Synthesis, Characterization and Photocatalytic Activity of β-Ca$_{2-x}$Zn$_x$SiO$_4$ (x = 0, 0.01 and 0.025)

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The compound of β-Ca$_2$SiO$_4$ has been considered as one of the important portand cement components. The existence of metals in the cement raw materials causes β-Ca$_{2-x}$M$_x$SiO$_4$ formation possibility. The β-Ca$_{2-x}$Zn$_x$SiO$_4$ (x = 0, 0.01 and 0.025) has been prepared and characterized, and aplied for degradation of Congo red. The samples were synthesized by heating stoichiometric amounts of Zn(NO$_3$)$_2$·6H$_2$O, CaCO$_3$ and SiO$_2$ at 950 ºC 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-Ca$_2$SiO$_4$. The SEM micrographs depicted the aggregated irregular shape particles having size about 0.2 μm. 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 (Ca$_2$SiO$_4$) 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 Ca$_2$SiO$_4$ has five phases (α, α′$_H$, α′$_L$, β and γ phase) [7,8]. Two of these phases occur naturally as larnite minerals (β-Ca$_2$SiO$_4$ monoclinic space groups P2$_1$/n) and calcio-olivine (γ-Ca$_2$SiO$_4$ orthorhombic space group Pbnm). Synthetic Ca$_2$SiO$_4$ is usually prepared by solid state reactions of CaO and CaCO$_3$ and SiO$_2$ at temperatures over 1450 ºC. Cooling from 1450 ºC to room temperature usually produces γ-Ca$_2$SiO$_4$ [8], while annealing γ-Ca$_2$SiO$_4$ at lower temperature can cause a transition to β-Ca$_2$SiO$_4$, although the conversion is often incomplete.

Many attempts were made to prepare pure phase β-Ca$_2$SiO$_4$ but the results are inconsistent [8-10]. Efforts include dehydration of calcium silicate hydrates at low temperatures (~ 800 ºC) [11], or use of starting materials which is more reactive such as Ca(NO$_3$)$_2$ and colloidal silica at 750 ºC [12]. Although it is generally accepted that β-Ca$_2$SiO$_4$ does not form during heating, but appears as a metastable phase in the stability field γ-Ca$_2$SiO$_4$

during cooling [8,13]. It has been reported that reacting CaC$_2$O$_4$ with SiO$_2$ amorphous at 950 ºC under atmospheric CO$_2$ produces a pure β-Ca$_2$SiO$_4$ 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-Ca$_2$SiO$_4$ 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 [SiO$_4$] tetrahedra [3]. Henning [16] summarized that structure of β-Ca$_2$SiO$_4$ may be stabilized by the addition of 0.5 % by weight of Cr$_2$O$_3$ or 0.4 % by weight of B$_2$O$_3$. The compound of β-Ca$_2$SiO$_4$ 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-Ca$_2$SiO$_4$ 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-Ca$_2$SiO$_4$ doped with heavy metals. Herein, we describe the synthesis of β-Ca$_2$SiO$_4$ doped with zinc. This work illustrates the synthesis and the characterization of β-Ca$_{2-x}$Zn$_x$SiO$_4$ (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$_x$SiO$_4$, x = 0, 0.01, and 0.025) were prepared by the solid state reaction of stoichiometric amounts of SiO$_2$ (Merck 99.8 %), CaCO$_3$ (Merck 99.5 %) and Zn(NO$_3$)$_2$·6H$_2$O (Merck $\geq$ 99.0 %) at 950 ºC for 4 h followed by air quenching to avoid the formation of β-Ca$_2$SiO$_4$.

The formation of β-Ca$_{2-x}$Zn$_x$SiO$_4$ 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 absorbtions were colected by using a Pharmaspec UV-1700 spectrophotometer.

RESULTS AND DISCUSSION

The powder X-ray diffraction patterns for β-Ca$_{2-x}$Zn$_x$SiO$_4$ (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$_x$SiO$_4$ (x = 0, 0.01 and 0.025) are composed of β-Ca$_2$SiO$_4$, since powder X-ray diffraction patterns are matched with the PDF of β-Ca$_2$SiO$_4$ (PDF 01-077-409) [3,18-20]. In case of Zn doped samples (β-Ca$_{2-x}$Zn$_x$SiO$_4$ with x = 0.01 and 0.025), there is no evidence for any unreacted CaO, ZnO or SiO$_2$. 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$_x$SiO$_4$ (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 µm. The homogeneity of samples was checked
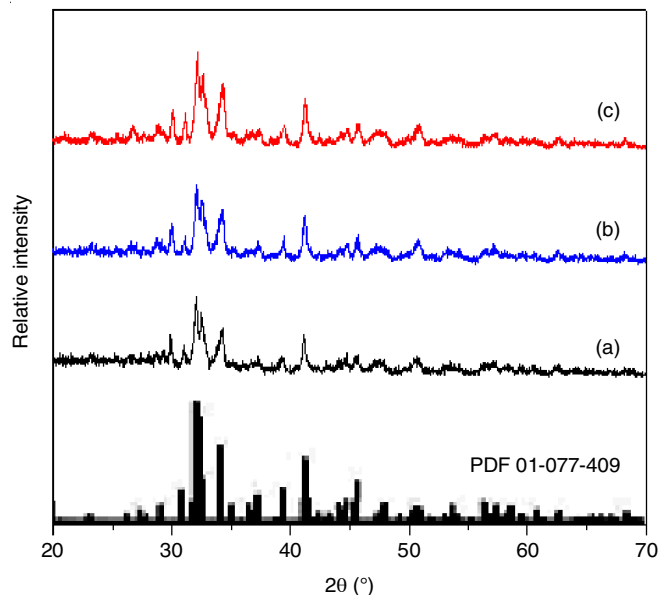

