysis have evidenced that calcination does involve a CaO crystallographic transformation (Rodriguez-Navarro et al., 2009). These observations show that a metastable CaO^* structure grows on each rhombohedral cleavage face of the calcite pseudomorph. The mechanically unstable CaO^* structure becomes progressively strained until a critical stress is reached, which is relieved by a collapse into the stable CaO cubic form as CO_2 is desorbed (Beruto et al., 1976, 2004; Searcy and Beruto, 1976). Structural transformation is seen to occur extremely fast for calcination under vacuum and does not play any rate-limiting role (Rodriguez-Navarro et al., 2009). However, Hyatt et al. (1958) already hypothesized in 1958 that the structural transformation $\text{CaO}^* \leftrightarrow \text{CaO}$ should be taken into account in the reaction mechanism for calcination under CO_2 , which lead these authors to formulate the rate equation:

$$r = \frac{r_0}{1 + \lambda P} \left(1 - \frac{P}{P_{eq}}\right) \quad (5)$$

where r_0 and λ were temperature dependent empirical parameters. Eq. (5) fitted well to experimental data on the calcination rate of single calcite crystals in CO_2 enriched environments although mostly at temperatures well over the equilibrium temperature (Hyatt et al., 1958). The data reported by Hyatt et al. (5) will be reviewed in detail in Section 3 within the context of the proposed kinetic model.

1.1. The Ca-looping technology

In order to retrieve reliable values of the activation energy by minimizing the elusive influence of CO_2 partial pressure in the kinetic equation (Eq. (3)), and also to avoid the technical difficulty of accurately controlling it, calcination kinetic studies have been traditionally carried out in the limit $P/P_{eq} \ll 1$ (Criado et al., 1995). Yet, the recently emerged Ca-looping (CaL) technology based on the multi-cyclic calcination/carbonation of limestone for CO_2 capture from coal fired power plants has conferred an extraordinary relevance to the analysis of limestone calcination at high CO_2 partial pressure. The first conceptual study of the CaL process appeared in a 1999 publication by Shimizu et al. (1999). Accordingly, CO_2 would be chemisorbed on the surface of CaO particles fluidized in a gas–solid reactor (carbonator) by the postcombustion gas stream at atmospheric pressure and temperatures around 650 °C. The carbonated solids are circulated into a second gas–solid reactor (calciner) operated also at atmospheric pressure. In this reactor, CaO is regenerated by calcination of the partially carbonated solids under CO_2 at partial pressure close to atmospheric pressure for it to be efficiently captured, compressed and stored. The progressive loss of CaO carbonation activity with the number of calcination/carbonation cycles is counterbalanced by the continuous purge of poorly active sorbent, which is replaced by fresh limestone directly fed into the calciner. Pilot-scale tests ($\sim 1\text{--}2 \text{ MW}_{th}$) currently in operation (Arias et al., 2013; Ströhle et al., 2014) are demonstrating a high and sustainable CO_2 capture efficiency. Hopefully, the low cost, wide availability and harmlessness towards the environment of natural limestone, as well as the synergy of the technology with the cement industry, would render the CaL technology competitive as compared with more mature CO_2 capture technologies.

The reaction equilibrium (Eq. (4)) imposes a minimum temperature $T \approx 895 \text{ °C}$ for calcination of limestone under CO_2 at atmospheric pressure ($P=1 \text{ atm}$). On the other hand, the calciner reactor in pilot-scale tests is operated in the fast fluidization regime, which provides a high efficiency of heat and mass transfer in the typically short residence times (of just a few minutes). Calcination of the partially carbonated solids (with a typical molar carbonate content of 15% after many cycles) is conceivably attained at about $T \approx 900 \text{ °C}$ in relatively short times as inferred from thermogravimetric analysis (TGA) tests (Martinez et al.,

Download English Version:

<https://daneshyari.com/en/article/154674>

Download Persian Version:

<https://daneshyari.com/article/154674>

[Daneshyari.com](https://daneshyari.com)