

基于粉煤灰高效催化的莫来石多孔陶瓷孔结构构筑与分离性能

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摘 要: 随着碳减排政策的实施和水处理标准的提升, 多孔陶瓷在水处理中的应用受到越来越广泛的关注。传统的多孔陶瓷材料受到原料来源、制备能耗等方面的限制, 在水处理行业的规模化应用受到极大限制, 因此开发低制备成本、高渗透通量的多孔陶瓷成为亟待解决的问题。本文以粉煤灰为主要材料、氟化铝(AlF_3)为催化剂, 制备了高孔隙率、高通量莫来石多孔陶瓷, 研究了 AlF_3 催化莫来石晶须的形成机理及莫来石多孔陶瓷孔结构构筑过程。随着莫来石晶须的生长, $1\,200\,^\circ\text{C}$ 烧结多孔陶瓷的孔隙率从 56.4% 增加到 57.6%, 平均孔径从 $0.75\,\mu\text{m}$ 增加到 $1.24\,\mu\text{m}$ 。考察了莫来石多孔陶瓷在乳化液处理中的选择渗透性, 当跨膜压力低于 0.25 bar 时其截留率超过 90.2%。

关键词: 多孔陶瓷; 孔隙率; 粉煤灰; 烧结; 莫来石晶须

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1 Introduction

Porous ceramics are widely used in various environmental applications such as solid-liquid separation and hot gas filtration due to their high mechanical strength, excellent chemical resistance and high thermal stability, compared with polymeric membrane^[1-2]. In general, commercial porous ceramics are usually prepared with alumina (Al_2O_3), zirconia (ZrO_2), silica (SiO_2) or silicon carbide (SiC) particles. The pores in these ceramics are made via particle-packing of inorganic powders. The resultant ceramics are characterized in terms of low porosity, high self-mass, low permeability and high filtration resistance. The sintering temperature of Al_2O_3 and SiC exceeds $1\,600\,^\circ\text{C}$, which is a high energy-consumption process^[3-4]. It is thus necessary to develop novel porous ceramics with a high porosity, a high mechanical strength and a low energy-consumption.

Mullite is an aluminosilicate ceramic with a composition ranging from $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ to $2\text{Al}_2\text{O}_3\cdot \text{SiO}_2$. Mullite ceramics are widely used as a catalyst carrier, a lightweight structure and a molten metal filter^[5]. Mullite whiskers ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$)-based porous ceramics have attracted recent attention in the treatment of various wastewaters. Compared with conventional porous

ceramics made via particle-packing, mullite whisker-based porous ceramics are constructed by whiskers interlocking, leading to fibrous porous structures with a high porosity, a high pore connectivity, and a low bulk density^[6].

According to the previous studies^[7-11] on the preparation of mullite whisker-constructed porous ceramics, a vital step is the growth of mullite whiskers with a high aspect ratio, a high fracture strength and a uniform distribution in porous ceramics. Usually, high-purity materials are chosen as raw materials so as to obtain mullite ceramics with a high fraction of mullite whiskers. Dong *et al.*^[12] prepared porous alumina/mullite membrane supports with a flexural strength of (13.4 ± 0.7) MPa and an open porosity of 72.8% when the ceramics were sintered at $1\,600\,^\circ\text{C}$ with fine alumina powder and silica sol as raw material. Abdullayev *et al.*^[13] prepared porous mullite-alumina ceramics with $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$, Na_2SO_4 , $\text{AlF}_3\cdot 3\text{H}_2\text{O}$ and amorphous SiO_2 from waste rice husk, and the as-prepared mullite-alumina had a compressive strength of 25.7 MPa and a porosity of 70.6%. Clearly, the mullite whiskers-constructed porous ceramics show a high porosity, compared with the particles-packed porous ceramics. However, these porous mullite ceramics are rarely used in industries due to the great cost of high-purity starting materials.

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Mullite whiskers can be also synthesized with industrial solid wastes and mineral materials containing Al-Si resources, such as bauxite^[14], clay^[15], coal gangue^[8], fly ash^[16] and kaolin clay^[17]. Fly ash is a primary byproduct of coal combustion. The recycling of fly ash can achieve environmental and economic benefits. The element analysis indicates that fly ash is constituted mostly of unburned carbon, metal oxides (*i.e.*, Si, Al and Fe) and other inorganic substances^[18–19]. Fly ash can be thus used for the manufacturing of mullite porous ceramics because of the high fraction of aluminosilicate.

In the manufacturing of mullite porous ceramics with low-cost materials, several catalysts (*i.e.*, AlF_3 , MoO_3 , WO_3 and V_2O_5) can be used to enhance the growth of mullite whiskers and then the rapid construction of fibrous porous ceramics^[20–21]. Fu *et al*^[10] prepared mullite porous ceramics with great porous structures with fly ash, $\text{Al}(\text{OH})_3$ and MoO_3 as raw materials. The addition of MoO_3 enhances the formation of a sub-stable and low-viscosity liquid phase, favoring the formation of a novel mullite whisker-interlocked structure with a higher porosity. Compared with MoO_3 , AlF_3 is considered as a more effective catalyst for the growth of mullite whiskers. Li *et al*^[22] prepared mullite whisker reinforced ceramics by a reactive sintering process with fly ash solid waste as a starting material and AlF_3 as a catalyst. At a catalyst fraction of 6%, a whisker-constructed porous ceramic with a porosity of 26.8% and a flexural strength of 59.1 MPa was obtained. AlF_3 catalyst accelerates the formation of mullite whiskers and then the construction of fibrous structure. However, it is still necessary to clarify the catalytic mechanism of AlF_3 during sintering and the construction process of the fibrous structure. Especially, the pore characteristics of the fibrous structure (*i.e.*, pore size and pore connectivity) depend on holding time during sintering. However, the influence of holding time on the growth of mullite whiskers and the permeance-selectivity of the fibrous structure is still unclear.

In this work, a mullite whisker-constructed porous ceramic was prepared with fly ash as a major material and $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ as a catalyst. The influences of sintering temperature and holding time on the microstructure, phase composition and filtration performance of the porous ceramics were investigated to clarify the growing mechanism of mullite whiskers based on solid-vapor reaction.

2 Experimental

2.1 Starting materials

Fly ash was obtained from a thermal power plant (Zibo, China). Table 1 shows the oxide composition. SiO_2 and Al_2O_3 were the major constituents. 30% (in

mass fraction) $\text{Al}(\text{OH})_3$ (Sinopharm Chemical Reagent Co., Ltd., China) was supplied to increase the fraction of Al_2O_3 in the mixture, as shown in Table 2. The resultant Al_2O_3 obtained from $\text{Al}(\text{OH})_3$ had a higher chemical activity, which was contributed to the mullitization of fly ash at a low sintering temperature. $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ powder (99% purity, Sinopharm Chemical Reagent Co., Ltd., China) was used as a catalyst for the growth of mullite whiskers. To form green body of porous ceramics with a high fracture strength, sodium carboxymethylcellulose (CMC, purity 99%, 800–1 200 mPa·S, Sinopharm Chemical Reagent Co., Ltd., China) was used as a binder.

