RESEARCH NOTES

Preparation of Macroporous TiO₂ Ceramic Based on Membrane Jet-flow Emulsification*

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Abstract A novel method to prepare macroporous TiO₂ ceramic, based on membrane emulsification was reported. To solve the paradox between the instability of nonaqueous emulsion and long emulsification time required by the membrane emulsification, a two-stage ceramic membrane jet-flow emulsification was proposed. Discussion was conducted on the evolution of droplet size with time, which followed the Ostwald ripening theory. And a monodispersed nonaqueous emulsion with an average droplet size of 1.6μm could be prepared. Using the emulsion as a template, TiO₂ ceramics with an average pore size of 1.1μm were obtained. The material could be prospectively used for preparation of catalysts, adsorbents, and membranes.
Keywords nonaqueous emulsion, ceramic, membrane emulsification, jet-flow

1 INTRODUCTION

Porous materials have recently received much attention because of their application in a wide variety of fields, such as biosensors, catalysts, adsorbents, chromatographic materials, and photonic crystals. Several approaches are currently available for the preparation of ordered structures with different length scales. Mesostructures can be obtained by the self-organization of the surfactant molecules, and colloidal templates are usually used to prepare ordered macroporous materials[1,2]. Imhof and Pine[3] have proposed a famous method — the emulsion templating approach, for preparing highly ordered macroporous materials. In this approach, the sol-gel process is used to deposit an inorganic material on the exterior of the droplets in a nonaqueous emulsion. The preparation of monodispersed nonaqueous emulsion is one of the key processes.

Membrane emulsification (ME) is a new emulsification technique based on membrane structure, which has received increasing attention over the last 10 years, because it consumes less energy, has low shearing stress and controllable droplet size of the emulsions[4]. However, low flux of the dispersed phase, resulting in a long emulsification time, has hindered the application of this technology. Especially in the preparation of nonaqueous emulsions, the problem has become more obvious because of nonaqueous emulsions being unstable.

In the previous study[5], a membrane jet-flow emulsification to resolve the paradox between the flux and the droplet size, in conventional membrane emulsification, was proposed. A monodispersed O/W emulsion could be obtained under jet flow by a two-stage membrane jet-flow emulsification process. The main purpose of this study was to prepare a monodispersed nonaqueous emulsion with the help of membrane emulsification under jet-flow, to investigate the stability of the nonaqueous emulsion, and to prepare an ordered macroporous TiO₂ ceramic based on this method.

2 EXPERIMENTAL

The formamide was used as the continuous phase, the isooctane as the dispersed phase. The surfactant was a symmetric triblock copolymer, poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) with a relative molecular weight of 5,800 (Aldrich). The membrane jet-flow emulsification apparatus with a stirring vessel of 300 ml was used in this study, which was smaller than that used in the previous studies[5,6]. Two ceramic membranes with a pore size of 0.16μm and 1.5μm were separately used in the two stages. Titanium terabutoxide [Ti(OC₄H₉)₄] was a precursor of TiO₂ and the sol was a mixture containing Ti(OC₄H₉)₄, acetylacetone, water, and formamide (molar ratio of Ti : acetylacetone : H₂O = 1 : 1 : 3.5 and the Ti molar concentration of 1.5mol·L⁻¹). The mixture contained a considerable amount of butanol, produced by the hydrolysis reaction. Because butanol destabilizes the emulsion, it was removed by double extraction with the help of hexanes. The resulting yellow liquid was often turbid. To obtain a clear yellow sol, the sol was heated briefly to 90℃. The emulsion was then added into the sol under stirring. Thirty percent ammonia was added and the mixture formed a gel after about 3h. The template was removed by heating at a temperature of 40℃ for 24h. The ordered macroporous ceramic could be obtained by calcining the gel at the temperature of 400℃ in a furnace for 4h.

The droplet sizes of the emulsions were analyzed through a microscope. As an index of monodispersion,

a coefficient of dispersion (α) was adopted[7]. $\alpha = S_d/D_d$, where S_d is a standard deviation of droplet diameter, and D_d is the average droplet diameter of an emulsion. The smaller the α value, the narrower the droplet size distribution and the better monodispersed the emulsion. Generally, monodispersed emulsion could be defined as $\alpha \leqslant 0.35$. Scanning electron microscopy (SEM) was utilized to determine the macroporous structure of the TiO₂ ceramic.

