



# Preparation of monolithic aluminium titanate with well-defined macropores via a sol–gel process accompanied by phase separation



Xingzhong Guo<sup>\*</sup>, Wenjun Zhu, Xiaobo Cai, Shengxing Liu, Hui Yang

School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

## ARTICLE INFO

### Article history:

Received 6 February 2015

Revised 21 April 2015

Accepted 7 June 2015

Available online 19 June 2015

### Keywords:

Aluminium titanate

Monolith

Sol–gel

Phase separation

## ABSTRACT

Monolithic aluminium titanate with well-defined macropores has been prepared through a sol–gel process accompanied by phase separation, using poly(ethylene oxide) (PEO) to induce the phase separation and formamide (FA) to control the gelation of  $\text{Al}_2\text{O}_3$ – $\text{TiO}_2$  system. Appropriate amounts of PEO and formamide allow the formation of aluminium titanate xerogel with cocontinuous macroporous structure and a monolithic shape. The pore size of the resultant dried gels is in the range of 2–3  $\mu\text{m}$  and the porosity is above 60%. The as-dried gel is amorphous and completely transforms into a single phase  $\text{Al}_2\text{TiO}_5$  after heat-treated at 1300 °C. The macroporous structure is well maintained while the skeleton becomes smooth after heat-treatment.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Aluminium titanate ( $\text{Al}_2\text{TiO}_5$ , AT) is known as a promising refractory ceramic due to its low coefficient of thermal expansion, low thermal conductivity, high melting temperature and high thermal shock resistance [1–4]. Based on these excellent properties,  $\text{Al}_2\text{TiO}_5$  ceramics have many industrial applications, such as kiln furniture, pouring spouts for foundry and thermal protection layers in internal combustion engines [5–8]. Recent research shows that porous aluminium titanate is a good candidate for use as catalyst supports and particle filters. For example, porous aluminium titanate with honeycomb structure has been successfully used as substrate material for diesel particulate filters, exhibiting better performance than cordierite and SiC [9–11]. One common method for the fabrication of porous aluminium titanate is solid-state sintering from  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  powder, using some modifying agents like  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  to improve the stabilization of  $\text{Al}_2\text{TiO}_5$  and pore-forming agents like spherical corn starch [12–15]. However, porous aluminium titanate material with cocontinuous macroporous structure has not been reported yet. Compared with the tradition solid-state sintering method, the sol–gel technique has attracted great interests as a promising method for the preparation of  $\text{Al}_2\text{O}_3$ – $\text{TiO}_2$  binary system due to its relatively low sintering temperature and high compositional homogeneity. Some studies also focus on the synthesis of aluminium titanate by sol–gel process in order to obtain  $\text{Al}_2\text{TiO}_5$  at low temperature and improve the

properties of  $\text{Al}_2\text{TiO}_5$  [16–19]. Sung et al. [20] synthesized mesoporous  $\text{Al}_2\text{O}_3/\text{TiO}_2$  by a combination of sol–gel reaction and evaporation-induced self-assembly process. Chu et al. [21] reported porous  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite nanostructures through a sputter-deposition and a sol–gel process. Dionysiou et al. [22] synthesized porous  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite membranes by an acetic acid-based sol–gel method. Innocenzi et al. [23] reported a low temperature sol–gel method for the synthesis of  $\beta$ - $\text{Al}_2\text{TiO}_5$  thin films, the obtained products present a high homogeneity. However, only powder and film but not monolithic aluminium titanate material were obtained. Moreover, compared with the monoliths composed of conventional particle-packed structure, the monoliths with cocontinuous macroporous structure display a superior performance for the applications in various kinds of fields due to the unique macrostructure [12,14]. For instance, when used as support materials, a monolithic shape provides suitable mechanical strength and the presence of interconnected macropores leads to high permeability and allows facile fluid transport [24,25].