Table 1 Oxide compositions of fly ash powder

Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	TiO_2	Others
Mass fraction/%	44.10	34.80	7.48	7.25	1.41	4.96

2.2 Specimen preparation

Fly ash, $\text{Al}(\text{OH})_3$ and $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ powders were weighed according to the composition design in Table 2, and 2% CMC was dissolved in deionized water, and then all the raw materials were stirred and ground in a high-energy ball mill at 200 r/min for 24 h. After mixing, the slurry was dried by a rotary evaporator and sieved with a stainless-steel screen to obtain a homogeneous mixture. The mixture was poured into a stainless-steel mold to form cylindrical samples with the diameter of 50 mm at 20 MPa. Finally, the specimens were sintered in a muffle furnace (KSL-1 750X, Hefei Kejing Material Technology Co., Ltd., China). To avoid the mass losses of gaseous substance during sintering, the specimens were sealed in alumina crucibles. During sintering, the specimens were heated to 800 °C slowly from room temperature at a heating rate of 100 °C/h, and held at 800 °C for 30 min to decompose the CMC binder. Afterwards, the specimens were sintered at 1 100 °C and 1 200 °C. The formation and growth of mullite whiskers were carried out at different holding time (*i.e.*, 2 h, 4 h and 6 h). After sintering, the specimens were firstly cooled to 600 °C at a rate of 100 °C/min, and then were cooled naturally to room temperature. Fig. 1 shows a detailed description for the processing of the porous ceramics.

Table 2 Composition design for synthesis of porous ceramics

Materials	Fly ash	$\text{Al}(\text{OH})_3$	$\text{AlF}_3 \cdot 3\text{H}_2\text{O}$
Mass fraction/%	60	30	10

2.3 Characterizations

The microstructures of the porous ceramics were determined by a model LEO-1 503 scanning electron microscope (SEM, LEO Co., Germany). The phase composition of the porous ceramics was determined by a model D/Max 2 550HB X-ray diffractometer (XRD, Rigaku Co., Japan) with Cu K α radiation, operating at 15 mA and 30 kV. The scanning range was from 10° to 90° at a rate of 4 (°)/min. The thermal properties of the mixed

powders were analyzed in air from room temperature to 1 200 °C by a model Q100 comprehensive thermal analyzer (TA, New Castle, USA). The open porosity P and bulk density ρ of the porous ceramics were determined based on the Archimedes principle. The open porosity and the bulk density of the porous ceramics were calculated by

$$P = \frac{W_1 - W_2}{W_1 - W_3} \times 100\% \quad (1)$$

$$\rho = \frac{\rho_{\text{water}} * W_2}{W_1 - W_3} \quad (2)$$

where P is the open porosity, ρ is the bulk density, ρ_{water} is the density of the water, W_2 , W_1 and W_3 are the masses of the dried, saturated and immersed (in water) samples, respectively. The shrinkage percentage S and

mass loss T of the sintered porous ceramics are expressed by

$$S = \frac{L_0 - L}{L_0} \times 100\% \quad (3)$$

$$T = \frac{M_0 - M}{M_0} \times 100\% \quad (4)$$

where L_0 and M_0 are the diameter and mass before sintering, respectively. L and M are the diameter and mass after sintering, respectively. The pore size distribution of the porous ceramics was determined by a mercury-pressure method (AutoPore IV 9510, Microtrac Co., USA). The length and diameter of the mullite whiskers were statistically analyzed using a software named IMAGE-PRO.

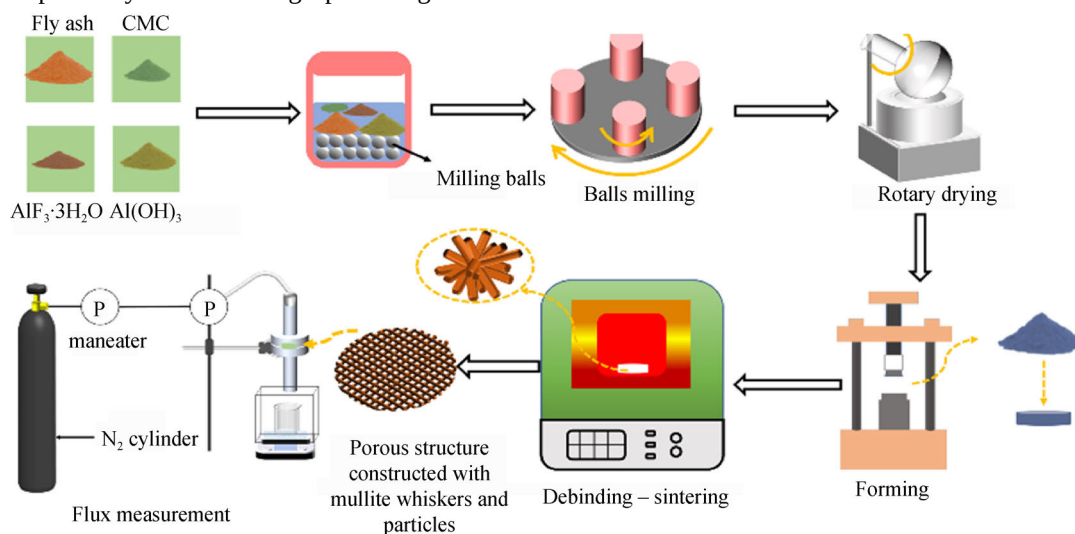


Fig. 1 Schematic diagram for the processing of the porous ceramics

Oil-in-water emulsions separation test was conducted to investigate selective performance of the porous ceramics. Five emulsions with different concentrations (*i.e.*, 200, 400, 600, 800 mg/L and 1 000 mg/L) were prepared with diesel and sodium dodecylbenzene sulfonate as raw materials. They were stirred by a digital high-speed disperser and homogenizer at 11 000 r/min for 10 min. The permeate flux was calculated by

$$J = \frac{V}{A \cdot t} \quad (5)$$

where V (L) represents the permeate volume, A (m²) represents the effective membrane area, and t (h) denotes the sampling time. In addition, the oil droplet retention rate R can be calculated by

$$R = \left(1 - \frac{C_p}{C}\right) \times 100\% \quad (6)$$

where C (mg/L) represents the feed concentration and C_p (mg/L) represents the oil concentration contained in the permeate. The oil concentrations of the emulsion before and after filtration were quantified by petroleum ether

extraction-ultraviolet spectrophotometer. During the test, the specimens with the diameter of 50 mm and the thickness of 5 mm were used.

