

Synthesis, Characterization and Photocatalytic Activity of β -Ca_{2-x}Zn_xSiO₄ (x = 0, 0.01 and 0.025)

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The compound of β -Ca₂SiO₄ has been considered as one of the important portland cement components. The existence of metals in the cement raw materials causes β -Ca_{2-x}M_xSiO₄ formation possibility. The β -Ca_{2-x}Zn_xSiO₄ (x = 0, 0.01 and 0.025) has been prepared and characterized, and applied for degradation of Congo red. The samples were synthesized by heating stoichiometric amounts of Zn(NO₃)₂·6H₂O, CaCO₃ and SiO₂ at 950 °C for 4 h followed by air quenching. The samples were characterized by using XRD, SEM, EDA and UV-visible spectroscopic methods. The XRD patterns indicate that the samples are isomorphous with β -Ca₂SiO₄. The SEM micrographs depicted the aggregated irregular shape particles having size about 0.2 μ m. The EDA measurements revealed that the bulk compositions of materials are as expected. The doping of zinc increases the E_g of the sample and decreases the photocatalytic power for degradation of Congo red under sunlight.

Keywords: Portland Cement, Dicalcium silicate, Zn doping, Congo red.

INTRODUCTION

Dicalcium silicate (Ca₂SiO₄) is a main component of Portland cement and is being investigated for use as a host [1-3]. It has been proposed that it may be a suitable host for metal from industrial waste [4-6]. The compound of Ca₂SiO₄ has five phases (α , α' _H, α' _L, β and γ phase) [7,8]. Two of these phases occur naturally as larnite minerals (β -Ca₂SiO₄ monoclinic space groups P2₁/n) and calcio-olivine (γ -Ca₂SiO₄ orthorhombic space group Pbnm). Synthetic Ca₂SiO₄ is usually prepared by solid state reactions of CaO and CaCO₃ and SiO₂ at temperatures over 1450 °C. Cooling from 1450 °C to room temperature usually produces γ -Ca₂SiO₄ [8], while annealing γ -Ca₂SiO₄ at lower temperature can cause a transition to β -Ca₂SiO₄, although the conversion is often incomplete.

Many attempts were made to prepare pure phase β -Ca₂SiO₄ but the results are inconsistent [8-10]. Efforts include dehydration of calcium silicate hydrates at low temperatures (~ 800 °C) [11], or use of starting materials which is more reactive such as Ca(NO₃)₂ and colloidal silica at 750 °C [12]. Although it is generally accepted that β -Ca₂SiO₄ does not form during heating, but appears as a metastable phase in the stability field γ -Ca₂SiO₄

during cooling [8,13]. It has been reported that reacting CaC₂O₄ with SiO₂ amorphous at 950 °C under atmospheric CO₂ produces a pure β -Ca₂SiO₄ powder [3]. A more promising way to prepare single phase samples with orthorhombic β structure is by adding dopant cations including Na, K, Fe, Cr and B. To date, the role of impurity culture in stabilizing β -Ca₂SiO₄ has not been fully determined [14].

Natural larnite was first reported by Tilley [15] and its structure consists of interconnected Ca polyhedra skeletons and isolated [SiO₄] tetrahedra [3]. Henning [16] summarized that structure of β -Ca₂SiO₄ may be stabilized by the addition of 0.5 % by weight of Cr₂O₃ or 0.4 % by weight of B₂O₃. The compound of β -Ca₂SiO₄ is believed to be a desirable component in many types of cement and consequently its production has received great attention. One method used to increase the amount of β -Ca₂SiO₄ present in cement is to add a number of secondary cations. Heavy metals can be stabilized into cement matrix by solidification/stabilization process [17]. It is possible to prepare β -Ca₂SiO₄ doped with heavy metals. Herein, we describe the synthesis of β -Ca₂SiO₄ doped with zinc. This work illustrates the synthesis and the characterization of β -Ca_{2-x}Zn_xSiO₄ (x = 0, 0.01 and 0.025) [12] and their application as photocatalysts.

EXPERIMENTAL

The samples were prepared by solid-state reaction methods. Zinc-doped β -dicalcium silicate (β -Ca_{2-x}Zn_xSiO₄, $x = 0, 0.01$, and 0.025) were prepared by the solid state reaction of stoichiometric amounts of SiO₂ (Merck 99.8 %), CaCO₃ (Merck 99.5 %) and Zn(NO₃)₂·6H₂O (Merck ≥ 99.0 %) at 950 °C for 4 h followed by air quenching to avoid the formation of β -Ca₂SiO₄.