The sol–gel process accompanied by phase separation is a new method for the fabrication of porous monoliths. In this approach, a sol–gel reaction progresses in parallel with the phase separation, each separated phase is interconnected in three-dimensional space, which is spontaneously formed along with the process of freezing the phase-separating transient morphology. Finally, the “cocontinuous” structure in micrometer scale could be gained, which derived from spinodal decomposition induced by the polymerization along with gelation [26–28]. By using the polymerization-induced phase separation technique, several kinds

<sup>\*</sup> Corresponding author.

E-mail address: [gxzh\\_zju@163.com](mailto:gxzh_zju@163.com) (X. Guo).

of porous monoliths have been prepared, including silica [26], titania [28–34], alumina [35], zirconia [36], iron(III) oxides [37]. Recently, porous monoliths of binary system based on  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$ , such as mayenite [38], mullite [39],  $\text{Ca}(\text{Si}, \text{Ba}, \text{Mg})\text{TiO}_3$  [40,41] and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [42] have been synthesized. However, it is not easy to obtain aluminium titanate binary system with cocontinuous structure since the mechanism of phase separation of  $\text{Al}_2\text{O}_3$  system is quite different from that of  $\text{TiO}_2$  system in the presence of poly(ethylene oxide) (PEO). In  $\text{Al}_2\text{O}_3$  system, PEO is preferentially dissolved in liquid phase after reaction and the phase separation is dominated by the enthalpic contribution [40]. On the other hand, in  $\text{TiO}_2$  system, PEO is distributed into the gel phase after reaction and the phase separation is controlled by entropic contribution [28]. The phase separation induced by PEO will be a result of both enthalpic and entropic contribution in  $\text{Al}_2\text{O}_3$ – $\text{TiO}_2$  binary system.

In this work, we prepare monolithic aluminium titanate with well-defined macropores by combining the sol–gel route with phase separation for the first time. The phase separation is induced by the addition of PEO and the gelation is accelerated by formamide (FA). The effects of PEO and FA on the gel morphologies and the influence of heat-treatment condition on the crystalline phase and macroporous structure are investigated. The mechanism of PEO-induced phase separation of  $\text{Al}_2\text{O}_3$ – $\text{TiO}_2$  binary system is discussed. The resultant aluminium titanate monoliths possess controllable macroporous structure and high porosity and will find applications in catalyst supports and filters for motor vehicles.

## 2. Experimental

### 2.1. Materials

Aluminium chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) and titanium tetrabutoxide ( $\text{Ti}(\text{OBU})_4$ ) were used as aluminum source and titanium source, respectively. Mixture of distilled water and ethanol ( $\text{C}_2\text{H}_6\text{O}$ ) was used as solvent. Poly(ethylene oxide) (PEO) with average molecular weight ( $M_w$ ) of  $1 \times 10^5$  was used as a phase separation inducer. Citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) and formamide (FA) were added as a chelating agent and a gelation agent, respectively. 2-Propanol was used for solvent exchange. All reagents were of analytical purity grade and used as received from Sinopharm Chemical Reagent Co., Ltd. (China).

### 2.2. Sample preparation

The starting compositions were listed in Table 1. In a typical synthesis,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (1.448 g) and citric acid (0.630 g) were dissolved in a mixture of distilled water (0.80 mL) and ethanol (2.50 mL).  $\text{Ti}(\text{OBU})_4$  (1.04 mL) was slowly added with vigorous stirring under ice-cooled condition. The molar ratio of  $\text{AlCl}_3/\text{Ti}(\text{OBU})_4$  was fixed as 2/1 to keep the stoichiometry. After obtaining a light yellow solution, PEO ( $W_{\text{PEO}}$  g) was added followed by stirring at room temperature about 1 h to dissolve PEO completely. Then,

FA ( $V_{\text{FA}}$  mL) was added. After mixing for 2 min, the obtained homogeneous solution was sealed and kept at 60 °C for 24 h for gelation and aging. The resultant wet gels were solvent-exchanged with 2-propanol every 12 h for 3 days and then evaporation-dried at 60 °C for 48 h to obtain the aluminum titanate inorganic–organic hybrid xerogels. Some samples were subsequently heat-treated at various temperatures up to 1300 °C for 2 h with a heating rate of 5 °C  $\text{min}^{-1}$ .