Fig. 1. XRD patterns of β-Ca$_{2-x}$Zn$_x$SiO$_4$ with x = (a) 0, (b) 0.01 and (c) 0.025 and the powder diffraction file of β-Ca$_2$SiO$_4$ (PDF 01-077-409) [Ref. 19,20]

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

The band gaps of β-Ca$_{2-x}$Zn$_x$SiO$_4$ 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 Zn^{2+} ion concentration. The doping Zn onto β-Ca$_2$SiO$_4$ increases the bandgap. However, the band gap of zinc-doped β-Ca$_2$SiO$_4$ indicates the compound is photocatalytically working well under UV light.
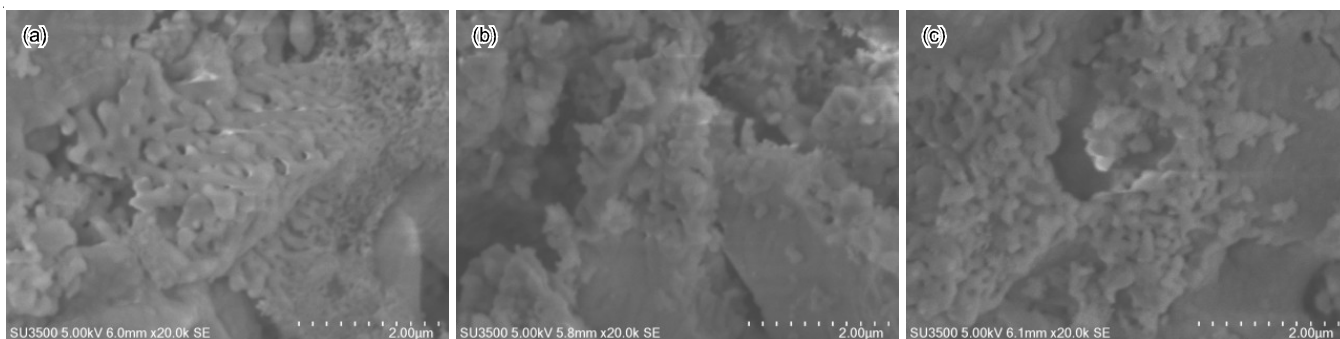

Fig. 2. SEM micrograph of β-Ca$_{2-x}$Zn$_x$SiO$_4$ with x = (a) 0, (b) 0.01 and (c) 0.025
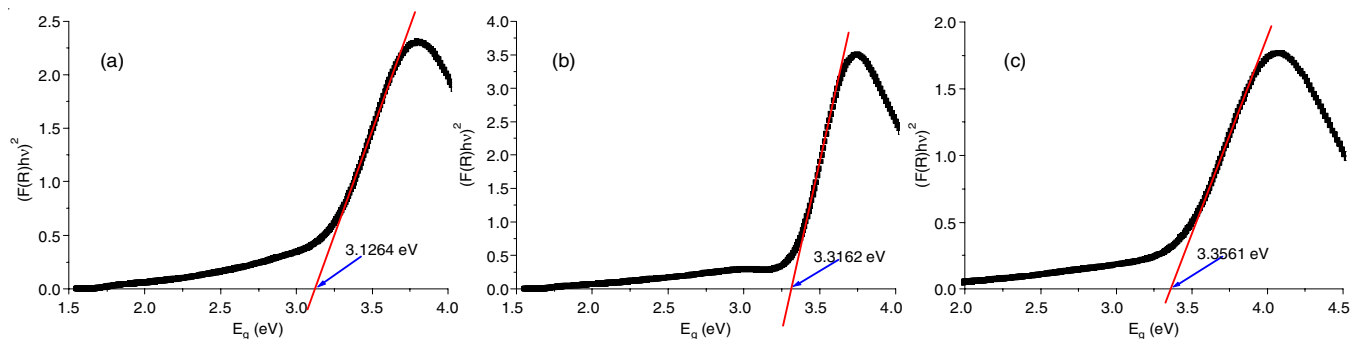