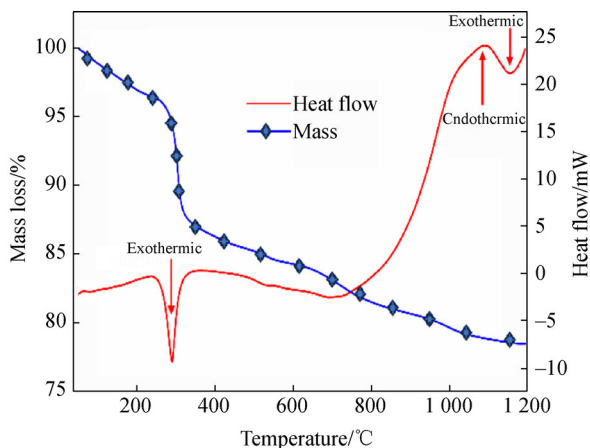
3 Results and discussion

3.1 Microstructure and composition

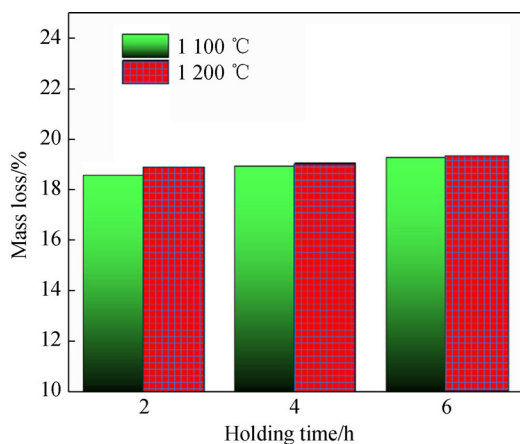
Fig. 2(a) shows the TG-DSC curve of a mixed material with $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ fraction of 10%. Clearly, a mass loss of 4% occurs from room temperature to 290 °C, indicating the removal of the chemically bounded water and consequently the formation of aluminum fluoride (AlF_3) from $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$. A mass loss of 10% accompanied by an endothermic peak occurs at 296 °C, which corresponds to the dehydration of $\text{Al}(\text{OH})_3$. In this dehydration reaction, $\text{Al}(\text{OH})_3$ produces Al_2O_3 with a highly chemical reactivity, thus accelerating the formation and growth of mullite whiskers. The mass loss at 300–900 °C is mainly due to the release of gas from the reaction among AlOF , F and SiF_4 . When the temperature exceeds 1 000 °C, an exothermic peak appears, corresponding to the formation of mullite whiskers^[15]. The gas AlF_3 acts as a catalyst for the formation and

growth of mullite whiskers.

In Fig. 2(b), the mass losses of the specimens sintered at 1 100 °C increase from 18.7% to 19.0% with the increase of sintering time, while the mass losses of the specimens sintered at 1 200 °C increase from 19.0% to 19.1%. The mass loss can be due to the dehydration of $\text{Al}(\text{OH})_3$ and $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ as well as the pyrolysis of CMC. Since the same starting materials are used for all the specimens (see Table 2), the mass loss is similar at different sintering time. At 1 200 °C, the sublimation of AlF_3 at a high temperature increases, and the mass loss reaches approximately 20%.



(a) TG-DSC



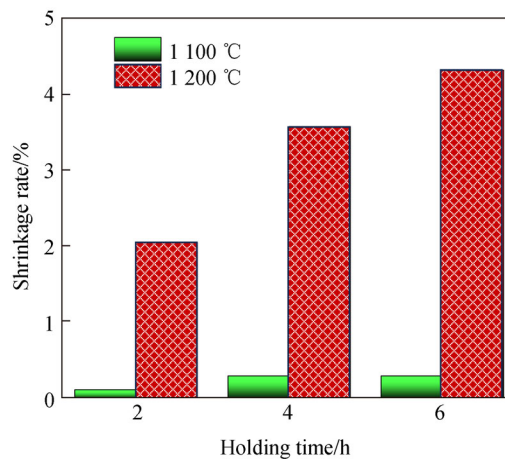
(b) Mass loss of porous ceramics

Fig. 2 TG-DSC curve of a mixture with $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ fraction of 10% and mass loss of porous ceramics at different holding time (i.e., 2–6 h)

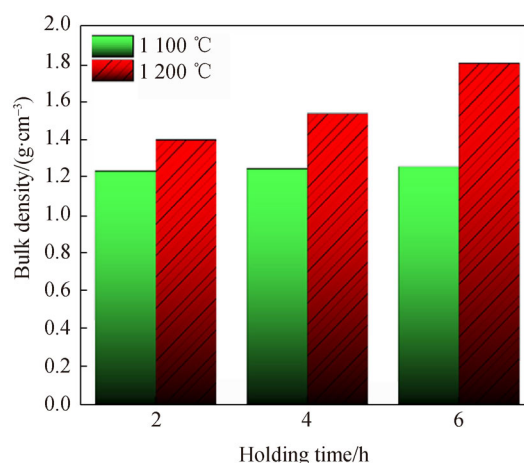
Fig. 3 shows the shrinkage and bulk density of the porous ceramics sintered at different temperatures and holding time. In Fig. 3(a), for the specimen sintered at 1 100 °C, only a slight shrinkage of approximately 0.2% occurs with the increase of holding time. For the specimen sintered at 1 200 °C, the shrinkage increases from 2.0% to 4.2% with the increase of holding time, indicating an accelerated densification of the specimens. From some previous studies^[23] on the sintering of fly ash-based porous ceramics, the densification process of fly ash-based porous ceramics can be affected by a liquid

phase that is generated during sintering. In the final stage of sintering, the liquid phase enhances the particle rearrangement, the mass diffusion and migration, thus accelerating the densification of the particles. Especially, more silica-rich liquid phases appear when the ceramics are sintered at 1 200 °C, which is responsible for the enhanced shrinkage of the porous ceramics.

Although the sublimation of AlF_3 , bulk density of porous ceramics increases with increasing the holding time, as shown in Fig. 3(b). For the specimens sintered at 1 200 °C, the bulk density increases from 1.39 g/cm³ to 1.79 g/cm³ with the increase of sintering time from 2 h to 6 h. Such an increase is ascribed to the rapid shrinkage of the materials (see Fig. 3(a)), where the shrinkage increases from 2.0% to 4.2%. The specimens exhibit the similar bulk density of approximately 1.24 g/cm³ because of the slight shrinkage for the specimens sintered at 1 100 °C.



