



A comparative study on the synthesis mechanism and microstructural development of hierarchical porous mullite monoliths obtained by the sol–gel process with three different silicon sources

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Abstract

Hierarchical porous mullite monoliths have been prepared via a sol–gel process accompanied by phase separation. Propylene oxide (PO) acted as an acid scavenger to mediate the gelation, poly(ethylene oxide) (PEO) as the phase-separation inducer and network former, aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) as the aluminum source. The route was improved by using hypotoxic tetraethylorthosilicate (TEOS) and nontoxic aqueous colloidal silica (Aq) instead of tetramethoxysilane (TMOS). The synthesis mechanism and microstructural development were comparatively investigated by scanning electron microscopy (SEM), thermogravimetry-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and nitrogen adsorption–desorption. It was found that the mixing degree of precursors and concurrent process of gelation and phase separation are key elements to get well-defined hierarchical porous mullite monoliths. In addition, the monoliths with high relative crystallinity are more likely to be obtained under low transformation temperature in organic silicon sources system.

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1. Introduction

Mullite is the only stable crystalline phase of the binary system Al_2O_3 – SiO_2 at atmospheric pressure, which is widely used in industrial ceramics [1]. In fact, it could be considered as a solid solution, $\text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}\text{O}_{10-x}]$, where x denotes the number of oxygen vacancies per unit cell, and the stable composition ranges from 0.25 to 0.40, corresponding to mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (60% alumina) and $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (67% alumina) [2–5]. In recent decades, mullite has attracted considerable attentions because of its desirable physical and chemical properties, such as high chemical and thermal stability, high melting point, high electrical resistivity, high transmittance in the mid-IR range, low density, very low thermal expansion coefficient and conductivity, good

mechanical strength and dielectric properties, creep resistance and good stability in harsh chemical environments [3,4,6,7]. Based on these excellent properties, mullite has been recommended for electronic, optical and high-temperature structural applications, for example, coatings for aircraft and gas turbine engines, efficient catalytic converters, kiln furniture, hot gas filters, etc [1,3,8]. The techniques for preparing ordinary mullite material include spray pyrolysis, sol–gel, mixture of solid reagents, and coprecipitation of mixed salts, etc [2].

With the development of porous materials, many other synthesis methods have been used to produce porous mullite, such as gel freeze-drying [9], starch consolidation [10,11], slip casting [12], gel casting [13], reaction forming [14], adding pore-forming agent [15], fused deposition [16], hydrothermal treatment [17], calcinations [18], leaching method [19], and chemical processing route [20], etc. Among all these methods, sol–gel process is the best to generate products with high purity

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and homogeneity. Meanwhile, the sol–gel process accompanied by phase separation has been developed to be one of the most promising techniques to fabricate hierarchically porous monoliths. Up till now, macroporous monoliths, for instance, Al_2O_3 [21], SiO_2 [22,23], alumina–silica gel [24], TiO_2 [25–28], ZrO_2 [29,30], carbon [31], Fe_3O_4 [32], $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) [33], calcium phosphate [34], LiFePO_4 [35], yttria-stabilized ZrO_2 (YSZ) [36], cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) [37], mayenite ($12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$) [38], aluminum phosphate (AlPO_4) [39], etc, have been successfully prepared. These porous monoliths have unparalleled characteristics, like precise controlling of compositions at molecular level, low-temperature wet chemical reaction, particularly, well-defined hierarchical pore structure [37]. Compared with single-sized pore materials, the hierarchical porous monoliths with a gradient distribution of interconnected macropores, mesopores or micropores have preferable properties, such as, an increasing mass transport through the macropores and an adjustable specific surface area derived from mesopores and micropores [40]. These properties allow them to be widely used in HPLC separation, catalysis, capillary electrochromatography, controlled drug delivery devices and so on.

Recently, Guo et al. [1] first proposed the preparation of hierarchical macro-mesoporous mullite monoliths materials via a sol–gel process accompanied by phase separation. However, the silicon source, TMOS, is expensive and poisonous. So far, Campos et al. [4] have studied the influence of gelation temperature for mullite crystallization using fully hydrolyzed silica. Sedaghat et al. [41] have made a comparative study on microstructural development of alumina–mullite nanocomposites, via the sol–gel process by using colloidal silica and TEOS. But they only synthesized mullite particle or alumina–mullite nanocomposites without bimodal porous structure. Svinka et al. [12] have evaluated the effect of various types of SiO_2 source (SiO_2 , SiC and Si_3N_4) on the bending strength of porous corundum–mullite ceramics, while the method was slip casting, and the microstructure of this material was single-sized pore.

