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An evaluation on sol-gel chemical processing of refractory barium hexa aluminate fibrous structures

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In this research barium hexa aluminate fibrous refractory products were produced by a chemical processing route. Boehmite was used as aluminum precursor while barium nitrate was used as barium precursor and the final solution had made according to stoichiometric BaO.6Al₂O₃ composition. It was found that two different gels could be obtained during this route. Mainly the secondary gel was trapped into the initial gel structure. Finally gels were heated at various temperatures (1350, 1650 °C) to following the formation of the barium hexa aluminate in fibrous structure due to sintering. Then the crystallization of transitional phases such as 3BaO.Al₂O₃ and BaO.Al₂O₃ to BaO.6Al₂O₃ were followed at different sintering temperatures by X-ray diffractometry (XRD) and Fourier transform infrared (FTIR) spectroscopy. Also scanning electron microscopy (SEM) was used to study the microstructural changes and micrographies. The produced gels were characterized by thermo gravimetrical and differential thermal analysis (TG/DTA). The results showed that BaO.6Al₂O₃ was the major phase at higher temperatures and fibrous structure appeared in final samples.

Key words: Sol-gel process, Scanning electron microscopy, X-ray diffraction, Aluminum oxide, Barium hexa aluminate.

Introduction

Today's it is well known that metal aluminates has found extensive application in refractories, high alumina cements and engineering ceramics such as pigments, glazes, combustion catalysts and display phosphors. Several barium compounds such as barium aluminates and titanates have interesting as starting materials in refractories and engineering ceramics processing. According to BaO-Al₂O₃ binary phase diagram, barium oxide (BaO), barium mono aluminate (BA: BaO.Al₂O₃) and especially barium hexa aluminate (BA₆: BaO.6Al₂O₃) are refractory materials and their melting points are 1920, 1800 and 1900 °C respectively [1, 2]. Today's several types of stoichiometric and non stoichiometrics barium aluminates were known. The formation of pure phases with these compositions depends on the used preparation route and experimental conditions. Barium aluminates are the most widely used group of aluminates which used as starting chemicals in various industrial applications from catalysts to structural ceramics due to their superior high temperature physical, mechanical and chemical properties. In BaO-Al₂O₃ system, the compounds often have 1:4.5 to 1:6.6 stoichiometric ratios and also have been considered as a binder in refractory castable production and engineering ceramics [3, 4]. Recently, new attentions have been focused on the production of nano sized barium hexa aluminate refractory powders.

These products have significant specific surface area ($\sim 20 \text{ m}^2\text{gr}^{-1}$) and could be used in catalyst applications in methane gas combustion systems. Also the high thermal stability of barium hexa aluminates make them as suitable materials for catalyst/catalyst supports were used in effective high temperature combustion of lean fuels such as in gas turbines with minimum CO and NO_x emission [5, 6]. In past years, noble metals such as Pt or Pd were used for this application, since the using of these metals cause to sintering or evaporation and then fast deterioration of the catalyst system at working temperatures higher than 1000 °C. While barium hexa aluminates not only withstand at temperatures higher than 1400°C, but also have a higher catalytic activity compared to the noble metals.

Barium hexa aluminates have the same lattice structure as calcium or strontium hexa aluminates. These materials have hexagonal lattice structure and D_{6h}^4 space group which has two molecules in each unit cell. BaAl₁₂O₁₉ solid solutions are similar to β -type alumina (NaAl₁₁O₁₇) and often appear in various stoichiometric compositions from Ba_{1.21}Al₁₁O_{17.71} to Ba_{0.75}Al₁₁O_{17.25} [7, 8].

In recent years different methods have been introduced and examined to prepare barium hexa aluminates via sol-gel chemical processing. In this case the properties of the end-products strongly depend on the followed synthesis routes, nature and history of the precursors. So that a careful choice of reagents and preparation routes are essential to produce the desired end-materials. Early work in this field established in 1997 [9, 10]. In overall classification, different methods such as using of primary fractions (primary nucleation) as aerogel, xerogel, pH, micro emulsion and reversible nano emulsion

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which directly affect nano structured systems [11]. All these efforts are the basis of the production and processing of new nano sized powders. However some important defects such as porosities and fractures appear in the structure of primary prepared nano ceramic fibres.

