



# Preparation of macroporous cordierite monoliths via the sol–gel process accompanied by phase separation

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Received 24 May 2013; received in revised form 13 August 2013; accepted 15 August 2013

Available online 5 October 2013

## Abstract

Monolithic cordierite with a cocontinuous macroporous structure has been successfully prepared by the sol–gel process accompanied by phase separation in the presence of poly(acrylamide) (PAAm). Propylene oxide (PO) acts as an acid scavenger to mediate the gelation of MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> ternary system, while PAAm works as a phase-separation inducer as well as a network former. The dried gel and that heat-treated at 800 °C are amorphous, and the sapphirine begins to precipitate at 900 °C, then transforming to orthorhombic β-cordierite at 1100 °C. After heat-treated at and above 1200 °C, the resultant β-cordierite further transforms to stable hexagonal α-cordierite. Heat-treatment changes the macroporous structure of cordierite monoliths such as macropore size and its distribution. The macroporous cordierite monolith after heat-treated at 1200 °C is found to possess a total porosity of 54%, interconnected macropores and dense solid skeletons.

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**Keywords:** Cordierite; Monoliths; Sol–gel; Phase separation

## 1. Introduction

Cordierite (nominal composition 2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>) is one of the useful crystalline phases in MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> ternary system, and is known as an advanced material with numerous important applications because of its excellent properties, such as low thermal expansion coefficient, excellent thermal shock resistance, low dielectric constant, good chemical durability, excellent refractoriness, and mechanical properties.<sup>1–5</sup> For instance, cordierite with honeycomb structure has been successfully used as a substrate material for diesel particulate filters (DPFs) and steam engine heat exchanger.<sup>6,7</sup> In addition, cordierite is expected to be a substrate material for integrated circuit boards replacing alumina.<sup>8,9</sup>

Porous cordierite has become the new development of cordierite materials for particle filters, catalyst supports and heat insulations, under severe conditions such as high temperature and high thermal shock.<sup>10–15</sup> Numerous techniques have been mentioned in the literature for the synthesis of porous

cordierite, such as, gel freeze-drying,<sup>10</sup> starch consolidation,<sup>11</sup> gel casting,<sup>12</sup> in situ solidification,<sup>13</sup> solid phase reaction,<sup>14</sup> and pore-formed processing.<sup>15</sup> However, porous cordierite materials with cocontinuous structure and controllable macroporous morphology have not been reported in the open literature. Moreover, studies on the preparation of a stable cordierite by sol–gel process with controlling the hydrolysis and polycondensation of three precursor compounds, have already been reported.<sup>16–20</sup> There have been yet no studies on the fabrication of macroporous cordierite monoliths by the sol–gel process accompanied by phase separation.

The sol–gel process accompanied by phase separation has been developed to be a new synthetic technique to fabricate porous monoliths having unparalleled characteristics, such as precise controlling of compositions at molecular level, low-temperature wet chemical reaction, and well-defined hierarchical pore structure with cocontinuous macropores in a monolithic shape.<sup>21–31</sup> The macroporous monoliths such as silica,<sup>21–26</sup> alumina,<sup>27</sup> titania,<sup>28</sup> zirconia,<sup>29</sup> carbon,<sup>30</sup> iron oxides,<sup>31</sup> and mullite,<sup>32</sup> have been successfully synthesized by the technique. So far, the theoretical justification has been established on fabrication of porous monoliths by the sol–gel process accompanied by phase separation.<sup>21–24</sup> It can be expected that

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more and more macroporous monolithic materials will be fabricated by the technique.

Epoxide-mediated sol–gel reaction using aqueous solution of metal salts as precursors was first reported by Gash et al.<sup>33</sup> The process combines a protonation reaction with a subsequent irreversible ring-opening reaction of a cyclic ether. It will uniformly raise the pH of solution, promotes the hydrolysis and condensation of aquo-cations, and allows the preparation of monolithic gels of metal hydroxides or oxyhydroxides. Some metal oxide monoliths such as porous alumina,<sup>27</sup> iron-based xerogel<sup>31</sup> and mullite<sup>32</sup> have been reported by means of this reaction.

In this study, we demonstrate the preparation of macroporous cordierite materials by combining the phase separation with the sol–gel route. The MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> ternary system with a silicon alkoxide and metal chlorides as additional precursors, is adopted to synthesize the cordierite monoliths in the presence of propylene oxide and poly(acrylamide). The resulting cordierite monoliths possess a cocontinuous controllable macropores, high porosity and dense skeletons. To the best of our knowledge, it is the first report to fabricate such macroporous cordierite monoliths. The cordierite material having well-defined macropores in a monolithic form will be designed so as to improve the performance of existing materials in various application fields.