The formation of β -Ca_{2-x}Zn_xSiO₄ was monitored by powder X-ray diffraction using a XRD Rigaku Multiflex. Energy Dispersive Analysis (EDA) were performed with an EDAX PV9900 system on a Jeol JCM-6000 Scanning microscope operating at 5 kV. UV-Vis absorptions were collected by using a Pharmaspec UV-1700 spectrophotometer.

RESULTS AND DISCUSSION

The powder X-ray diffraction patterns for β -Ca_{2-x}Zn_xSiO₄ ($x = 0, 0.01$ and 0.025), recorded using a conventional Cu radiation on a Bragg-Brentano diffractometer are shown in Fig. 1. The patterns indicate that all samples are isomorphous. It is demonstrated that prepared β -Ca_{2-x}Zn_xSiO₄ ($x = 0, 0.01$ and 0.025) are composed of β -Ca₂SiO₄, since powder X-ray diffraction patterns are matched with the PDF of β -Ca₂SiO₄ (PDF 01-077-409) [3,18-20]. In case of Zn doped samples (β -Ca_{2-x}Zn_xSiO₄ with $x = 0.01$ and 0.025), there is no evidence for any unreacted CaO, ZnO or SiO₂. Since β -phase is present in portland cement we have limited present studies to compositions with $x < 0.025$, *i.e.* where the samples contain only β -phase.

Scanning electron micrographs of selected β -Ca_{2-x}Zn_xSiO₄ ($x = 0, 0.01$ and 0.025) samples (Fig. 2) indicates that the materials consist of aggregated irregular shape particles having size about 0.2 μ m. The homogeneity of samples was checked

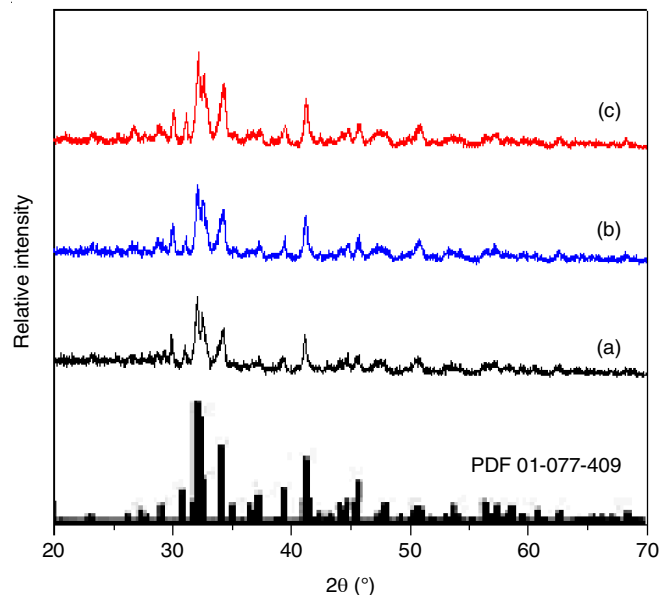


Fig. 1. XRD patterns of β -Ca_{2-x}Zn_xSiO₄ with $x =$ (a) 0, (b) 0.01 and (c) 0.025 and the powder diffraction file of β -Ca₂SiO₄ (PDF 01-077-409) [Ref. 19,20]

using EDA technique. These measurements revealed that the bulk compositions of materials are as expected.

The band gaps of β -Ca_{2-x}Zn_xSiO₄ for $x = 0, 0.01$ and 0.025 are 3.1264 eV, 3.3162 eV and 3.3561 eV, respectively (Fig. 3). This E_g 's are much lower as compared to that of Basavaraj *et al.* [21] finding (5.10 eV). In general, the band gap energy is larger with the more of Zn²⁺ ion concentration. The doping Zn onto β -Ca₂SiO₄ increases the bandgap. However, the band gap of zinc-doped β -Ca₂SiO₄ indicates the compound is photocatalytically working well under UV light.