In the present article efforts have been made for preparation of barium hexa aluminate fibrous structures by sol-gel chemical processing route. This method is based on the formation of a primary gel that needed to obtain an expected barium hexa aluminate phases by gel segregation. This can be done by introducing a secondary gel maker and forced shear stresses lead to formation of two segregated gels. After drying, hydrolysis process was done simultaneously with pyrolysis on heat treating. The heat treating program included three stages. At first stage (from room temperature to 600 °C) evaporation of volatile matters such as water, alcohol and burning out of organic binder were happened by slow heating (1 K/min) and caused to less fractures, defects and pores formation during sintering. At the second stage from 600 °C to the final selected sintering temperatures (1350-1650 °C), the heating rate was 10 K/min. Finally for completion of barium hexa aluminate phase transformation, the soaking time was set for 3 hours and then the samples were cooled down in the furnace to room temperature. The investigation was focused on understanding the mechanisms of gel formation, phase formation temperatures and transitions during barium hexa aluminates formation via sol gel process and sintering.

Experimental Procedures

Barium carbonate (Merck-AG) was used as barium source and nano boehmite (10 to 20 nm, Keith Ceramics, UK) as aluminum precursor respectively. Nitric acid (99%) was used for barium nitrate formation and also to establish the pH of the initial gel. Distilled water was used as solvent and ethanol (99%) was used as dispersant agent. Finally poly vinyl alcohol (PVA, MW = 145,000) was used as an organic binder in secondary gel making process.

All phase analyses were performed by Cu-K α radiation and X-Ray Philips diffractometer (XRD). Scanning electron microscopies and micrographies were done by SEM/ EDAX (Cambridge S360 system) at 10-20 keV. The fourier transform infrared (FTIR) spectra of samples were recorded by Perkin Elmer P-500 Spectrophotometer and by using KBr pellet method.

Initial gel preparation

At first, the initial gel was prepared by the following procedure. Barium carbonate and boehmite were weighted according to the stoichiometric composition of barium hexa aluminate. 150 ml of distilled water and ethanol were mixed with 15 : 1volume ratio in a mixer with a 100 rpm rotation rate. Then barium carbonate were weighted and gradually introduced to sol. The solution was mixed up for 30 minutes. After sol homogenization, nitric acid was



Fig. 1. Preparation chart of barium hexa aluminate samples.

added by droplet. Barium carbonate reacted with nitric acid according to the following reaction (Eq. 1) and $Ba(NO_3)_2$, CO_2 and water were produced:

$$BaCO_3 + 2HNO_3 \rightarrow Ba(NO_3)_2 + CO_2 + H_2O$$
(1)

Extra nitric acid was added in order to pH adjustment and completion of the reaction. To increase the rate of reaction and dissolution of the secondary gel, the temperature was fixed at 70 °C. When the sol became fully colourless and the gas evaluation stopped, the reaction was completed. At this stage boehmite was gradually added to the sol according to the stoichiometric composition of barium hexa aluminate. Finally the solutions were mixed for 1 hour and then the initial gel was produced during the homogenizing. A digital pH meter was used for pH measurements and pH was fixed at 3-4 during these reactions.

Secondary gel preparation

In this stage for producing the secondary gel, 5 grs of poly vinyl alcohol (PVA) was added to initial gel at 70 °C temperature and agitation increased up to 1500 rpm. With increasing the PVA content, the initial gel agglomerates from the solution due to the forced shear stresses caused by agitation. In this step the initial gel was agitated for one hour. At last the morphology of agglomerates became fibrous with different sizes were dispersed in the secondary gel. Finally the end-produced gels were placed into an alumina crucible and heated under certain heat treating program in an electric resistance furnace. Fig. 1 shows the overall flowchart of the applied process.

Results and Discussion

STA results

The STA data of the precursors are shown in Fig. 2.



Fig. 2. Thermal analysis studies of dried barium hexa aluminate precursor (heating rate = 5 K/min).



Fig. 3. X-ray diffraction patterns of precursors heated at (a) $250 \,^{\circ}$ C, (b) $550 \,^{\circ}$ C, (c) $800 \,^{\circ}$ C, (d) $1350 \,^{\circ}$ C, (e) $1450 \,^{\circ}$ C, (f) $1550 \,^{\circ}$ C and (g) $1650 \,^{\circ}$ C.