In this paper, the route to fabricate hierarchical porous mullite monoliths has been improved by using hypotoxic organic silicon source (TEOS) and even nontoxic inorganic silicon source (Aq) instead of TMOS. Compare to the traditional approach, well defined macropores and mesostructured skeletons have been prepared with a lower cost, in a more easily handled and environment friendly way. In addition, a comparative study has been made, which is on the synthesis mechanism and microstructural development. This paper may provide an insight on the synthesis of hierarchical porous monoliths with various existing materials, via the sol–gel process accompanied by phase separation.

2. Experimental

2.1. Chemicals

Aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$: Guangdong Guanghua Sci-Tech Co., Ltd, $\geq 97\%$) was used as aluminum source. Tetramethylorthosilicate (TMOS, Aldrich, 98%), tetraethylorthosilicate (TEOS, Beijing Chemical Plant) and aqueous

colloidal silica (Aq, Jinan Yinfeng Silicon Products Co., Ltd, 30% solution) were used as silicon sources. A mixture of distilled water and ethanol (EtOH, Beijing Tongguang Fine Chemicals Company, $\geq 99.7\%$) were used as the solvent. Propylene oxide (PO: Sinopharm Chemical Reagent Co., Ltd, $\geq 99.5\%$) was added to initiate the gelation reaction, and poly(ethylene oxide) (PEO, Changchun Huagao Fine Chemicals Company) with viscosity-averaged molecular weight (Mv) of 1×10^6 was used as a phase separation inducer.

2.2. Synthesis

In this paper, the method of preparing hierarchical porous mullite monoliths reported by Guo et al. [1] had been improved. The amounts of silicon sources were different, while the processes were similar. Take the inorganic silicon source for example. First, moderate PEO was dispersed in 10.5 mL of EtOH, then 8.55 g of H_2O was added. After completely dissolved, the resultant transparent solution was cooled to 0°C in an ice–water bath. 10 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was slowly added under stirring condition. Subsequently, 1.9 g of Aq was dropped into the solution under the same condition. At this moment, homogeneous and transparent multi-component solutions were prepared through the hydrolysis of the precursors. Then 9.0 mL of PO was added under the condition of ice–water bath. After stirring for 1 min, the resultant homogeneous solution was transferred to a sealed container and kept at 40°C for gelation. The gelation and phase separation proceeded spontaneously, and eventually induced the transition from sol–gel to gel. The wet gel was aged for 72 h and evaporation-dried for 120 h at the same temperature. Some of the dried gels were heat-treated at various temperatures between 800°C and 1300°C for 5 h in air at a heating rate of $10^\circ\text{C}/\text{min}$. The compositions of different solution are listed in Table 1.

2.3. Characterization

The microstructures of the fractured surfaces of the samples were observed by scanning electron microscope (SEM) taken by a Hitachi S-4800 scanning electron microscope (25 kV). Thermogravimetry-differential thermal analysis (TG-DTA) of the dried gels was performed on a Thermo plus TG/DTA6200 (Rigaku Corp., Japan) at a heating rate of $10^\circ\text{C}/\text{min}$. Nitrogen was continuously supplied at a rate of 100 mL/min. X-ray diffraction (XRD) patterns were recorded on XRD-7000 (Shimadzu, Japan) by using $\text{Cu K}\alpha$ radiation (at a tube voltage of 40 kV and a tube current of 30 mA) at a scan rate of $10^\circ/\text{min}$ through each step of 0.02° , and the 2θ angles range from 5° to 80° . The relative crystallinity was estimated by comparing the six peaks areas ($2\theta=16.39^\circ$, 26.35° , 33.26° , 35.25° , 40.81° , 60.74°) of these samples with sample E-4-b after heat-treated at 1300°C (relative crystallinity, 100%). The IR spectra were recorded on Thermo Fisher Scientific FT-IR spectrometer (Nicolet iS5) with samples pressed in KBr pellets. The nitrogen adsorption–desorption isotherms were measured at 77 K on a Micrometrics QUADRASORB SI surface area analyzer and pore size analyzer. All samples were degassed at 573 K for 3 h

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