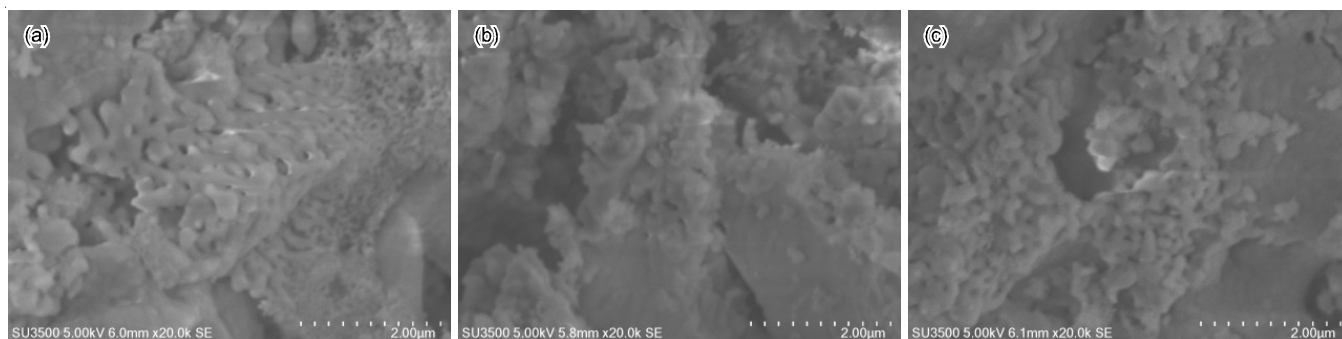


Fig. 2. SEM micrograph of β -Ca_{2-x}Zn_xSiO₄ with $x =$ (a) 0, (b) 0.01 and (c) 0.025

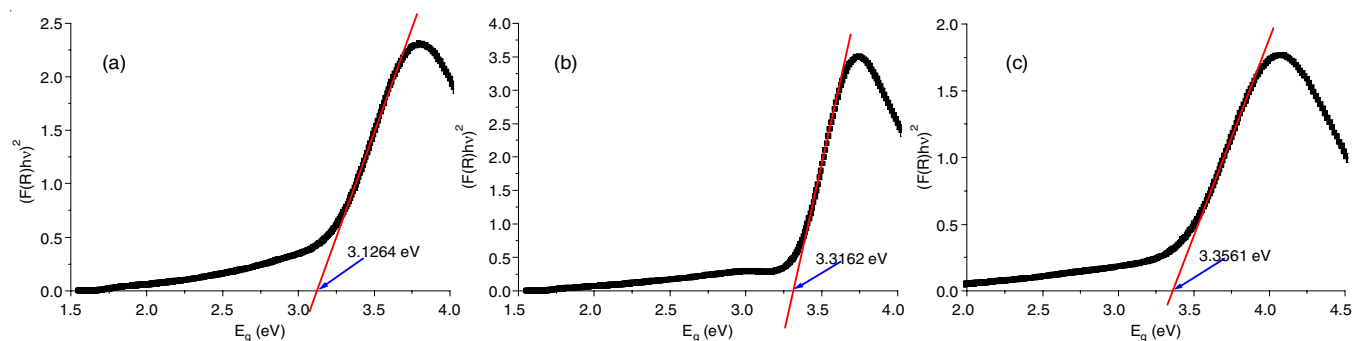


Fig. 3. Band gaps of β -Ca_{2-x}Zn_xSiO₄ for $x =$ (a) 0, (b) 0.01 and (c) 0.025

The photocatalytic experiments were undertaken in the dark and under sunlight. In dark experiment, the reduced concentration of Congo red solution is assumed to be caused by the catalyst absorption process. Fig. 4 shows that the catalyst $\beta\text{-Ca}_{2-x}\text{Zn}_x\text{SiO}_4$ for $x =$ (a) 0, (b) 0.01, and (c) 0.025 can absorb Congo red in the dark. Congo red absorption rate is relatively large at absorption time between 0 to 20 min. The absorption rate then decreases sharply between 20 min and 40 min, and the subsequent absorption progressed slowly.

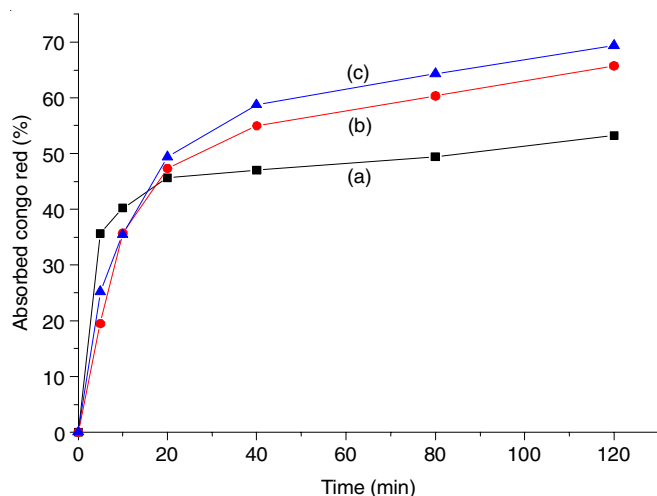


Fig. 4. Percentage of the absorbed Congo red in aqueous solution after photocatalytic reaction by using $\beta\text{-Ca}_{2-x}\text{Zn}_x\text{SiO}_4$ for $x =$ (a) 0, (b) 0.01 and (c) 0.025 as catalysts, in the dark

