



Effect of synergistic interaction between Ce and Mn on the CO₂ capture of calcium-based sorbent: Textural properties, electron donation, and oxygen vacancy

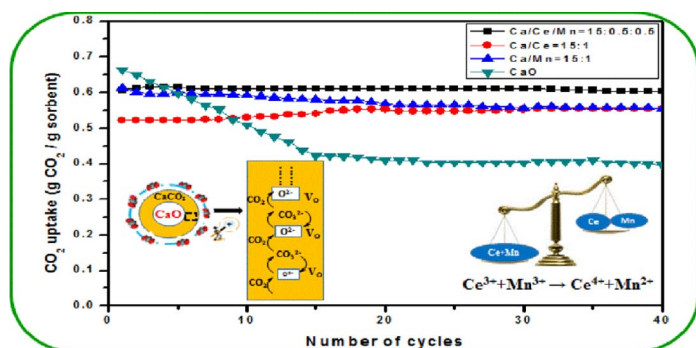


Hongxia Guo^a, Xiaochen Kou^a, Yujun Zhao^a, Shengping Wang^{a,*}, Qi Sun^{a,b}, Xinbin Ma^a

^a Key Laboratory for Green Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

^b National Institute of Clean-and-Low-Carbon Energy, Beijing 102209, China

GRAPHICAL ABSTRACT



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ABSTRACT

The diffusion of CO₂ and mobility of O²⁻ are the keys to capture of CO₂ for CaO-based sorbents. We present a (Ce-Mn)-doped calcium-based sorbent, and investigate the effect of Ce and Mn incorporation on CO₂ capture. Interaction between Ce and Mn promotes electron donation from Ca atom to surface oxygen atoms. The stronger the electrons transfer, the stronger interaction between CaO and CO₂ is, thus improving CO₂ adsorption. Electron transfer between Ce and Mn facilitates oxygen vacancy generation, which improves diffusion and mobility of O²⁻. In addition, CeO₂ and Ca₂MnO₄ prevent CaO crystallite growth and agglomeration. The (Ce-Mn)-doped sorbents exhibited excellent long-term durability with carbonation capacity of about 0.61 g-CO₂/g-ads after 40 cycles.

1. Introduction

Increasing CO₂ concentration in the atmosphere is one of the most important factors of global warming. Therefore, the issue of greenhouse gas effect has attracted extensive attention. Carbon capture/storage (CCS) is regarded as a promising solution to constrain CO₂ emissions

and mitigate the climate change [1–3]. Calcium looping is a viable technique for CO₂ adsorption in terms of their low cost and regeneration [4–6]. However, the major challenge for the CaO-based sorbents is the fast decay of CO₂ capture performance with the number of cycles, and the carbonation/calcination loop is far from reversible in practice. Thus, the development of the calcium-based sorbents maintaining high

* Corresponding author.

E-mail address: spwang@tju.edu.cn (S. Wang).

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reactivity is extremely urgent for the CO₂ capture [7–12].

It is well known that adding inert materials into CaO to form doped sorbent is one of the most effective ways to improve the stability of calcium-based sorbents, such as Zr [13–17,20,23,24,26], Mg [19], Al [20–22], Ce [18,23], Mn [25], and so on. Our group [18] had synthesized a series of Ce-doped sorbents by a simple sol-gel method, and the sample (Ca/Ce = 15:1) showed a favorable absorption capacity and cycle durability, maintaining a CO₂ uptake capacity of 0.59 g-CO₂/g-ads after 18 cycles. However, CeO₂ is unstable at high temperature because of the progressive agglomeration of its particles, and the cost is relatively high [27]. Manganese oxides possess high Tammann temperature, environmental compatibility, low cost, and non-toxicity, which have also been exploited as a suitable material for CO₂ adsorption. Sun et al. [25] investigated the effect of manganese salts including Mn(NO₃)₂ and MnCO₃ on the CO₂ capture performance of calcium-based sorbent during cyclic calcination/carbonation reactions. The carbonation conversion with Mn(NO₃)₂ as manganese salts diminished from 0.74 to 0.42 after 10 cycles, and there was also a remarkable decrease of 0.46 in that of MnCO₃-doped CaCO₃. Due to its relatively low performance, the challenge remains to further enhance the sorption capacity and stability.

The oxygen vacancy is favorable to the diffusion of CO₂ and mobility of O²⁻ according to the proposed adsorption mechanism of CO₂. The process is shown as follows:



The diffusion of CO₂ and mobility of O²⁻ are key to the capture of CO₂ in the early stage of diffusion-controlled carbonation reaction [28–30].

It is noted that doping cerium can bring a large number of oxygen vacancies and an improved oxygen transport capacity ($\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$) [31,32]. Taking into account the possibility of multiple valences for Mn as well as the redox couple associated with Ce, the synergistic effect would be anticipated from the combination of Mn oxides with CeO₂, which may promote the generation of oxygen vacancy [33]. Thus, a motivative assumption is that (Ce-Mn)-doped oxide as an additive of the calcium-based sorbent would be promising in the field of CO₂ capture. On the other hand, the introduction of Mn decreases the cost of the process, because Mn is abundantly distributed in the natural environment. Therefore, it is very urgent to develop a (Ce-Mn)-doped CaO-based nanosorbent with excellent capacity and good stability employing relatively low-cost, environmentally benign additives.