### 2.3. Characterization

Morphologies of samples before and after heat-treatment were observed by a field-emission scanning electron microscope (FE-SEM: SIRION-100, FEI Co., Holland). Thermogravimetric-differential scanning calorimetry (TG-DSC: SDT-Q600, TA Instrument, USA) to 1000 °C was performed on the sample at a heating rate of 5 °C  $\text{min}^{-1}$  with continuously supplying air. Chemical bonding information on the dried gels was investigated with Fourier transform infrared spectroscopy (FT-IR: Nicolet 5700, ThermoFisher Co., USA) using the KBr pellet technique. The crystalline phase was confirmed by powder X-ray diffraction (XRD: Empyrean 200895, PANalytical B.V., Holland). Macropore size distributions were evaluated by mercury porosimetry (AutoPore IV 9510, Micromeritics Instruments, USA). The porosity (%) was calculated as  $[(1 - \rho_b)/\rho_s] \times 100$ , where  $\rho_b$  and  $\rho_s$  refers to the bulk and skeletal density, respectively.

## 3. Results and discussion

### 3.1. Preparation of monolithic gels

The starting solutions with compositions listed in Table 1 were homogeneous and light yellow in colour. The solution gelled in about 25 min after the addition of FA (AT03), while the gelation was not observed without FA. However, without the addition of citric acid, only friable opaque gels were formed as aggregates of  $\text{TiO}_2$  precipitates. In the present system, citric acid acts as a chelating agent as well as an acid catalyst to control the hydrolysis reaction of two precursors (titanium tetrabutoxide and aluminum chloride). The citric acid can decrease the reactivity of titanium alkoxide species by coordinating to the Ti atoms, and the acidic condition is also needed to further stabilize the chelated species and decrease the reactivity during hydrolysis [31,43]. Meanwhile, the citric acid can also induce the hydrolysis of aluminum chloride due to the catalyst effect in the mixture solution of water and ethanol. As a result, a comparable hydrolysis rate could be acquired between titanium and aluminum precursors, and a translucent sol could be obtained after co-hydrolysis [44]. The addition of FA triggered the sol–gel transition of the binary system, while the addition of PEO induced the phase separation of the system. The cooperative adjustment of PEO and FA corresponding to phase separation and sol–gel transition allowed the obtaining of the white gels in a monolithic shape [35,45]. The Ti–Al complex gels with

**Table 1**  
Starting compositions of the reaction mixtures.

Materials	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (g)	$\text{Ti}(\text{OBU})_4$ (mL)	$\text{C}_6\text{H}_8\text{O}_7$ (g)	$\text{H}_2\text{O}$ (mL)	Ethanol (mL)	FA (mL)	PEO (g)
AT01	1.448	1.04	0.630	0.80	2.50	0.40	0
AT02	1.448	1.04	0.630	0.80	2.50	0.40	0.020
AT03	1.448	1.04	0.630	0.80	2.50	0.40	0.040
AT04	1.448	1.04	0.630	0.80	2.50	0.40	0.080
AT05	1.448	1.04	0.630	0.80	2.50	0.40	0.160
AT06	1.448	1.04	0.630	0.80	2.50	0.20	0.080
AT07	1.448	1.04	0.630	0.80	2.50	0.30	0.080
AT08	1.448	1.04	0.630	0.80	2.50	0.50	0.080

Download English Version:

<https://daneshyari.com/en/article/828441>

Download Persian Version:

<https://daneshyari.com/article/828441>

[Daneshyari.com](https://daneshyari.com)