Fig. 3. Band gaps of β-Ca$_{2-x}$Zn$_x$SiO$_4$ for x = (a) 0, (b) 0.01 and (c) 0.025

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 β-Ca$_{2-x}$Zn$_x$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.
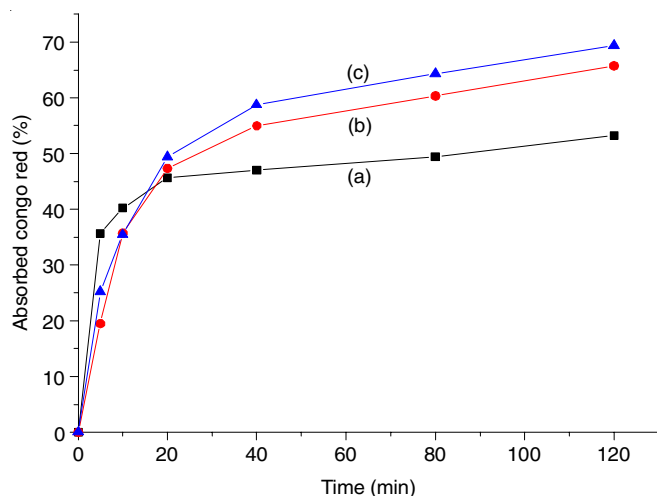

Fig. 4.   Percentage of the absorbed congo red in aqueous solution after photocalytic reaction by using β-Ca$_{2-x}$Zn$_x$SiO$_4$ for x = (a) 0, (b) 0.01 and (c) 0.025 as catalysts, in the dark

The experiments conducted in sunlight, Congo red concentration is decreased as a result of the absorption and photodegradation process with batches of photocatalysts β-Ca$_{2-x}$Zn$_x$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 absorpstion and photodegradation, respectively.
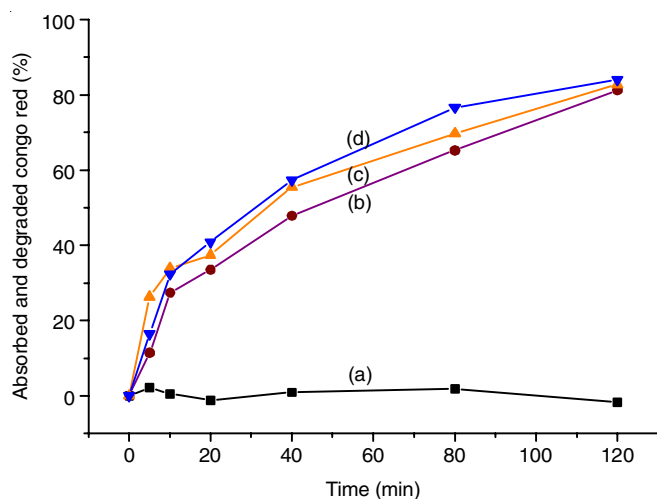

Fig. 5.   Percentage of the absorbed and degraded congo red in aqueous solution after photocatalytic reaction without catalysts (a) and by using β-Ca$_{2-x}$Zn$_x$SiO$_4$ for x = (b) 0, (c) 0.01 and (d) 0.025 as catalysts, under sunlight

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 β-Ca$_2$SiO$_4$ catalysts. However, doping Zn onto β-Ca$_2$SiO$_4$ lowers the absorbtion and the degradation of Congo red about 15 %.
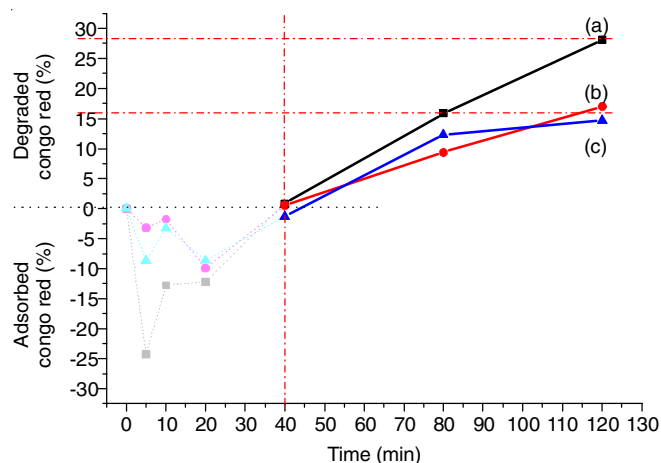

Fig. 6.   Percentage of the degraded congo red in aqueous solution after photocatalytic reaction by using β-Ca$_{2-x}$Zn$_x$SiO$_4$ for x = (a) 0, (b) 0.01 and (c) 0.025 as catalysts, under sunlight

Conclusion

The β-Ca$_{2-x}$Zn$_x$SiO$_4$ has been prepared and characterized, and applied for the degradaton of Congo red. The samples are isomorphous with β-Ca$_2$SiO$_4$. The particles are aggregated irregular in shape having size about 0.2 μm. 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.

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