In this work, we consider use of a novel (Ce-Mn)-doped calcium-based sorbent for CO₂ capture, and examine the roles of textural properties, electron donation, and generation of oxygen vacancy. The X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂ physisorption measurement, X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), and UV-visible diffuse reflectance spectra (UV-vis DRS) were employed to elucidate the relationship of synergistic interaction and CO₂ adsorption performance.

2. Experimental section

2.1. Sorbent preparation

All the sorbents were synthesized using an improved sol-gel combustion method, and a typical synthesis process of (Ce-Mn)-doped sorbent is as follows. The precursors used in the sorbent were Ca(NO₃)₂·4H₂O (Tianjin Yuanli Chemical Co. Ltd., AR grade), Ce(NO₃)₃·6H₂O (Tianjin Kernel Chemical Reagent Co. Ltd., AR grade), and Mn(NO₃)₂·4H₂O (Macklin, AR grade, 50 wt%) solution. Initially,

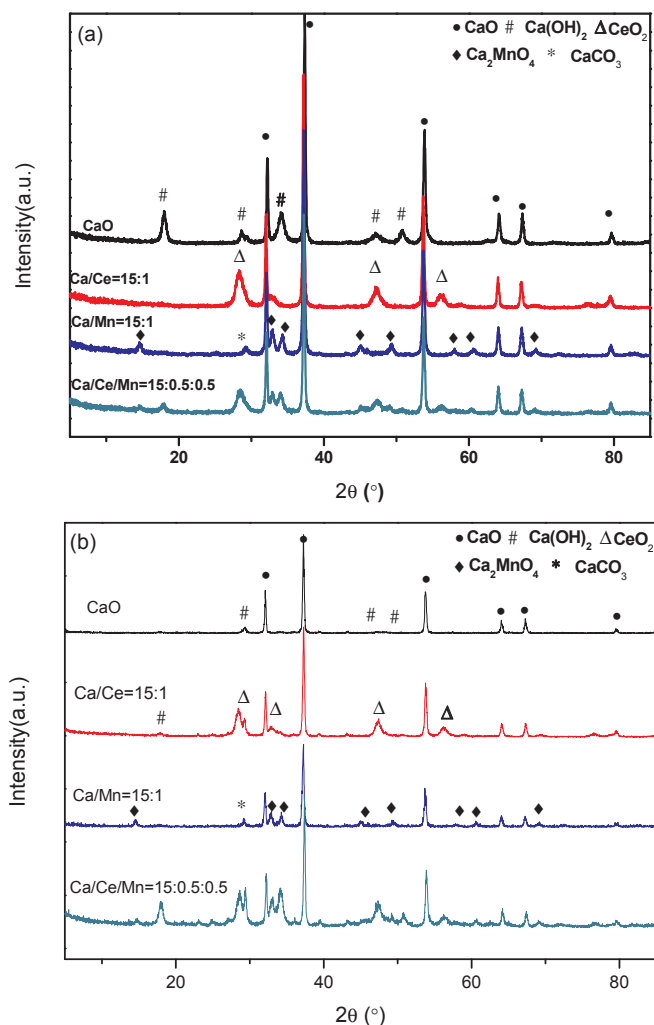


Fig. 1. XRD patterns of various (a) fresh and (b) used sorbents after 40 cycles.

predetermined amounts of metal precursors (Ca/Ce/Mn = 15:0.5:0.5) and citric acid monohydrate (Tianjin Yuanli Chemical Co. Ltd., AR grade) were dissolved in deionized water. Then metal precursors and polyethylene glycol 6000 (Tianjin Kernel Chemical Reagent Co. Ltd., AR grade, 1 wt% in the mixture) were mixed together. The solution was heated to 70 °C under stirring for 10 min, after that the citric acid was added with citric acid/total metal cations = 2. The mixture was continuously stirred at 70 °C for 3 h. In order to improve the ionization degree of the citric acid, the pH value was adjusted to ~10 by dropwise addition of aqua ammonia (Tianjin Kernel Chemical Reagent Co. Ltd., AR grade). A viscous gel formed after the superfluous water evaporation. The gel was dried at 100 °C for 24 h obtaining a low-density foam. The foam was crushed and calcined at 700 °C (2 °C min⁻¹) for 4 h. Ce-doped and Mn-doped sorbents were prepared using the same procedure. Pure CaO was also obtained and used as a reference.

2.2. Sorbent characterization

XRD patterns were acquired on a Rigaku D/max-2500 diffractometer, operating at 40 kV and 30 mA, with filtered Cu K α radiation. The data was collected in the 5–85° 2 θ range, at a scanning speed of 8° min⁻¹. Crystalline phases were identified by matching with the reference data from International Centre for Diffraction Data Powder Diffraction Files (ICDD-PDF).

The surface morphology of samples was characterized using SEM (Hitachi S4800 field-emission microscope at 3.0 kV).

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