The small endothermic peak near to 110 °C in DTA is attributed to 10% weight loss of the initial in TG curve and related to free water evaporation. As it can be seen, 40% weight loss between 200 and 700 °C is due to decomposition of precursors and burning out of organic materials and binders. Also the endothermic peak between 200 and 350 °C proves the remove of moisture from boehmite and the exothermic peak between 450 and 550 °C is related to burning of polymeric matrix. The next endothermic peak may be caused by nitrogen dioxide (NO₂) removal from barium nitrate and barium aluminate formation. Also the exothermic peak near to 1200 °C may be caused by barium hexa aluminate formation.

Phase and microstructural studies

In this work the effects of various calcination temperatures on barium hexa aluminate formation were studied by phase studies and microstructural evolutions. Fig. 3 shows the X-ray diffraction patterns of as-received and calcined precursors at different temperatures. The precursor is dried at 250 °C for 2 hrs contains barium nitrate and boehmite. But after increasing the calcination temperature



Fig. 4. Scanning electron microscopy of samples heated at 1650 °C at different magnifications.

up to 520 °C, the structural water of boehmite removed and γ -Al₂O₃ formed. Also in this pattern barium nitrate peaks remains. Then barium aluminate and α -Al₂O₃ phases were appeared at 800 °C and finally at higher temperatures the contents of these phases decrease and barium hexa aluminate phase contents increases. It can be seen that barium hexa aluminate phases often present in nonstoichiometric forms such as BaAl_{9.2}O_{14.8} and BaAl_{13.2}O_{20.8} (Fig. 3). Sundaresan and Aksoy reported that different sol-gel processes based on molecular and colloidal type could be performed [13]. In molecular gel systems, it is generally accepted that nucleation controls the reaction rate. In this system seeding or doping of gel agents increases the kinetic of reactions. In the colloidal systems kinetic of reactions and transformation to acceptable compositions could be controlled by ions diffusion rate from interface or first produced layer on the external surface of grains. Diffusion coefficients of Ba²⁺ and Al³⁺ ions into produced layers determine the type of Al-rich or Ba-rich phases [11-13] in final products.

SEM micrographs from produced barium hexa aluminate powders were recorded and are shown in Fig. 4. As it shows, there is not any fracture in the fiber and they tied together to construct the main fibrous structures.

FTIR results

In this research the formation mechanism of barium hexa aluminates from precursors followed by fourier transform infrared spectroscopy (FT-IR) studies. Fig. 5 illustrates the FT-IR spectra of precursor and calcined powders at 250, 520 and 800 °C. FT-IR analysis was used to follow the dehydration reaction of the precursor and the formation of Al-O-Ba bands. Common bands exist in precursor spectrum such as the broad O-H band centered



Fig. 5. Fourier transform infrared (FTIR) spectra of fired precursors at different temperatures.

around 3400 cm⁻¹, the 1630 cm⁻¹ H₂O vibration band, the bands related to NO₃⁻¹ groups at 1384 cm⁻¹, the 1200-1400 cm⁻¹ regions corresponding to C-H and C-O bands and also very broad and strong peak observed in the 400-900 cm⁻¹ region can be due to several M-O stretching and bending vibrations which could not be resolved in the present case. And a broad band between 400 and 980 cm⁻¹, in this region most of the vibrations for Al-O bending modes appear with symmetries E_{1u} and A_{2u} [5, 14].

As it has been shown there is little difference between FT-IR spectra of precursor and sample dried at 250 °C, although in the FT-IR spectra of sample calcined at 520 °C group of NO_3^- has been detected but the peaks of carbon and hydrate compounds have been eliminated and in higher calcination temperatures NO_3^- group peaks has no more existed.

Conclusion

Fibrous barium hexa aluminate refractories (BaO.6Al₂O₃) have been synthesized by a sol-gel chemical processing

route at 1200 °C. It has been found that at first different barium aluminates and α -Al₂O₃ have been formed and at higher temperatures also barium hexa aluminates in stoichiometric and non-stoichiometric phases such as BaAl₉₂O_{14.8} and BaAl₁₃₂O_{20.8} have been appeared. Scanning electron microscopy studies showed that fibrous structures had not any fractures and two kinds of fibers, like main fibers which are larger in size and aspect ratios in comparison with minor ones had been produced, which are tied together and form the main fibrous bonny like refractory structures.

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