(a) Shrinkage



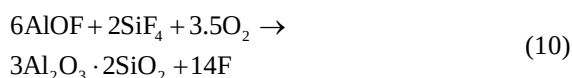
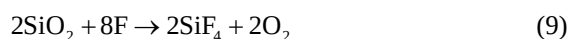
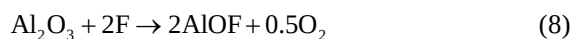
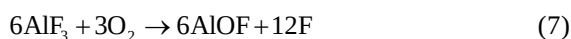
(b) Bulk density

Fig. 3 Shrinkage and bulk density of porous ceramics at different holding time (i.e., 2–6 h)

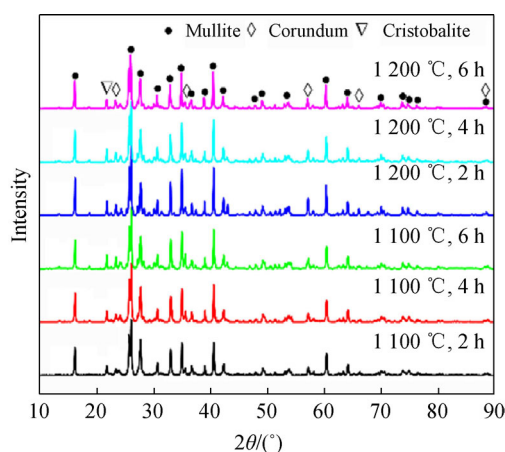
Fig. 4 shows the phase compositions of the porous ceramics sintered at 1 100 °C and 1 200 °C. In Fig. 4(a), the porous ceramics are comprised of mullite (PDF 00-015-0776), corundum (PDF 97-000-9770) and cristobalite (PDF 97-002-4587). The peak intensity of

mullite increases with the increase of sintering temperature and holding time, indicating an enhanced synthesis of mullite phase. The quantity analysis is conducted by a normalized reference intensity (RIR) method, which can confirm the content of mullite phase in porous ceramics^[24–25]. In Fig. 4(b), the mullite content of the specimen sintered at 1 100 °C increases from 80.9% to 84.3% because of the enhanced mass diffusion by the liquid phase (see Fig. 3(b)). The mullite content of the specimen sintered at 1 200 °C increases from 83.2% to 86.1%. It is thus indicated that the high sintering temperature and long holding time are beneficial to the formation of mullite phase.

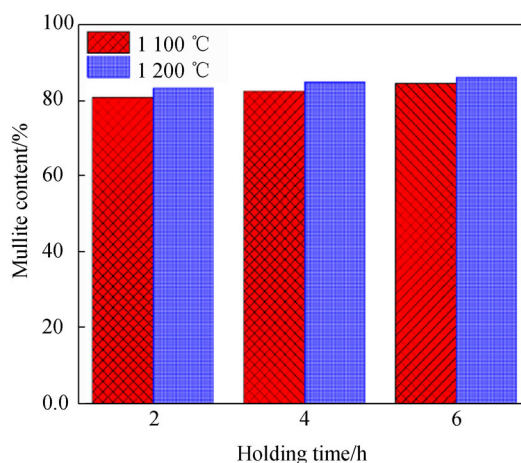
According to some previous studies on the synthesis of mullite whiskers, the formation process of mullite whiskers can be expressed by^[9, 16, 26]:



The corundum phase is derived from the decomposition of $\text{Al}(\text{OH})_3$, which is characterized by a high reactivity, compared with the fused alumina. During sintering, the resultant corundum and cristobalite react with fluorine to yield AlOF and SiF_4 , respectively (see Eqs. (8) and (9)). Consequently, AlOF and SiF_4 react with oxygen to yield mullite whiskers under sealed conditions and release fluorine simultaneously. The morphologies and dimensions of mullite whiskers are sensitive to sintering temperature, holding time and fluorine concentration.



(a) XRD patterns of porous ceramics



(b) Mullite contents of porous ceramics

Fig. 4 XRD patterns and mullite contents of the porous ceramics at different holding time

Figs. 5(a)–5(f) show the microstructures of the porous ceramics sintered at 1 100 °C and different holding time. In Figs. 5(a)–5(c), a mass of mullite whiskers form and distribute uniformly throughout the porous ceramics. In Figs. 5(d)–5(f), some slight and short whiskers form at a holding time of 2 h (see Fig. 5(d)), and then the whiskers grow both in the diameter and length directions with the increase of holding time (see Fig. 5(c) and 5(f)). All the three specimens are constructed with mullite whiskers and particles.

In Figs. 5(g)–5(l), the porous ceramics sintered at 1 200 °C present distinctly different morphologies, compared with that sintered at 1 100 °C. In Figs. 5(g) and 5(j), a plentiful of liquid phase forms, which encircles the as-synthesized mullite whiskers. In Figs. 5(h)–5(i), a liquid phase is consumed with the formation and growth of mullite whiskers when the holding time is increased because of the enhanced growth kinetics. In Figs. 5(k) and 5(l), the mullite whiskers exhibit greater length and diameter, compared with that sintered at 1 100 °C (see Figs. 5(c) and 5(f)).

Moreover, the specimen sintered for 6 h is constructed by mullite whiskers due to the rapid consumption of silica-rich liquid phase and the growth of mullite whiskers (see Figs. 5(i) and 5(l)), which is different with the specimen sintered at 1 100 °C (see Figs. 5(c) and 5(f)). From some previous studies^[27–29] on the growth of mullite whiskers, the whisker aspect ratio is related to sintering temperature and concentration of the atmosphere provided by the additives. All the specimens are sintered under the same atmosphere conditions (the same composition and sealed conditions), thus the microstructure difference is resulted from the sintering temperature.

In Fig. 6(a), the diameter and length of the mullite whiskers both distribute in a narrow size range for the specimen sintered at 1 100 °C for 2 h and 4 h. The diameter and length of the whiskers increase, and the size values randomly distribute in a large range when the holding time increases. Fig. 6(b) shows the distribution of aspect ratios of the specimens, which is calculated according to the size values in Fig. 6(a). The aspect ratios of the specimens sintered for 4 h and 6 h

are 6.5 and 4.2, respectively. The decline in aspect ratio can be ascribed to the rapid growth of mullite whiskers in diameter. It is speculated that the mullite whiskers form in the initial stage of holding time (*i.e.*, 0–4 h), and

then they grow rapidly in diameter in the final stage of holding time (*i.e.*, 4–6 h). Thus, the porous ceramics sintered at 1 100 °C are constructed with mullite whiskers and particles.

