



Evaluation of the effect of inert support on the carbonation reaction of synthetic CaO-based CO₂ sorbents

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HIGHLIGHTS

- CaO-based sorbents have been produced on to MgO and Ca₁₂Al₁₄O₃₃ inert supports.
- The CaO content of the material determined its chemical stability.
- Materials kinetic parameters for the carbonation reaction have been determined.
- Sorbent particles have been produced from materials in powder form.
- A complete particle reaction model has been developed.

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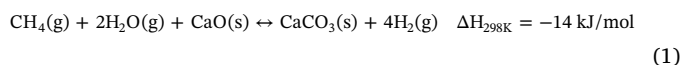
ABSTRACT

Calcium oxide has been proved to be a suitable sorbent for high temperature CO₂ capture processes based on the cyclic carbonation-calcination reaction. In this work several synthetic sorbents have been prepared with CaO contents between 40 and 95% wt. on to two different inert supports MgO and Ca₁₂Al₁₄O₃₃. The effect of CaO content and inert nature on materials CO₂ carrying capacity and reactivity towards carbonation reaction has been assessed. The materials have been texturally characterised. A complete kinetic study has been performed and the Random Pore Model has been applied to determine the intrinsic rate parameters for the carbonation reaction. Suitable particles for operation in fixed bed reactor have been produced from some selected powdered materials, and a complete particle reaction model that incorporate the intrinsic kinetic data has been developed and validated.

1. Introduction

The separation of a pure CO₂ stream, combined with a well managed geological storage site is still considered to be a major mitigation option for climate change [1,2]. The carbonation reaction serves as the basis for several high temperature CO₂ capture systems when it is coupled with a calcination step to produce a pure CO₂ stream. The use of the carbonation-calcination loop of CaO/CaCO₃ is now accepted as a viable technique for the capture of CO₂ in post-combustion [3,4] or in pre-combustion [4,5] routes. In this context, the sorption enhanced steam methane reforming (SER) arises as a novel intensified process that combines the H₂ production with inherent CO₂ capture [5] in a single system. In the SER process, the reforming, water gas shift (WGS) reactions, and the removal of CO₂ take place simultaneously in one single stage in presence of a catalyst and a CO₂ sorbent (Eq. (1)). The use of a calcium-based material allows the CO₂ to be removed from the gas phase as soon as it is produced, forming CaCO₃ [5–12]. According

to thermodynamic predictions and experimental results, it is possible to obtain more than 95% vol. H₂ (on a dry basis) using CaO as sorbent [5,6] in a wide range of temperatures from 923 K to 1023 K. The CO₂ sorption reaction (i. e. the carbonation of CaO) is exothermic and supplies “in situ” the heat required to carry out the endothermic reforming process.



As a product gas with almost pure H₂ is obtained directly from the reformer, the downstream purification process is simplified. The presence of sorbent minimizes the formation of coke allowing for a reduction of the steam excess in the reformer and the operation at lower temperature favours the use of cheaper materials in the reactor units [5,6,13–15]. Focused on combining hydrogen production and CO₂ separation, the use of CaO-sorbents in natural gas reforming or water gas shift processes was first proposed in the mid-90s [8,16]. The inherent

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Nomenclature

a, b	stoichiometric coefficients for carbonation reaction
C	concentration of CO_2 (kmol/m^3); b bulk concentration; e equilibrium
D	effective product layer diffusivity (m^2/s)
D_o	pre-exponential factor in Eq. (9) (m^2/s)
D_p	$bM_{\text{CaO}}DC/ap$ apparent product layer diffusion (m^2/s)
$E_{a_{K, D}}$	activation energy for the kinetic regime, K ; and for the combined diffusion and kinetic regime, D , (kJ/kmol)
h_{K-D}	product layer thickness (m); K - D transition between reaction regimes
k_{s_o}	pre-exponential factor in Eq. (8) (m^4/kmols)
k_s	rate constant for surface reaction (m^4/kmols)
$L_{o, N}$	initial total length of pore system (m/m^3); N pore length for cycle N
M_{CaO}	molecular weight of CaO (kg/kmol)
R_i	pore radius (m)
$S_{o, N}$	initial reaction surface (m^2/m^3); N reaction surface for cycle N

t	time (s)
$V_{\text{CaO}, \text{CaCO}_3}^M$	molar volumes (m^3/kmol)
X_{carb}	CaO molar conversion ($\text{mol CaO reacted/mol material}$); N , relative to cycle N ; K - D transition between reaction regimes; r residual CaO conversion
X_{max}	maximum CaO molar conversion according to their composition
Z	ratio volume fraction after and before reaction

Greek letter

α	volume fraction of CaCO_3 invading a pore volume
β	$2k_{s,ap}(1-\varepsilon)/M_{\text{CaO}}bDS_o$
δ	decrease in pore radius upon carbonation (m)
ε	porosity
$\nu_o(r)$	pore radii distribution
ρ	density $\text{kg CaO}/\text{m}^3$ material
τ	$k_s(C_b - C_e)S_o t / (1 - \varepsilon)$
ψ	$4\pi L_o(1 - \varepsilon)/S_o^2$

advantages associated to these concepts (namely higher hydrogen yields, process simplification or absence of water gas shift catalysts among others) have contributed to their great advancement in terms of materials development and conceptual process design, as reviewed by Harrison [5].

