

## Effect of Precursor pH on One-dimensional Growth of Mullite Prepared by Sol-Gel Method with $\text{WO}_3$ Catalyst

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**Abstract:** One-dimensional mullite particles were synthesized by sol-gel method from hydrous aluminum chloride ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) and tetraethoxysilane (TEOS) as raw materials and  $\text{WO}_3$  as catalyst.  $\text{WO}_3$  had a desired effect on the anisotropic growth of mullite particles by forming aluminum tungstate ( $\text{AlWO}_4$ ) as growth template at low temperature, which was greatly dependent on the precursor pH. NMR results indicate that the pH during gelation can highly influence the homogeneity of precursor, mullite formation and microstructural features. One-dimensional mullite particles are significant only when the precursor pH is lower than 7. Morphology of the mullite particles synthesized with  $\text{pH} \geq 7$  transforms from anisotropy to isotropy and platelike.

**Key words:** mullite; sol-gel; one-dimensional growth;  $\text{WO}_3$ ; pH

One-dimensional nano-sized mullite particles are attractive to high temperature applications owing to its relatively high chemical stability, good refractory properties, high temperature mechanical strength and low thermal expansion coefficient<sup>[1-3]</sup>. During all the reported processes of preparing mullite fibers, sol-gel method is the ripest technique due to its good homogeneity, low crystallization temperature and high purity of products<sup>[4-5]</sup>. Some investigations have been in progress on the morphology development of mullite by  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  sol-gel system at different pH conditions<sup>[6-7]</sup>. Generally, it is well accepted that the hydrolysis and condensation of source materials (consequently the homogeneity) are significantly dependent on pH conditions, further influencing the crystallization sequence and morphology evolution of mullite products.

Recently, it is reported that  $\text{WO}_3$  is an effective catalyst inducing the one-dimensional growth of mullite by forming  $\text{AlWO}_4$  as growth template<sup>[5,8-9]</sup>. However, in the present work, the morphology of mullite particles prepared by  $\text{WO}_3$ -catalyzed sol-gel system is greatly dependent on the precursor pH. One-dimensional nanocolumns were synthesized largely only under acidic conditions. Although the effect of precursor pH on synthesizing and morphology of sol-gel processed mullite has

been studied widely<sup>[6-7]</sup>. It is noticed that the relationship between precursor pH and catalytic effect in  $\text{WO}_3$ -catalyzed sol-gel system have not been well characterized. The variations of morphologic development in different pH range is not explained as yet. In this study, one-dimensional mullite nanocolumns were prepared by sol-gel method with 5mol%  $\text{WO}_3$  as catalyst. Citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) and ammonia water ( $\text{NH}_4\text{OH}$ ) were added into the precursor sols to control the pH in the range from 1 to 14. The catalytic effect of  $\text{WO}_3$ , synthesizing behavior and morphology evolution under different pH conditions have been extensively investigated.

## 1 Experiment

Commercially available  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and TEOS were used as the raw materials with  $n(\text{AlCl}_3) : n(\text{TEOS}) : n(\text{H}_2\text{O}) = 3 : 1 : 80$ . Ammonium tungstate ( $\text{N}_5\text{H}_{37}\text{W}_6\text{O}_{24} \cdot \text{H}_2\text{O}$ ) was employed as catalyst resource of  $\text{WO}_3$  whose concentration was 5mol% of Al. Precursor pH of the sols were controlled at pH = 1, 4, 7, 10, 14. The source solutions were mixed and stirred at room temperature for 8h and then kept at room temperature for 4-10d. The obtained gels were baked at 80°C for 7d then transferred into a graphite crucible. The crucible was

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placed into a tube furnace and heated at a rate of 10°C/min up to 1400°C and the chamber was flushed with pure N<sub>2</sub> atmosphere at a flow rate of 1500 mL/min. Finally, the furnace was allowed to cool down naturally to room temperature.