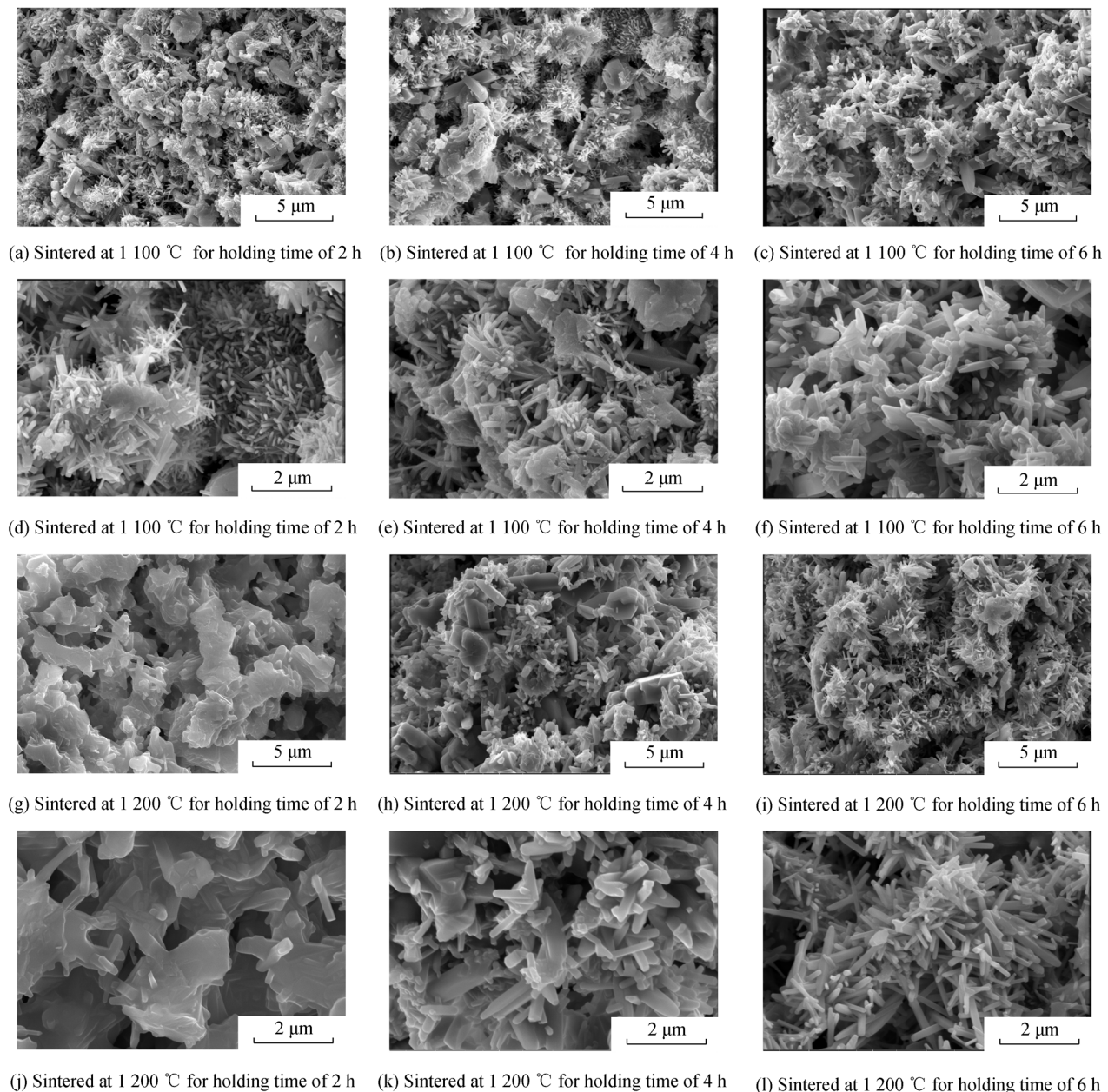


Fig. 5 Microstructures of the porous ceramics sintered at 1 100 °C and 1 200 °C and different holding time

For the porous ceramics sintered at 1 200 °C, the size distribution of the mullite whiskers is shown in Figs. 5(c) and 5(d). In despite of the difference in holding time, the diameter of the mullite whiskers is 0.1–0.3 μm, and the length of the whiskers is 0.2–1.4 μm. In Fig. 6(d), the aspect ratio of the porous ceramics increases from 4.4 to 7.2, which accords with the morphology variation in Figs. 5(j) and 5(l). Thus, a long holding time favors the growth of mullite whiskers in the specimen sintered at 1 200 °C. Compared with the specimen sintered at 1 100 °C, the specimen sintered at 1 200 °C is constructed with

mullite whiskers due to the growth of a high fraction of mullite whiskers.

Fig. 7 shows the formation and growth of mullite whiskers based on the evolution in microstructures and phase compositions of the porous ceramics. When the porous ceramics are sintered at 1 100 °C, the mullite whiskers grow and construct a porous structure with mullite whiskers and particles. For the porous ceramics sintered at 1 200 °C, the growth of mullite whiskers is enhanced due to the formation of silica-rich liquid phase, thus having the structure of the porous ceramics with a high porosity and a superior pore connectivity.