3 RESULTS AND DISCUSSION

In these experiments, the stable emulsions were prepared with formamide as the continuous phase, isooctane as the dispersed phase, an emulsifier concentrate of 2%, and a ZrO₂ membrane with nominal size 0.16μm was used in the first stage. Fig.1 shows the emulsion prepared at a pressure of 0.09MPa, and the rotate speed of 300r·min^{-1}. As shown in this figure, the average droplet size of the emulsion was 3.2μm and the α was 0.563. The emulsion prepared was not monodispersed because of the higher pressure, however the flux could reach 201.4L·m^{-2}·h^{-1}. Using the secondary jet-flow membrane emulsification, monodispersed emulsion with small droplet size could be obtained. Fig.2 shows the droplet size of the emulsion prepared by using an α-Al₂O₃ ceramic membrane, having a nominal pore size of 1.5μm, at 150kPa pressure, with 300r·min^{-1} stirring speed. The average droplet size of the emulsion was 1.6μm, which was slightly bigger than the membrane pore size. The α of the emulsion was 0.22, which meant the emulsion was monodispersed. The flux reached 176.4L·m^{-2}·h^{-1}, which was attributed to the larger pore size and higher

pressure. The stability of the emulsion is shown in Fig.3. The cube of average droplet diameter of the emulsion linearly increased with time, which followed the famous Ostwald ripening theory[8]. And the coefficient of dispersion (α) had little changes from 0.22 to 0.24, which meant the emulsion had always been kept monodispersed during the 960min. Therefore, the stability of the emulsion could meet the demands of the sol-gel process.

Figure 3 Evolution of the structure of the nonaqueous emulsion with time
□ the cube of average droplet diameter of the emulsion;
■ the α of the emulsion

A light-scattering particle sizer (Zetasizer 3000, Malvern Instruments, Malvern, UK), determined the particle size of the sol. The evolution of the sol with time is shown in Fig.4. The particle size of the sol was about 4nm initially, and it became more than 10nm after 10 days. The result indicated that the particle size increased with time because of coalescence. Generally the sol was stable and no precipitation emerged in several weeks, however, it was recommended to use the sol in three days to obtain the ordered porous material.
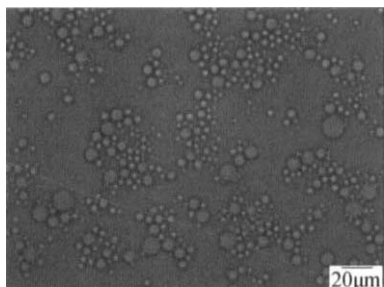

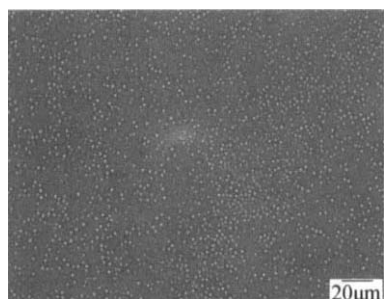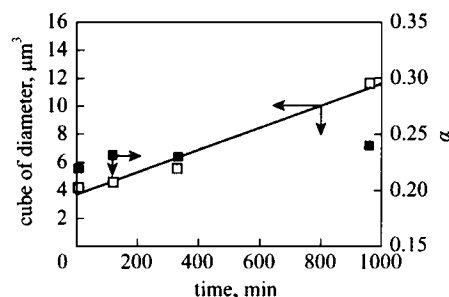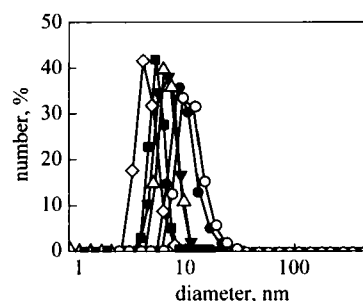**Figure 1 The optical microscope photographs of the emulsion prepared by first membrane jet-flow emulsification**

Figure 2 The optical microscope photographs of the emulsion prepared by secondary membrane jet-flow emulsification

Figure 4 Evolution of particle size number distribution with time
(H₂O/Ti molar ratio was 3.5)
◇ the first day; ■ the second day; △ the fourth day;
▼ the fifth day; ● the tenth day; ○ the eleventh day

The emulsion was concentrated by centrifuging and then dispersed in the sol, and the stable gel could be obtained by adding 30% ammonia into the mixture. The template was removed after heating to a temperature of 40℃ for 24h, and then the gel was calcined at a temperature of 400℃ in a furnace, for 4h, to obtain macroporous ceramic. Fig.5 shows the scanning electron micrographs of the surface and cross-section. The TiO₂ ceramic with the pore size of 1.1μm was obtained by the calcining process, which was about 0.69