The thermal analysis of the gels has been carried out up to 1200°C in N<sub>2</sub> atmosphere at a rate of 10°C/min by Differential Scanning Calorimetry (TG/DSC, NETZSCH STA 409 PC/PG, Germany). The nuclear magnetic resonance (NMR, Avance 300, Bruker, Germany) was carried out on a spectrometer operating at 104.2 MHz for <sup>27</sup>Al. The phase transformation and microstructure of mullite particles was studied by X-ray diffractometer (XRD, D8 Advance, Bruker AXS, Germany) and scanning electron microscope (SEM, LEO 1530, Germany) equipped with the energy dispersive X-ray spectra (EDS).

## 2 Results and discussion

Figure 1 shows the TG/DSC analysis of all the as-dried gels prepared under different pH conditions. The endothermic peaks occurred at 200°C were considered as the dehydration of aluminum hydrate and absorbed water. A sharp exothermic peak at about 822°C followed by a small one at about 962°C were observed for as-dried gel with precursor pH = 1 (acidic sample hereinafter). According to Schmücker, *et al.*<sup>[10]</sup>, the first peak was related to the formation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the second one indicated the formation of mullite phase. With the increase of pH to 14 (basic sample hereinafter), the formation temperature of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and mullite gradually raised to 943°C and 1082°C, respectively. The variation of formation temperatures are probably caused by the different precursor homogeneity, which can be demonstrated by NMR.

TG curves of all as-dried gels present almost the same mass loss (~22 wt%) with a sudden change of about 3 wt% at 860°C. Noticing that the molar concentration of WO<sub>3</sub> added in precursor is 5 mol% and the weight composition is calculated to be 4 wt%, which is close to the sudden weight loss rate. So it is probable that the delayed mass loss is deduced to the volatilization of WO<sub>3</sub>. Figure 2 shows the EDS results of acidic sample sintered at 800°C and 1000°C. It is clear that no tungsten could be detected after sintering at 1000°C. Combining the TG results, it is reasonable that the sudden mass loss happened at 860°C is caused by the volatilization of WO<sub>3</sub>.

Figure 3(a) shows the XRD patterns of acidic sample sintered at different temperatures. After sintering at

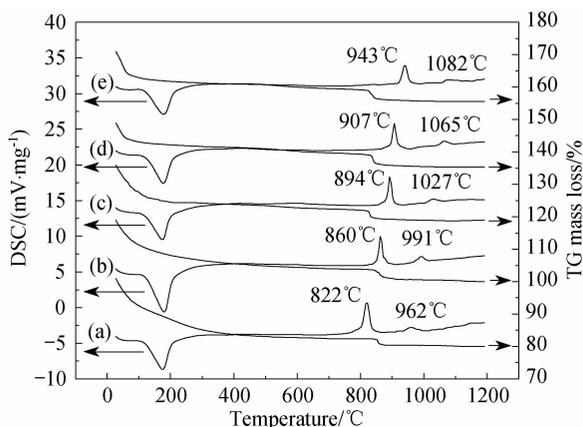


Fig. 1 TG/DSC curves of all as-dried gels prepared at (a) pH = 1, (b) pH = 4, (c) pH = 7, (d) pH = 10 and (e) pH = 14