With the objective of overcoming the decay in CO_2 capture capacity that present CaO based sorbents derived from natural limestones and dolomites, there has been an intense research in the recent years on the development of synthetic CaO -based sorbents, aiming for highly resistant to sintering materials with a sufficient CO_2 carrying capacity and reactivity to sustain CaL processes see for example the reviews by Liu et al. [17] and Erans et al. [18]. Different strategies have been adopted according to the literature to produce synthetic CaO -based sorbents as for example the use of sintering-resistant calcium precursors as nano-sized CaO/CaCO_3 [19], organometallic precursors [20,21] or precipitated CaCO_3 , whose reported results largely varied with the test conditions. Their performance has been related with their differences in pore structure/surface area, but not systematic analysis has been performed [17]. Sorbent doping has been also proposed as a method to improve the stability of CaO based sorbents without successful results [22,23], but it is the incorporation of CaO to an inert matrix the most extended and deeply tested strategy [17,24–31]. This strategy was derived from the expertise on dispersing active components on to porous inert matrix to synthesise diverse sorbents and catalysts, and it was supported by the observation of the better performance in terms of cyclic stability that presented calcined dolomites when compared with calcined limestones. The MgO in calcined dolomites would help to hinder the CaO/CaCO_3 sintering along cycling [8,16,32]. Since Ahiara et al. [33] incorporated CaO to an inert CaTiO_3 matrix to react with CO_2 , an important range of supports as for example MgO , MgAl_2O_4 , $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, SiO_2 , and ZrO_2 (doping with Zr [34]) among others have been evaluated. Some of them were able to reduce the sintering of CaO grain with temperature, and improved the cyclic reactivity of the sorbent. Also a various techniques have been developed for their production, as for example sol-gel combustion as a popular approach to produce nanomaterials, and a common route when mixed the CaO precursors with aluminium precursors to produce $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ materials, as CaO will react with Al_2O_3 after calcination [27–29,35]. Mixing on its different approaches has been also a common production route: dry mixing when all the precursors are mixed in dry form; suspension mixing of insoluble precursors in a solvent to be dried to form a powdered product [30]; hydrothermal route when mixed the solid precursors in water and then brought to an autoclave at mild

temperature and moderate pressure to form an hydro garnet that it is later calcined [36]; sol mixing when at least one of the precursors is soluble [27–29,35,37–39], and wet mixing when both precursors are soluble in the solvent and they are subsequently processed to form a dry product [40,41]. A common procedure to evaluate the performance of a given CO_2 sorbent is to evaluate the evolution of its CO_2 carrying capacity (mole basis expressed as moles CO_2 captured per mol of CaO in the material, or weight basis expressed as weight of CO_2 captured per weight of calcined sorbent) along multiple calcination/carbonation cycles [33, 42–46]. However, it is necessary to highlight that the evolution of sorbent CO_2 carrying capacity and the long term performance of the materials can be affected by the experimental conditions during the testing of the materials, not only due to the possible sintering phenomena that will take place in more or less extension depending on the calcination conditions (in terms of CO_2 partial pressure, presence of steam and temperature during calcination stage) [47–50] but also due to the partial reactivation of the sorbent that takes place when the carbonation reaction is extended beyond the fast reaction stage [45, 51, 52]. In this way, it is not possible to compare the performance of materials tested under diverse reaction conditions, but, there are some valid trends that can be derived from the data in the literature. As for example, according to the experimental results compiled by Liu et al. 2012 [17], the maximum CO_2 capture capacity of a sorbent is directly proportional to its CaO loading. According to the three dimensional percolation theory, these authors proposed that the maximum CaO content that can be allocated in a continuum framework of inert support was 82.77% wt. [40]. The stability and high efficiency CaO utilisation that presented materials with CaO contents between 52% and 75% weight was attributed to the fine dispersion of CaO in the sorbent that presented nanocrystalline domains of MgO adhered to their surfaces. In this way, co-precipitation could be a suitable synthesis method to produce highly dispersed CaO on to inert support. This was the case of materials obtained by Filitz et al. [53], Kierzkowska et al. [54] and Zhenissova et al. [31] that were prepared through co-precipitation of Ca containing salts for the active phase, and Mg or Al containing salts for the inert support to obtain the mixture of Ca^{2+} and Mg^{2+} or Al^{3+} in the crystalline lattice. The authors reported a good stability of the materials along several calcination/carbonation cycles.

As shown in the introduction section, there has been intense work on determining the effect that inert support has on the reactivity stabilization of synthetic sorbents [5,17,25,26], and although there is a growing interest on modelling the reaction of synthetic CO_2 sorbents and bi-functional CaO -based materials [55,56], there is scarce work on

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