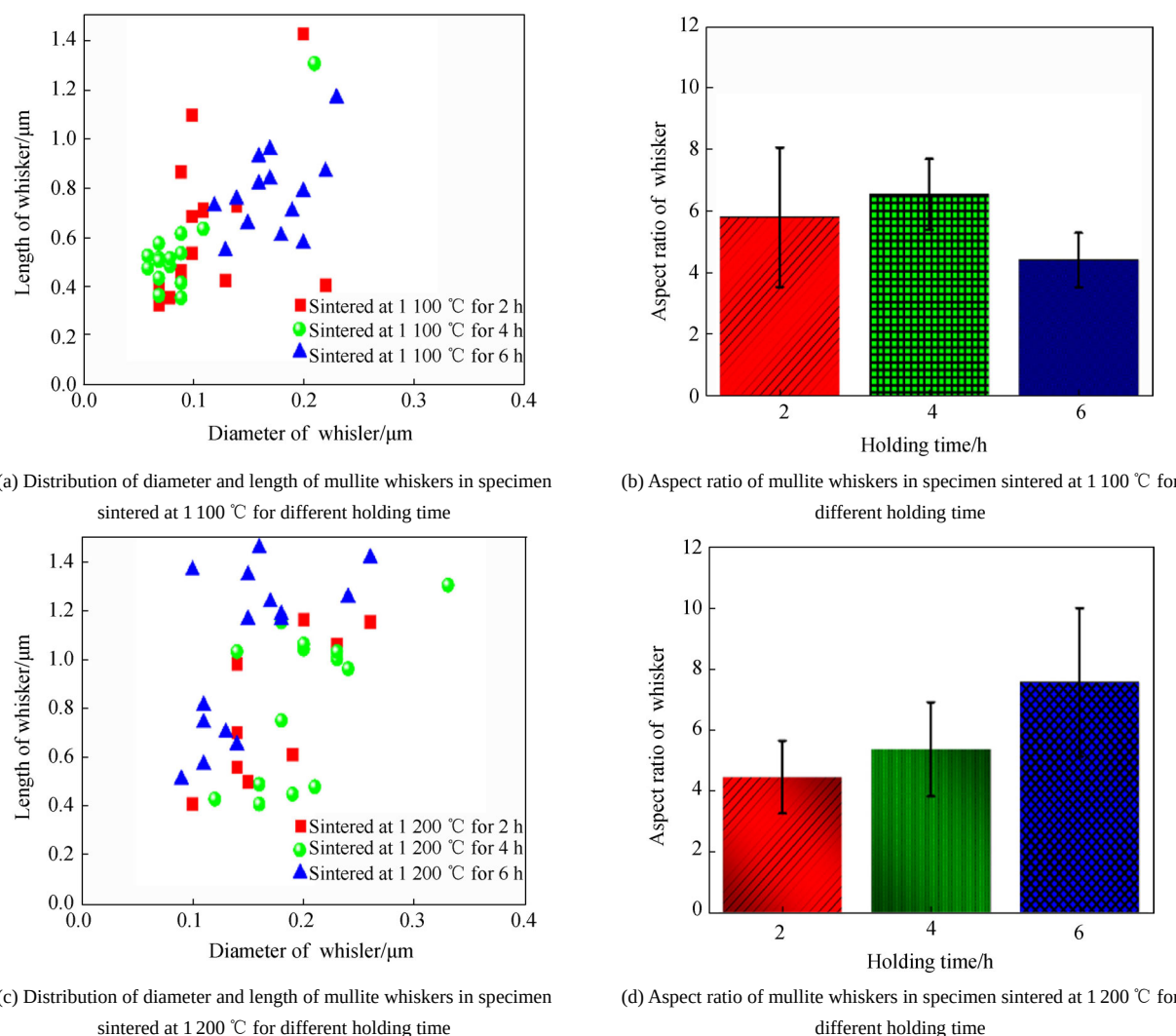


Fig. 6 Diameter/length distributions and aspect ratios of the mullite whiskers in the porous ceramics sintered at different sintering temperatures and holding time

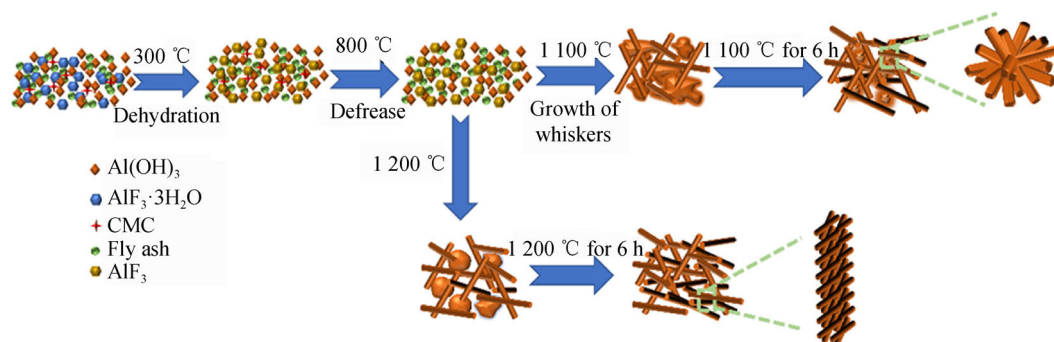


Fig. 7 Schematic diagram for formation of mullite whisker and microstructure evolution of fibrous porous ceramics

3.2 Pore structure and filtration properties

Fig. 8 shows the porosity and water absorption of the porous ceramics sintered at different temperatures and holding time. Clearly, the porosity increases from 55.2% to 55.8% for the porous ceramics sintered at 1 100 °C, and the porosity increases from 56.4% to 57.6% for the specimen sintered at 1 200 °C. Such an increase agrees with the microstructure variation of the porous ceramics (see Fig. 5). The specimens sintered at 1 200 °C displays

higher porosity than that sintered at 1 100 °C, which is ascribed to the rapid consumption of liquid phase during the formation and growth of mullite whiskers. The water adsorption of the porous ceramics increases from 42.8% to 44.6% for the specimen sintered at 1 200 °C due to the increase in porosity. Compared with porous ceramics formed by particle-accumulation, the pores are formed by a combination of whisker interlocking and particles accumulation. Thus, the growth of mullite whiskers

results in the increase in water adsorption of the porous ceramics. In addition, it is evident that sintering temperature is a key factor that can affect the porosity and water absorption of the porous ceramics, while the holding time has a slight effect.

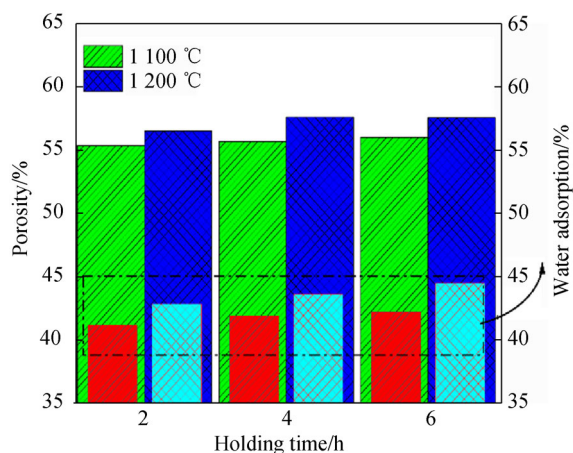


Fig. 8 Porosity and water adsorption of porous ceramics sintered at different temperatures and holding time

In Fig. 9, the majority of pores of the porous ceramics sintered at 1200 °C distribute in a narrow size range from 0.5 μm to 1.5 μm . The median pore size of the specimen increases from 0.75 μm to 1.24 μm with the increase of sintering time. Clearly, the growth of mullite whiskers leads to the increase in pore size of the porous ceramics because of the formation of the whisker-constructed fibrous porous structure.

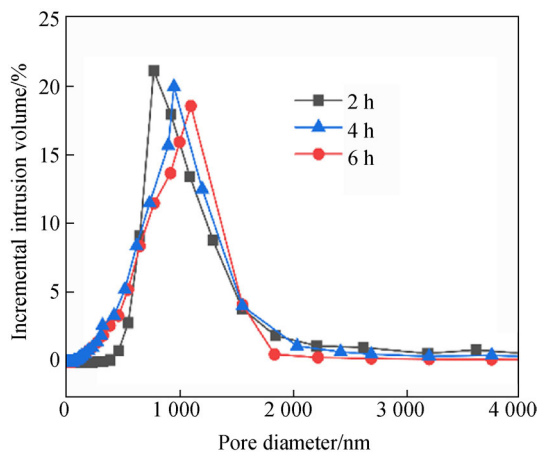


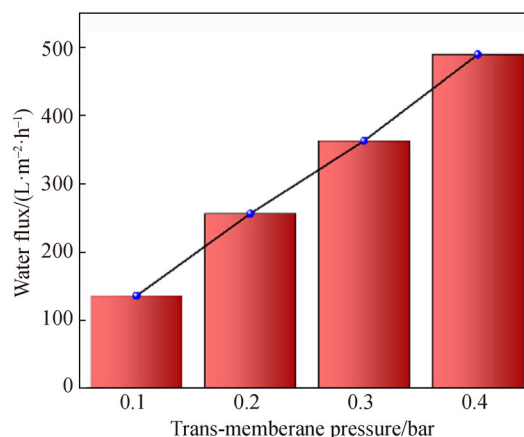
Fig. 9 Pore size distribution of porous ceramics sintered at 1200 °C at different holding time

In consideration of the high porosity and pore size distribution, the specimen sintered at 1200 °C for 6 h is chosen for the permeance-selectivity test (see Fig. 10(a)). In Fig. 10(b), the water flux increases from 118 $\text{L}/(\text{m}^2 \cdot \text{h})$ to 496 $\text{L}/(\text{m}^2 \cdot \text{h})$ with the increase of trans-membrane pressure (TMP), indicating that TMP is a sole parameter to determine the water flux of the porous ceramics. Assuming that the transport mechanism of the sample be consistent with the viscous flow model, the relationship between the flux and the TMP difference is consistent

with Darcy's law^[30] (see a straight line in Fig. 10(b)).