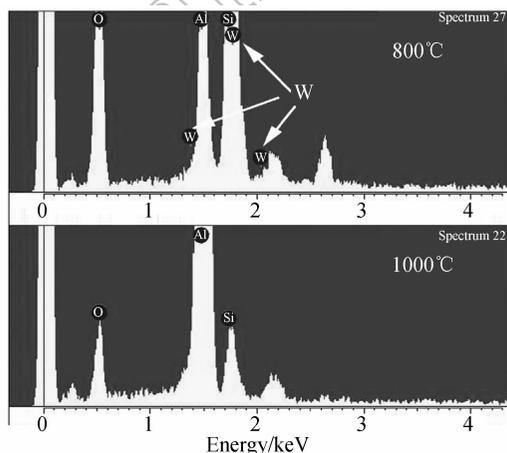


Fig. 2 EDS results of acidic sample sintered at 800°C and 1000°C

900°C, broad XRD peaks of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> coexisting with a trace amount of AlWO<sub>4</sub> are obtained simultaneously. Mullite phase is observed through sintering at 1000°C, coexisting with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Further increasing of sintering temperature from 1100°C to 1400°C leads to the disappearance of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and distinct split of (120) and (210) peaks, which is apparently corresponded to well-crystallized orthorhombic structure.

Figure 3(b) shows the XRD patterns of basic sample sintered at different temperatures. Broad peaks of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> appear at 1000°C. Mullite phase first appears at 1100°C coexisting with a large amount of corundum. Cristobalite phase is formed at 1200°C. Further increasing of heating temperature leads to the absorption of cristobalite and corundum by re-crystallization of mullite. It is noticed that no AlWO<sub>4</sub> phase is observed in the pH range. These differences may be due to the different homogeneities of precursors during gelation.

Figure 4(a) and (b) displays a large amount of anisotropic mullite nanocolumns prepared under acidic conditions. Further increasing of precursor pH leads to

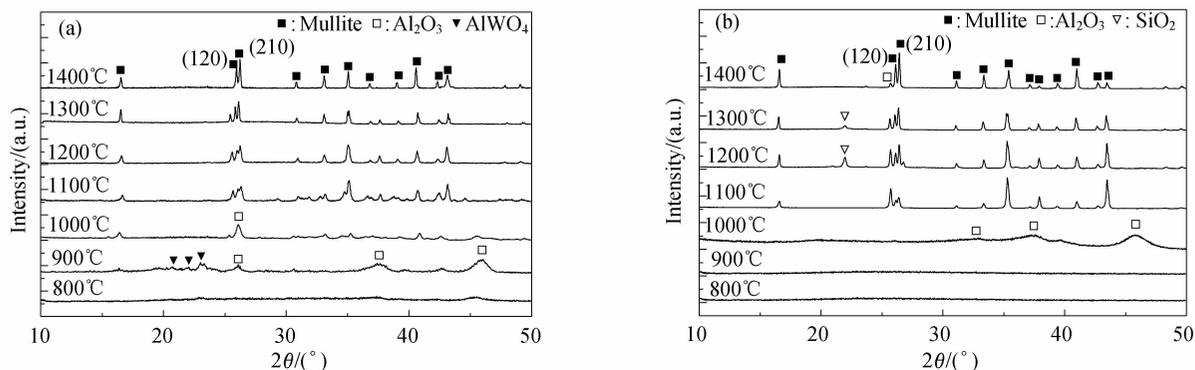


Fig. 3 XRD patterns of (a) acidic samples and (b) basic samples sintered at different temperatures

