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Characterizations of the thermal decomposition of nano-magnesium hydroxide by positron annihilation lifetime spectroscopy

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ABSTRACT

The thermal decomposition behavior of magnesium hydroxide ($Mg(OH)_2$) nanopowders was investigated by positron annihilation lifetime spectroscopy (PALS), X-ray diffraction (XRD), thermogravimetric and differential scanning calorimetry (TG-DSC) analysis, high-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). It was indicated that the microstructural changes started from 300 °C were earlier than the phase transformation from hexagonal $Mg(OH)_2$ nanopowders to face-centered cubic MgO occurred at about 380 °C during decomposition process. The variation of positron annihilation parameters revealed the production of new vacancy defects and the aggregation of vacancy clusters in grain boundary areas and microvoids between particles due to the removal of H_2O and rearrangement of interface atoms. A positron trapping model was proposed to help further understand the changes of microstructure and interfacial defects during $Mg(OH)_2$ thermal decomposition.

1. Introduction

Nano-magnesium hydroxide ($Mg(OH)_2$) is widely used in many industrial fields, such as flame-retardant [1], water treatment [2], biomedicine [3], and as the most important magnesium oxide (MgO) precursor [4,5]. As nano-MgO has high efficiency in antibacterial agents [6], catalysts [7], adsorbents [8], and optoelectronic materials [9], many different synthetic methods were developed to obtain MgO nanoparticles, such as microemulsion-based oil/water interface precipitation [10], hydrothermal reaction [11] and chemical precipitation [12]. Calcining or drying kinds of modified $Mg(OH)_2$ precursor is an easily accessible and cost-effective method to obtain MgO [13]. Pilarska et al. synthesized a plate morphology of poly(ethylene glycols)-modified $Mg(OH)_2$ particles and the calcinate MgO could be used as insulating materials because of its permittivity ε′ independent of frequency [5]. The resulting MgO properties strongly depend on the shape, agglomeration state, preparation process and decomposition process of $Mg(OH)_2$ [4,14]. However, in recent years, few work paid attention to the thermal decomposition behavior of nano-$Mg(OH)_2$.

The decomposition of $Mg(OH)_2$ is generally viewed as a two-phase process occurred in the temperature range of 280– 450 °C. The resulting MgO structure from $Mg(OH)_2$ decomposition maintains a distinct crystallographic relationship with original $Mg(OH)_2$, which is (0001) $Mg(OH)_2$ || (111) MgO and $[11\bar{2}0]$ $Mg(OH)_2$ || $[10\bar{1}]$ MgO [15]. Several kinds of decomposition mechanism have been proposed from kinetics, energetics, morphology and crystallography. A phase-boundary controlled mechanism was that the decomposition reaction proceeded by the advance of an interface two-dimensional reaction from the perimeter to the center of basal plane of hydroxide crystal [16]. In a homogenous mechanism, the migration of H_2O molecules from the planes to the surface was thought to control the structure change of $Mg(OH)_2$ to MgO [17]. The nucleation and development of MgO in two directions of interface were considered more acceptable because it could successfully describe the kinetics of $Mg(OH)_2$ decomposition [18]. McKelvy et al. [19] also discovered that the lamellar nucleation and growth processes governed dehydroxylation of lamellar $Mg(OH)_2$. However, the atomic-scale nature (defects) of the decomposition process lacks attention. The defects information in atomic-scale are important to the properties of MgO, e.g. the new introduced defects in MgO produced by $Mg(OH)_2$ decomposition contributed to the luminescence of MgO [4], and the interfacial defects in MgO nanocrystals were related to its ferromagnetism [20].

The principle of operation of positron annihilation lifetime spectroscopy (PALS) is to measure the spectrum of time intervals between start signals, generated by detecting prompt gamma rays following the emission of positrons, and stop signals from one of the annihilation gamma photons. A positron is the antiparticle of an electron, and it can get trapped by defects without positive charge, i.e. by vacancies or other open volume defects. Positrons can also get trapped by negative ions or by solute aggregates with higher positron affinity than the host atoms. Thus PALS is a unique and valuable technique to characterize the vacancy-type defects and open volume defects in solid based on the detection of γ-radiation [21,22], which convey information of the

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lifetime of positrons. In addition, the correct identification of defects with PALS requires the knowledge of accurate positron lifetimes for the various kinds of defects, which can be provided by first-principles calculations. In most studies, positron lifetimes are calculated using a simple practical method proposed by Puska and Nieminen [23,24] based on density function theory (DFT), where the electron and positron densities are determined without imposing self-consistency.

PALS method has been successfully used to study advanced semiconductor [25,26], nano-ceramic [27] and nano-porous material [28]. In hydrogenation-modified TiO_2, a huge number of oxygen vacancies introduction were found by PALS measurements, which retarded the charge recombination and improved the photocatalytic activity of TiO_2 [26]. In report of Dutta et al. [29], PALS results revealed that high temperature annealed ZnO semiconductor had a better crystallinity (or lower defect concentration). But no reports about the thermal decomposition of nanomaterials by PALS were found. Therefore, in this work, the thermal decomposition of $Mg(OH)_2$ nanopowders with different temperatures annealing were investigated by using PALS technique, X-ray diffraction (XRD), thermogravimetric and differential scanning calorimetry (TG-DSC) analysis, high resolution transmission electron microscopy (HRTEM), and scanning electron microscopy (SEM). The changes of microstructure and interfacial defects before and after decomposition from $Mg(OH)_2$ to MgO were discussed.