## 2. Experimental

### 2.1. Synthesis procedure

Magnesium chloride (MgCl<sub>2</sub>·6H<sub>2</sub>O, Aldrich, 99%), aluminum chloride (AlCl<sub>3</sub>·6H<sub>2</sub>O, Aldrich, 99%), and tetramethylorthosilicate (TMOS, Aldrich, 99%) were used as magnesium, aluminum, and silicon sources, respectively. Mixtures of distilled water (H<sub>2</sub>O) and ethanol (EtOH, Kishida Reagents Chemicals, 99.5%) were used as the solvents. Propylene oxide (PO, Aldrich, 99%) was used as a gelation agent, and poly(acrylamide) (PAAm, Aldrich, 50 wt.% in water) having average molecular weight (*M<sub>v</sub>*) of 1 × 10<sup>5</sup> was used as a phase-separation inducer. All the chemical reagents were used as received.

The starting raw materials of magnesium aluminum silicate gels prepared in this study are listed in Table 1. The sample gels were prepared as follows: MgCl<sub>2</sub>·6H<sub>2</sub>O, AlCl<sub>3</sub>·6H<sub>2</sub>O and PAAm were dissolved in a mixture of H<sub>2</sub>O and EtOH, and

TMOS was dropped into the solution under vigorous stirring condition. The container together with the whole mixed solution was firstly placed in water bath at 60 °C for 60 min to complete the dissolution of PAAm, and then cooled to room temperature, under continued stirring. Propylene oxide was then added to the transparent solution under vigorous stirring. After stirring for 1 min, the container was sealed and kept at 40 °C for gelation. After gelation, the wet gel was aged at 40 °C for 72 h and evaporation-dried at 60 °C. Some of the dried gels were heat-treated at various temperatures between 800 and 1300 °C for 5 h in air.

### 2.2. Characterization of materials

Macroporous morphology of the dried gels and crystalline monoliths after heat treatment were observed by a scanning electron microscope (SEM, JSM-6060S, JEOL Ltd., Akishima, Japan). Thermogravimetry-differential thermal analysis (TG–DTA) of the dried gels was performed on a Thermo plus TG 8120 (Rigaku Corp., Japan) at a heating rate of 5 °C/min. Powder X-ray diffractions (XRD) of the dried and heat-treated monoliths were performed with a RINT Ultima III diffractometer (Rigaku Corp., Akishima, Japan) using CuK<sub>α</sub> radiation ( $\lambda = 0.154$  nm) as an incident beam. Infrared (IR) transmittance spectra of the dried gels were measured by using the standard KBr-pellet technique with an infrared analyzer (FT-IR: IR Affinity-1, Shimadzu Corp., Japan). Macropore size distribution of the dried gel monolith was evaluated by mercury intrusion porosimetry (Pore-master 60-GT, Quantachrome Instruments, USA). The nitrogen adsorption–desorption of dried gels and crystalline monoliths were characterized by a nitrogen adsorption–desorption apparatus (BELSORP mini II, Bel Japan Inc., Toyonaka, Japan). Before each nitrogen adsorption–desorption measurement, the samples were degassed at 200 °C under vacuum for more than 6 h. Specific surface area and pore size distributions were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) respectively.

## 3. Results and discussion

### 3.1. Formation of macroporous morphology

In the present system containing three kind of precursors for respective metal oxides, the co-hydrolysis of aluminum chloride (AlCl<sub>3</sub>·6H<sub>2</sub>O) and magnesium chloride (MgCl<sub>2</sub>·6H<sub>2</sub>O) in the

Table 1  
Starting compositions of macroporous cordierite monoliths.

Compositions	AlCl <sub>3</sub> ·6H <sub>2</sub> O (wt.%)	MgCl <sub>2</sub> ·6H <sub>2</sub> O (wt.%)	TMOS (wt.%)	H <sub>2</sub> O (wt.%)	EtOH (wt.%)	PO (wt.%)	PAAm (wt.%)
N-1	21.1	8.4	10.3	31.6	23.3	5.3	0
N-2	20.0	8.0	9.8	30.0	22.1	5.1	5.0
N-3	19.1	7.6	9.4	28.6	21.1	4.7	9.5
N-4	18.5	7.4	9.1	27.8	20.5	4.6	12.1
N-5	18.2	7.3	8.9	27.3	20.1	4.5	13.7
N-6	17.8	7.1	8.7	26.7	19.7	4.4	15.6
N-7	17.4	7.0	8.5	26.1	19.3	4.3	17.4
N-8	16.7	6.7	8.2	25.0	18.4	4.1	20.9
N-9	16.0	6.4	7.9	24.0	17.7	4.0	24.0

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