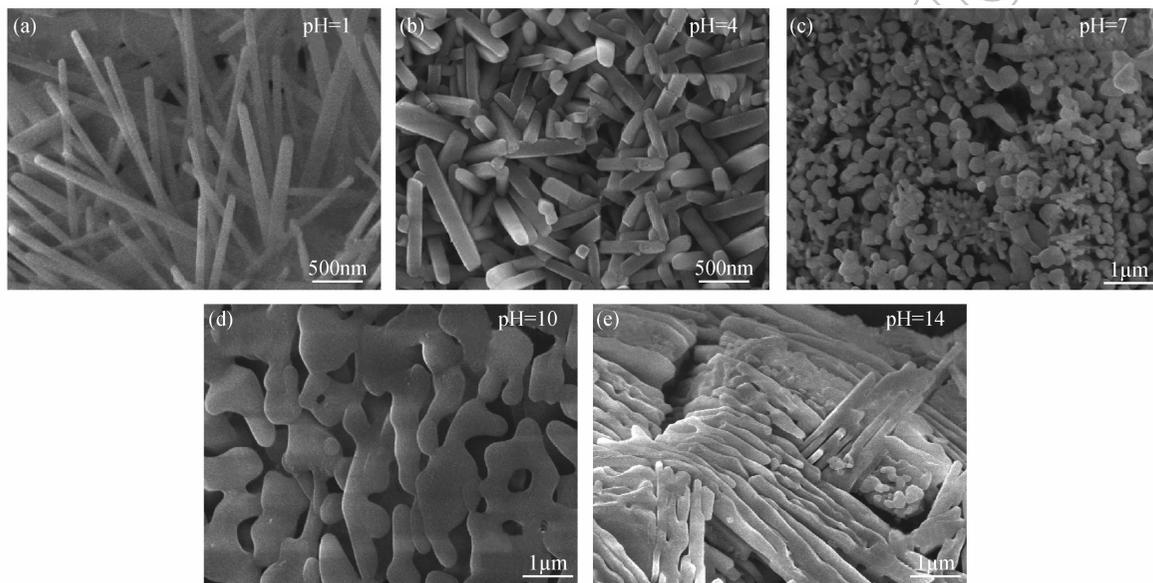


Fig. 4 SEM images of mullite precursors prepared at (a) pH = 1, (b) pH = 4, (c) pH = 7, (d) pH = 10 and (e) pH = 14 and sintered at 1400°C for 2h

the appearance of isotropic particles. For instance, in Fig. 4 (c), although mullite nanocolumns can be observed somewhere, isotropic particles have become the primary morphology. In Fig. 4(d) and (e), the anisotropic mullite particles have disappeared. A large amount of isotropic particles are observed in Fig. 4(d), and further develop to platelike, as shown in Fig. 4(e).

It has been reported that  $\text{WO}_3$  has a strong tendency to induce the one-dimensional growth of mullite by formation  $\text{AlWO}_4$  at low temperature of 1000°C<sup>[5,8-9]</sup>. However, in the present work,  $\text{AlWO}_4$  phase is formed only under acidic condition. The variations are probably caused by the different local homogeneity in the transformation from gel to mullite, which can be characterized by  $^{27}\text{Al}$  NMR spectra, as shown in Fig 5.

The NMR spectra of acidic sample (Fig. 5 (a)) heat-treated below 900°C are similar to those of amorphous aluminosilicate with three typical spectra peaks at  $\delta = 0, 28$  and  $60$ <sup>[11]</sup>. The resonances at  $\delta = 0$  and  $60$  are

attributed to  $\text{Al}^{3+}$  in 6- and 4-fold coordination, respectively. The resonance at  $\delta = 28$  was often ascribed to distorted tetrahedral site associated with  $\text{Al}^{3+}$  in triclusters causing by the incorporation of  $\text{Al}^{3+}$  in  $\text{Si}^{4+}$  sites<sup>[12]</sup>. The appearance of resonance at  $\delta = 28$  reveals that some  $\text{Al}^{3+}$  enter into silica gel network, indicating that the mullite precursor has near atomic level homogeneous mixing<sup>[11-12]</sup>. Sintering at 900°C leads to the disappearance of peak at  $\delta = 28$ , suggesting that amorphous aluminosilicate has transformed to  $\gamma\text{-Al}_2\text{O}_3$  at this temperature. No obvious changes are observed by sintering at 1100°C.