(a) Physical view of oil–water separation device



(b) Water flux of porous ceramics sintered at 1200 °C for 6 h

Fig. 10 Physical view of oil–water separation device and water flux of porous ceramics sintered at 1200 °C for 6 h

Figs. 11 (a) and (b) show the microstructure and particle size distribution of the oil-in-water emulsion (200 mg/L) used, where the sizes of the oil-droplets distributed from 5.0 to 10.0 μm . Fig. 11c shows the permeate flux of the porous ceramics sintered at 1200 °C for 6 h at the TMP of 0.2 bar. For the emulsion with a concentration of 200 mg/L, the permeate flux decreases from 210.61 to 192.35 $\text{L}/(\text{m}^2 \cdot \text{h})$ within the filtration time range, while the permeate flux decreases from 120.59 to 106.94 $\text{L}/(\text{m}^2 \cdot \text{h})$ for the emulsion with a concentration of 1000 mg/L. The oil droplets in the emulsions can block the connected pores in the porous ceramics, resulting in the decline of the permeate flux with the increase of the emulsion concentrations.

In Fig. 11(c), the permeate flux decreases slowly in the initial stage and then reaches a steady state afterwards. In the initial stage, the water can easily pass through the ceramic pores, producing high flux values, and the oil droplets block some pores. As a result, the permeate flux decreases and eventually reaches a steady state. The flux reduction is mainly due to ceramic fouling. The initial stage of membrane fouling is mainly consistent with the intermediate pore blocking model,

while the consequent stage is mainly consistent with the cake filtration model^[31–32].

Fig. 11(d) shows the oil rejection of the porous ceramics at different TMPs (*i.e.*, 0.1 bar to 0.4 bar). The high TMP induces the transformation of oil droplets and then their pass, thus the oil rejection decreases from appropriately 90% to 87%. In addition, the oil rejection increases slightly with the increase of oil concentration under the same TMP condition. A high oil concentration favors the rejection of oil droplets in the emulsions, which is consistent with the results reported by Rashad *et al.*^[33] in the filtration of

oil-in-water emulsions. The merge of small oil droplets induces the formation of large oil droplets, which cannot pass through the porous ceramics readily. Fig. 11(e) shows the morphologies of the emulsion before and after filtration, which further confirms the high oil rejection of the porous ceramics.

Table 3 shows the performances of the porous ceramics in this work and the other materials reported in the literatures^[11, 16, 34–37]. Clearly, we can prepare the porous ceramics with a high porosity and a high flux at a lower sintering temperature due to the formation of mullite whisker-constructed porous structures.

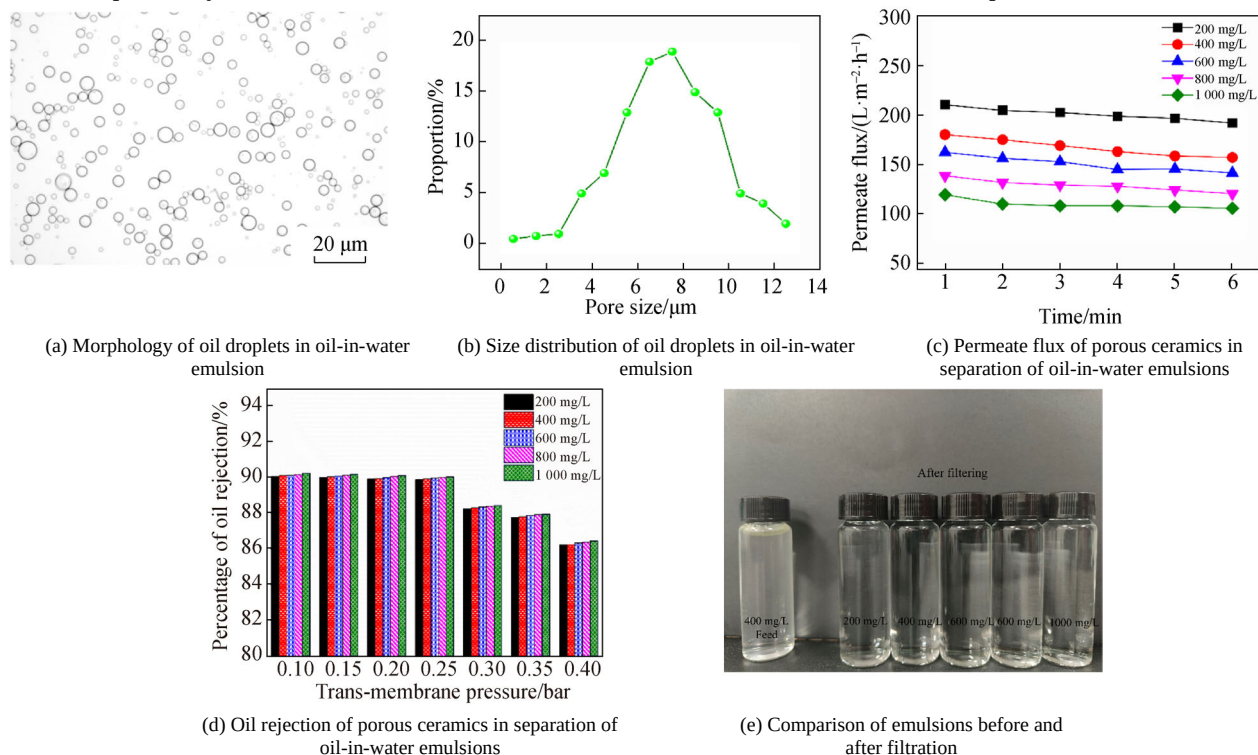


Fig. 11 Morphology and size distribution of oil droplets in oil-in-water emulsion, permeate flux and oil rejection of porous ceramics in separation of oil-in-water emulsions, and comparison of emulsions before and after filtration

Table 3 Comparison of the preparation parameters and performances of the mullite-based porous ceramics

Composition	Sintering temperature/°C	Porosity/%	Pore size/μm	Oily water flux/(L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Oil rejection/%	Reference
Mullite bonded porous SiC membrane	1 000	36–45	3–4	127–225	89–92	[11]
Mullite	1 350	41	0.25	35	90	[34]
Clay	1 000–1 100	26	0.67	30	84.1	[35]
Coal fly ash/bauxite	1 200	47.3	0.25		90	[36]
Fly ash/bauxite	1 400	51.9	0.93	6.19	96–98	[16]
Kaolin/quartz	900	30	1.30	466	85	[37]
Fly ash-AF	1 200	57.6	1.24	1 053	90	This work

4 Conclusions

A low-cost porous ceramic was prepared with fly ash as a major material and AlF₃·3H₂O as a catalyst. The following conclusions could be drawn:

1) Sintering temperature affected the shrinkage of

the porous ceramics. For the specimen sintered at 1 100 °C, only a slight shrinkage of approximately 0.2% occurred during sintering. For the specimen sintered at 1 200 °C, the shrinkage increased from 2.0% to 4.2% due to the formation of silica-rich liquid phase. Also, the high sintering temperature favored the formation of mullite phase. The fraction mullite phase reached 86.1% for the

specimen sintered at 1 200 °C for 6 h.