The experiments conducted in sunlight, Congo red concentration is decreased as a result of the absorption and photodegradation process with batches of photocatalysts $\beta\text{-Ca}_{2-x}\text{Zn}_x\text{SiO}_4$ for $x = 0, 0.01$ and 0.025 (Fig. 5). Compared to non-catalyzed solution, whose Congo red concentration did not change during the experiment, Congo red concentration is decreased dramatically between observations ranging from 0 to 40 min, and is decreased slightly on observations after 40 min caused mainly by absorption and photodegradation, respectively.

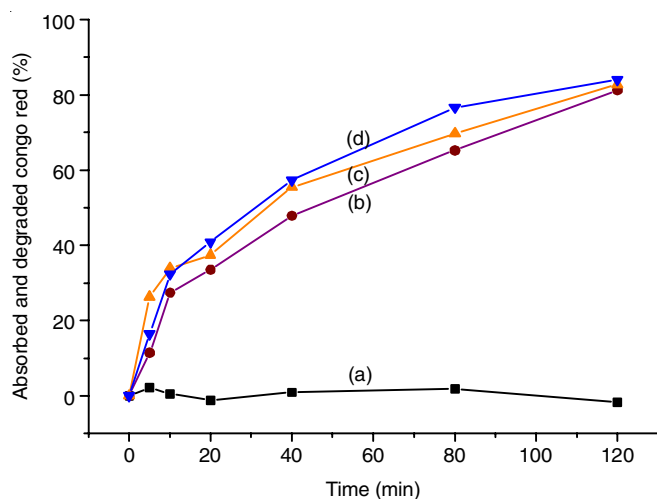


Fig. 5. Percentage of the absorbed and degraded Congo red in aqueous solution after photocatalytic reaction without catalysts (a) and by using $\beta\text{-Ca}_{2-x}\text{Zn}_x\text{SiO}_4$ for $x =$ (b) 0, (c) 0.01 and (d) 0.025 as catalysts, under sunlight

The process of absorption (major) and degradation (minor) occurring at experiments between 0 to 40 min can reduce Congo red concentration by up to 30 %. A similar amount also occurred in the absorption process (minor) and degradation (major) in experiments between 40 and 120 min (Fig. 6), by using $\beta\text{-Ca}_2\text{SiO}_4$ catalysts. However, doping Zn onto $\beta\text{-Ca}_2\text{SiO}_4$ lowers the absorption and the degradation of Congo red about 15 %.

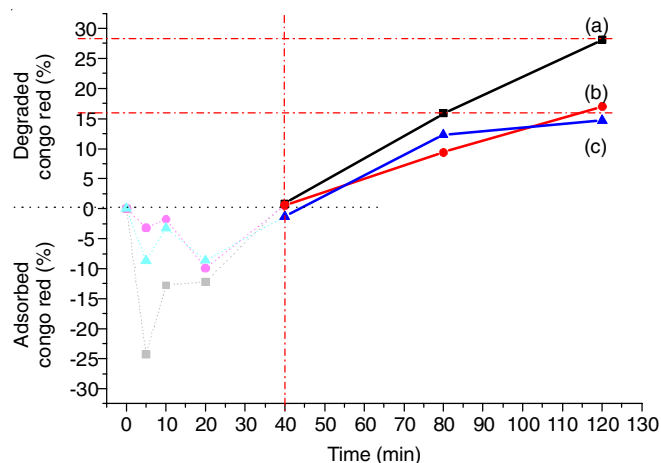


Fig. 6. Percentage of the degraded Congo red in aqueous solution after photocatalytic reaction by using $\beta\text{-Ca}_{2-x}\text{Zn}_x\text{SiO}_4$ for $x =$ (a) 0, (b) 0.01 and (c) 0.025 as catalysts, under sunlight

Conclusion

The $\beta\text{-Ca}_{2-x}\text{Zn}_x\text{SiO}_4$ has been prepared and characterized, and applied for the degradation of Congo red. The samples are isomorphous with $\beta\text{-Ca}_2\text{SiO}_4$. The particles are aggregated irregular in shape having size about $0.2\ \mu\text{m}$. The bulk compositions of samples are as expected. The doping of zinc increases the E_g of the sample, and decreases the photocatalytic degradation power of Congo red under sunlight.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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