On the contrary, the  $^{27}\text{Al}$  NMR spectra of basic sample (Fig. 5 (b)) heated at 200°C only display two strong peaks at  $\delta = 0$  and  $60$ . The absence of resonance at  $\delta = 28$  indicates less homogeneity and the segregation of alumina and silica components under basic condition<sup>[11-12]</sup>. With the temperature increasing from 400°C to 900°C, resonance at  $\delta = 28$  appears, although the peak

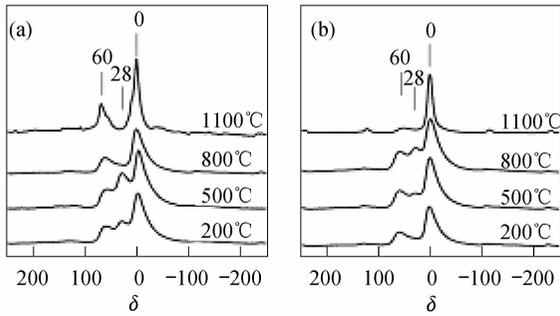


Fig. 5  $^{27}\text{Al}$  NMR spectra of (a) acidic sample and (b) basic sample heat-treated at different temperatures

is very weak. Only one strong peak at  $\delta = 0$  appears after sintering at  $1100^\circ\text{C}$ , which is caused by the formation of corundum.

It is well accepted that the aluminum coordination in aluminosilicate gel is related to their homogeneity. The resonances at  $\delta = 28$  and  $60$  reflect the uniform Al/Si dispersion of the precursor and the efficient incorporation of aluminum into the tetrahedral silicate network<sup>[11-12]</sup>. NMR results demonstrate that the homogeneity of acidic precursor is much higher than that of basic precursor, which is the cause of lower formation temperatures of  $\gamma\text{-Al}_2\text{O}_3$  and mullite under acidic condition.

According to the above results, the effect of precursor pH on one-dimensional growth of mullite prepared by  $\text{WO}_3$ -catalyzed sol-gel system may be speculated as follows: When gels are prepared at high acidic pH, the higher homogeneity leads to the earlier appearance of  $\gamma\text{-Al}_2\text{O}_3$ , which reacts with  $\text{WO}_3$  forming  $\text{AlWO}_4$  as a growth template and further induces the one-dimensional growth of mullite. While under basic condition, due to the less homogeneity of precursor and the segregation of alumina component, the formation temperature of  $\gamma\text{-Al}_2\text{O}_3$  is higher than the volatilization temperature of  $\text{WO}_3$ .  $\text{WO}_3$  has been volatilizing from gel before the formation of  $\text{AlWO}_4$ , leading to the absence of  $\text{AlWO}_4$  framework and the depression of one-dimensional growth

of mullite. The segregated alumina and silica components crystallize in their own paths to corundum and cristobalite. Mullite is formed largely later through solid state reaction of crystalline components.

### 3 Conclusions

One-dimensional mullite particles have been synthesized by simple sol-gel method.  $\text{WO}_3$  acted as an effective catalyst only under acidic condition due to the better homogeneity of precursor and earlier appearance of  $\gamma\text{-Al}_2\text{O}_3$ .  $\text{AlWO}_4$  has a three-dimensional framework, inducing one-dimensional growth of mullite particles. However, under basic condition,  $\text{WO}_3$  largely volatilized before the formation of  $\text{AlWO}_4$ , the lack of growth template led to the disappearance of anisotropic particles.

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## pH 值对溶胶-凝胶法制备莫来石纳米粉体微观形貌的影响

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**摘要:** 以氧化钨为催化剂, 利用溶胶-凝胶法制备了具有高长径比的一维莫来石纳米粉体。研究表明, 溶胶前驱体的 pH 值对氧化钨的催化作用有重要的影响。只有当溶胶前驱体的 pH 值小于 7 时, 才能形成  $\text{AlWO}_4$  生长模板引导一维莫来石颗粒的形成。随着溶胶前驱体 pH 值的逐渐升高, 前驱体的化学均匀度降低, 导致  $\gamma\text{-Al}_2\text{O}_3$  形成温度升高,  $\text{WO}_3$  在生成  $\text{AlWO}_4$  之前已经大量挥发。生长模板的缺失使莫来石粉体的微观形貌从各向异性向各向同性发展。

**关键词:** 莫来石; 溶胶-凝胶; 一维生长;  $\text{WO}_3$ ; pH 值

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