2) With the growth of mullite whiskers, the porosity of the porous ceramics increased from 56.4% to 57.6% for the specimen sintered at 1 200 °C, and the average pore size of the specimen increased from 0.75 to 1.24 μm . The growth of mullite whiskers increased both in porosity and pore size of the whisker-constructed porous ceramics.

3) The emulsion test indicated that the permeate flux decreased from 210.61 to 192.35 $\text{L}/(\text{m}^2 \cdot \text{h})$ for the specimen sintered at 1 200 °C. Oil rejection of the porous ceramics decreased from appropriately 90% to 87% as TMP increased from 0.1 to 0.4 bar. The decline was ascribed to the transformation of large oil droplets at a high TMP.

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Construction and Filtration Performance of Mullite Fibrous Porous Ceramics by *in-situ* Catalysis of Fly Ash

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Extended Abstract

Introduction Porous ceramics are widely used in a variety of environmental fields such as solid–liquid separation and hot gas filtration due to their high mechanical strength, excellent chemical resistance, and high thermal stability. Conventional porous ceramics are usually made of particle-packing of inorganic powders, which are usually characterized by a low porosity, a high self-weight, a low permeability and a high filtration resistance. It is thus necessary to develop novel porous ceramics with a high porosity, a high mechanical strength and a low packing density. Mullite whisker-based porous ceramics have attracted recent attention in the treatment of various wastewaters. Compared with porous ceramics prepared by conventional particle-packing, mullite whisker-based porous ceramics are constructed by whisker interlocking, resulting in fibrous structures with a high porosity, a high pore connectivity and a low packing density. However, these mullite porous ceramics are seldom used in industry due to the high cost of the high-purity starting materials. Fly ash is a major by-product of coal combustion. The elemental analysis shows that fly ash is mainly composed of unburned carbon, metal oxides (*i.e.*, Si, Al, and Fe) and other inorganic materials. Fly ash can be used to prepare mullite porous ceramics due to the presence the high content of aluminum silicates. However, the effect of holding time on the growth of mullite whiskers and the permeance-selectivity of the fibrous structures is still unclear. In order to elucidate the growth mechanism of mullite whiskers based on gas-solid reaction, the effects of sintering temperature and holding time on the microstructure, phase composition and filtration properties of the porous ceramics were investigated.

Methods Fly ash powder provided by Huaneng Thermal Power Plant in Zibo, China, and $\text{Al}(\text{OH})_3$ purchased from Sinopharm Chemical Reagent Co. Ltd., China, were used as major materials. $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ purchased from Sinopharm Chemical Reagent Co. Ltd., China, was employed as a catalyst for mullite whisker growth. In order to prepare porous ceramics with a high fracture strength, sodium carboxymethyl cellulose (CMC) from Sinopharm Chemical Reagent Co., China was chosen as a binder. Fly ash, $\text{Al}(\text{OH})_3$, $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ and CMC were mixed and ground in a ball mill, and then the slurry was dried with a rotary evaporator and sieved through a stainless steel sieve to obtain a homogeneous mixture. After dry pressing, the green body was sintered in a muffle furnace. The effect of holding time on the formation and growth of mullite whiskers was elucidated at different holding time (*i.e.*, 2, 4 h and 6 h). The microstructure of the porous ceramics was determined by scanning electron microscopy (SEM). The phase composition of the porous ceramics was analyzed by X-ray diffraction (XRD). The selectivity of the porous ceramics was investigated by oil-in-water emulsion separation experiments.

Results and discussion To clarify the growing mechanism of mullite whiskers based on solid-vapor reaction, the influences of sintering temperature and holding time on the microstructure, phase composition and filtration performance of the porous ceramics are investigated. The gas $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ acts as a catalyst for the formation and growth of mullite whiskers. The thermogravimetric analysis curves indicate that the mullite whisker growth follows a gas-solid reaction mechanism, where $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ acts as a catalyst for the formation and growth of mullite whisker. The mass loss of the samples sintered at different temperatures is similar while the shrinkage increases from 2.0% to 4.2% as the holding time increases. A liquid phase formed during the sintering process enhances the particles rearrangement, the mass diffusion and migration, and the densification of the specimens. The XRD patterns indicate that a

high sintering temperature and a long holding time were favorable for the formation of the mullite phase. The whisker aspect ratio is related to the sintering temperature and the concentration of the atmosphere provided by the additives. The analysis of the length-to-diameter ratio of the mullite whiskers reveals that the increase in holding time favors the growth of mullite whiskers. Based on the analysis of the pore structure of the porous ceramics, the sintering temperature is a key factor affecting the porosity, water absorption and pore size of the porous ceramics, while the holding time has a slight effect. According to the results of flux tests on the specimens sintered at 1 200 °C for 6 h, the permeation flux decreases from 210.61 L/(m²·h) to 192.35 L/(m²·h). When the trans-membrane pressure increases from 0.1 bar to 0.4 bar, the oil rejection of the porous ceramic reaches 90%.

Conclusions The sintering temperature affected shrinkage of the porous ceramics. For the specimen sintered at 1 100 °C, only a slight shrinkage of approximately 0.2% occurred during sintering. For the specimen sintered at 1 200 °C, the shrinkage increased from 2.0% to 4.2% due to the formation of silica-rich liquid phase. Also, the high sintering temperature favored the formation of mullite phase. The growth of mullite whiskers increased both in porosity and pore size of the whisker-constructed porous ceramics. With the growth of mullite whiskers, the porosity of the porous ceramics increased from 56.4% to 57.6% for the specimen sintered at 1 200 °C, and the average pore size increased from 0.75 to 1.24 μm. The emulsion test indicated that the permeate flux decreased from 210.61 to 192.35 L/(m²·h) for the specimen sintered at 1 200 °C. Oil rejection of the porous ceramics decreased from appropriately 90% to 87% as TPM increased from 0.1 to 0.4 bar.

Keywords: porous ceramics; porosity; fly ash; sintering; mullite whisker