2. Experimental

2.1. Sample preparation

Nano-sized $Mg(OH)_2$ powders (~30 nm particle size) synthesized by chemical coprecipitation with a purity of 99.9% were purchased from Beijing DK Nano Technology Co. LTD, China. After being milled in agate mortar, nanopowders were pressed into tablet under a static pressure of about 10 MP for 4 min. The tablet had a diameter about 10 mm and a thickness about 2 mm. The isochronally annealing experiments were carried on these samples at different temperatures in the range of 100– 520 °C in air for 2 h. The heating rate was about 5 °C/min.

2.2. Characterization

The PALS measurements were performed on annealed samples immediately after cool down in air. In the measurements, PALS is a conventional fast-fast coincidence system with a time resolution of about 280 ps. The isotope positron source was ^{22}Na with intensity about 7.4×10^5 Bq, which was sealed between two Kapton films. During the measurement, the positron source and two identical samples were set as a sandwich structure placed between two gamma ray detectors. Each positron annihilation spectrum was collected with a total count of 1×10^6 and analyzed by LT Version 9 program [30] to decompose several lifetime components. Before sample measurements, the spectrum of pure Si single crystal was measured to determine the components of positron annihilation in the source and Kapton films.

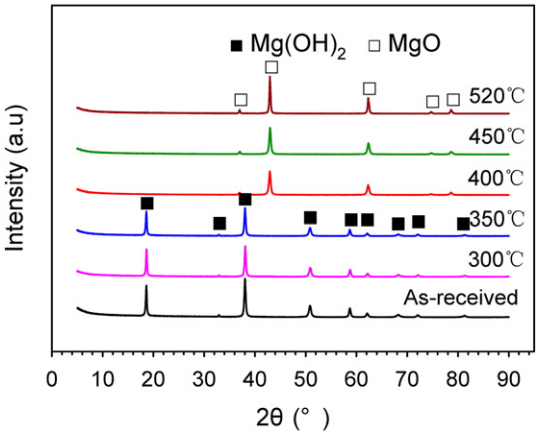

Fig. 1. XRD patterns of $Mg(OH)_2$ nanopowders annealed in air at different temperatures.

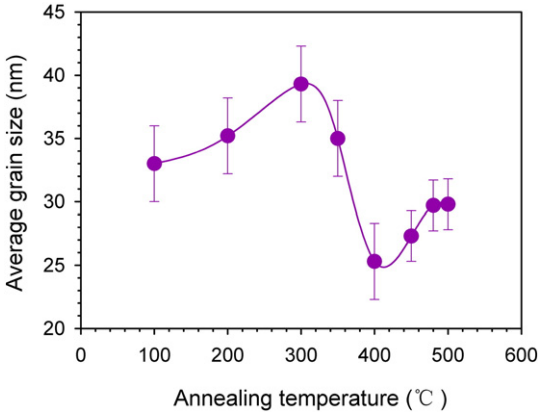

Fig. 2. The average grain size calculated from full width at half maximum of the diffraction peaks by Scherrer equation as a function of annealing temperatures.

XRD (Bruker D8 Advance, Cu Kα) was performed on samples annealed at different temperatures. The thermal decomposition behavior of the as-received $Mg(OH)_2$ nanopowders was studied by thermogravimetric (TG) and differential scanning calorimeter (DSC) analysis (NETZSCH STA 449C) in a temperature range of 20– 800 °C with heating rate of 5 °C/min under N_2 flow. The micromorphology of samples before and after annealing was characterized using HRTEM (JEM-2100, JEOL, Japan) and SEM (Sirion 200, FEI, Netherlands).

2.3. Theoretical calculation

The theoretical positron lifetimes of perfect $Mg(OH)_2$ and MgO lattices with and without vacancy defect were calculated, by using atomic superposition (ATSUP) method based on density function theory (DFT) [24]. In calculation models, the space group of $Mg(OH)_2$ and MgO are $D_{3d^3}-P\bar{3}m1$ and $Fm-3m$, respectively. The experimental lattice parameters of brucite structure $Mg(OH)_2$ and rock-salt structure MgO were $a = b = 3.147$ Å, $c = 4.768$ Å, and $a = b = c = 4.217$ Å, respectively. Perfect $Mg(OH)_2$ lattice was modeled by a $4 \times 4 \times 2$ supercell, which contained a total of 160 atoms. Perfect MgO lattice was modeled by a $2 \times 2 \times 2$ supercell, which contained a total of 64 atoms. The vacancy-type defects of V_{Mg}, V_{OH} and $V_{Mg\text{-}OH}$ in $Mg(OH)_2$ lattice and V_{Mg} in MgO lattice were constructed by removing the atoms of Mg, OH, and Mg-OH from the interior of perfect lattices, respectively.

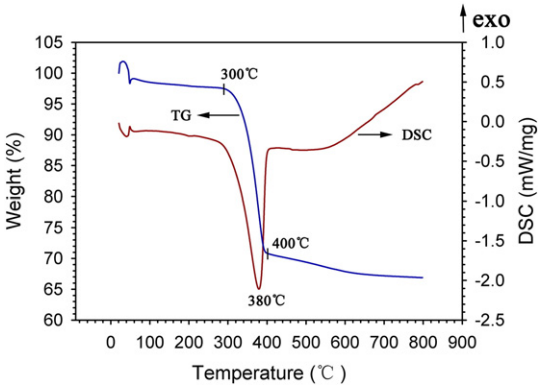

Fig. 3. TG and DSC curves of $Mg(OH)_2$ nanopowders in the temperature range of 25– 800 °C with a heating rate of 5 °C/min.